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THE KINETICS OF THE REACTIONS OF HYDROGEN ATOMS
WITH
ETHYLENE, VINYL FLUORIDE AND 1,1-DIFLUOROETHYLENE

by

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A THESIS

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ABSTRACT

Hydrogen atoms generated in a Wood-Bonhoeffer discharge were reacted with ethylene, vinyl fluoride and 1,1-difluoroethylene. The products of the ethylene reaction were: CH_4, C_2H_6, C_3H_8 and n-C_4H_{10}. The products of the vinyl fluoride reaction under similar conditions were: CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, C_2H_4, C_3H_6, C_2H_2 and HF. The products of the 1,1-difluoethylene reaction under similar conditions were: CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, C_2H_4, C_3H_6, C_2H_2, HF and C_2H_3F. With the exception of HF, all products were quantitatively studied over the temperature range 303°-603°K. The kinetics and mechanisms of the three reactions were studied in detail. The rate constants were calculated for each step of the mechanisms for three temperatures. Activation energies were also determined for each step. The calculation of the rate constants and testing of the mechanisms was accomplished by numerical integration of the simultaneous differential equations for each species involved in the reactions.

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CHAPTER I

INTRODUCTION

1. HYDROGEN ATOM PRODUCTION

Since the first report of the dissociation of molecular hydrogen on hot tungsten filaments in 1911[1], many methods have been developed for the generation of hydrogen atoms. Perhaps the most frequently used method is the so-called Wood's tube[2], in which a low pressure stream of molecular hydrogen passes over metallic electrodes held at a relatively high voltage. Other common methods include: (1) radio-frequency and high frequency microwave discharges, (2) mercury photosensitized decomposition of H_2 and hydrocarbons, (3) direct photolysis of H_2S, HBr and HI, (4) radiolysis of paraffins, (5) certain flame reactions and (6) shock tubes.

Le Roy and co-workers[3] developed the pyrolytic method for kinetic studies of atomic hydrogen reactions. They obtained hydrogen atoms at partial pressures of the order of 5×10^{-3} torr by passing hydrogen at 1 to 10 torr over a tungsten filament maintained at 1700°C.

In a Wood's tube (glow discharge), molecular hydrogen has been found to be up to 25% dissociated over the pressure range 0.1 to 1.0 torr[2,4,5]. This method has been extended to pressures as high as 20 torr by Harteck and Raeder[6]. Contamination from the electrodes and the limited pressure range are the major disadvantages of the Wood's tube.

In order to avoid contamination by the electrodes, the electrodeless radio-frequency and microwave discharges can be used. The theory of the electrodeless discharge was outlined as early as 1928, but an efficient way of producing high concentrations of hydrogen atoms by this method was first described by Jennings and Linnett[7] in 1958. They found that the discharge could be maintained by using 350 watts of 9.7 MHz radiation and a gas pressure of about 0.08 torr. This gave about 50-60 percent dissociation of

H_2 into H atoms. Dalgleish and Knox[8] found that mixtures of 10-15% H_2 in Ar (2 torr), when passed through an 18 MHz radio-frequency discharge (~100W), gave about 25% dissociation of H_2 into H atoms. Widespread use of microwave discharges for the dissociation of gases resulted from the development of powerful sources of microwave energy during World War II. Among the early users of this type of discharge were Nagle et al.[9] and Broida et al.[10], who found that a microwave discharge provides an efficient, stable source of hydrogen atoms. The microwave source has the advantage of having the energy readily and efficiently coupled to the gaseous discharge.

The mercury (Hg $^3P_1$) photo-sensitized decomposition of H_2 has proven to be a convenient source of hydrogen atoms[11,12]. Hydrogen atoms may also be produced by the mercury (Hg $^3P_1$) photo-sensitized decomposition of hydrocarbons[13] and fluoro-hydrocarbons[14,15]. The direct photolysis of substances like HBr[16,17], HI[18,19], formaldehyde[20], and H_2S[21,22] results in the production of hot ground state ($^2S_{1/2}$) hydrogen atoms. These hot atoms have excessive translational energy (from 22 to 40 kcal per mole) depending on the wave length of the photolysis source. In an excess of inert gas, these hot atoms will be deactivated rapidly by collisions and react as thermalized atoms[23].

Hydrogen atoms may also be produced by radiolysis. Yang[24] produced H atoms by gamma radiolysis of propane and studied the effect of C_2H_4 on the rate of H_2 production. Dorfman et al.[25] produced H atoms in hydrogen by a pulse of high energy electrons from a febetron generator. In principle, the radiolysis technique is very similar to the two preceeding photochemical methods. These techniques have been used primarily for measurements of competitive reactions yielding ratios of the rate constants of the competing reactions.

Hydrogen atoms are present after ignition of mixtures of H_2 and O_2[26]. The presence of an added compound can change the explosion limits of the thermal reaction and the relative rates of attack of H on the additive can be obtained by determining the relative rates of consumption of H_2 and the additive. Hydrogen atoms can be generated in the exhaust gas from low pressure hydrogen, hydrogen-CO, and hydrocarbon flames. Atomic hydrogen reactions can be studied at very high temperatures (up to 1600°K) by this method[27,28]. The thermal dissociation of hydrogen behind a shock wave was described by Gardiner and Kistiakowsky[29]. From measurements of the rate of dissociation of H_2 in shock tubes, rate constants for hydrogen atoms with O_2 can be determined for temperatures up to 2700°K[30].

2. HYDROGEN ATOM DETECTION AND CONCENTRATION MEASUREMENT

The detection of H atoms and determination of their concentration may be made by either physical or chemical methods.

(A) Physical Methods

i) Wrede Gauge Method

A fairly direct method of estimating the concentration of hydrogen atoms in a gas containing only H_2 and H has been devised by Wrede[31] and Harteck[32]. This method depends on the steady state pressure difference which is established when the stream of gas containing hydrogen atoms and molecules is diffused onto a catalyst through a slit or capillary whose width is smaller than the mean free path of the gas. The H atoms then recombine on a catalyst and only molecules effuse back into the main system creating a small pressure difference. This method can only be used at low pressures and for concentrations of atoms which are high enough to be of the same order of magnitude as that of the molecules. Hence, it is only practical with the discharge tube method of producing hydrogen atoms. Groth and Warneck[33] have shown that with this method it is possible to obtain reasonable response times at pressures of 1 torr or higher without loss of accuracy.

ii) Calorimetric Method

Bonhoeffer[34] first investigated the calorimetric detection of atomic hydrogen. This method is dependent upon a measurement of the heat released when atoms recombine on an efficient catalyst. Linnett and Marsden[35] measured the relative concentrations of H atoms by mounting the catalyst on the tip of a fine thermocouple and measuring the E.M.F. produced. Le Roy et al.[3] obtained the absolute concentration by using an isothermal calorimetric probe in which the detector was a platinum spiral. The spiral and a calibrated milliameter formed one arm of a wheatstone bridge. The other three arms consisted of a 1000 ohm standard resistance and two decade boxes. The spiral was maintained at a constant temperature by varying the current through the bridge. The tendency for increased spiral temperature, due to atom recombination on its surface, was offset by lowering the current in the spiral. In this manner, heat losses present in a normal thermocouple probe, were eliminated. The decrease in the power supplied to the detector gave a measure of the number of hydrogen atoms recombining on its surface per second. Smith et al.[36] found that elevated temperatures increased the efficiency and reduced the rate of surface poisoning of the catalyst. The possible errors, due to incomplete release of the heat of recombination on the surface and the change in thermal conductivity of the gas with its degree of dissociation, appeared to be small[37]. It was noted, however, that the diffusion effect could introduce serious errors if the gas flow was not rapid enough[37]. The calorimetric method was further used by Pospelra and Myasmikov[38] to measure the recombination of hydrogen atoms.

iii) Mass Spectrometric Method

The concentration of hydrogen atoms can be determined by mass spectrometry, provided that the molecular beam inlet is arranged so that the atoms can pass directly into the ionizing region of the spectrometer without surface collisions[39]. The mass spectrometer can be calibrated for hydrogen atoms by measuring the decrease in the mass spectrometric peak height for H_2 in the presence and absence of H atoms[40,41]. Niki et al.[41], also followed the H atom peak by using a time-of-flight mass spectrometer.

iv) Lyman α Photometry Method

In this method, the hydrogen atoms in the system are measured by their absorption of the Lyman α line (1215.78 Å) emitted from a hydrogen discharge lamp. This absorption can be measured by various vacuum ultraviolet detectors. This photometric technique has been found to be very sensitive and fast enough to follow the hydrogen atom decay.

Preston[42] was the first to use this method to determine hydrogen atom concentrations. A vacuum spectrograph was used as the detector. McNesby and Tanaka[43] used the Lyman α line as a photolysis source to obtain H (^2P) which was used as a reactive species. Myerson et al.[44] were the first to use this method with a photomultiplier tube as the detection device. Michael et al.[45,46] have developed an ionization detector employing ionization of NO for detection of the Lyman α line. Braun and Lenzi[47] have used a slightly different technique by measuring the reasonance fluoresence of the Lyman α excitation of H atoms. The atomic fluoresence arises from hydrogen atoms (^2P) excited by absorption of the Lyman α line. This fluoresence is detected by a photomultiplier tube set at an angle so as not to be affected by the Lyman α lamp.

The Lyman α photometric method has been used in discharge flow[45], mercury photosensitization[46], shock tube[44], photolysis[47], and pulse radiolysis[25] systems.

v) Electron Spin Resonance Method

The validity of absolute hydrogen atom concentration measurement in the gas phase by electron spin resonance (ESR) spectroscopy, using O_2 as a reference gas, has been established for many years[48,49,50,51]. The ESR spectrum of the hydrogen atom consists of a widely spaced doublet[52, 53, 54].

(B) Chemical Methods

i) Molybdenum Oxide Method

Melville and Robb[11] used a molybdenum oxide film as a detector responsive to hydrogen atoms. MoO_3 film turns bluish when attacked by all types of atoms or radicals and is especially sensitive when attacked by hydrogen atoms.

ii) HNO* Chemiluminesence

Two methods based on the emission from excited HNO* have been used to determine hydrogen atom concentrations.

The basic reaction (1-1) was studied by Thrush and Clyne[55],

$$H\cdot + NO \longrightarrow HNO^* \longrightarrow HNO\cdot + h\nu \qquad (1\text{-}1)$$

$$H\cdot + HNO\cdot \longrightarrow H_2 + NO \qquad (1\text{-}2)$$

where reaction (1-1) is the rate-determining step. They found that this reaction produced light in the visible and near infra-red region (5000 to 8000Å).

Thrush and Clyne[56] also investigated the reaction between hydrogen atoms and NO_2. They suggested the mechanism as (1-3a) followed by (1-1)

$$H\cdot + NO_2 \longrightarrow OH\cdot + NO \qquad (1\text{-}3a)$$

$$H\cdot + NO \longrightarrow HNO\overset{*}{\cdot} \longrightarrow HNO\cdot + h\nu \qquad (1\text{-}1).$$

The initial step has been found to be somewhat more complicated[8,48,57,58], as shown in (1-3b).

$$k = 2.9 \times 10^{13}\ \text{cc.mole}^{-1}\ \text{sec}^{-1}$$

$$2H\cdot + 3NO_2 \longrightarrow H_2O + O_2 + 3NO \qquad (1\text{-}3b)$$

$$H\cdot + NO \longrightarrow HNO\overset{*}{\cdot} \longrightarrow HNO\cdot + h\nu \qquad (1\text{-}1)$$

From the above, it is seen that the extinction of the HNO* chemiluminesence occurs at an NO_2 flow rate of 1.5 times the hydrogen atom flow rate.

Clyne and Stedman[59] studied the reaction of hydrogen atoms with NOCl and suggested the initial step as (1-4), followed by (1-1).

$$H\cdot + NOCl \longrightarrow NO + HCl \qquad (1\text{-}4)$$

$$H\cdot + NO \longrightarrow HNO\overset{*}{\cdot} \longrightarrow HNO\cdot + h\nu \qquad (1\text{-}1)$$

When the concentration of NOCl was equal to that of hydrogen atoms, the HNO emission was extinguished, thus allowing determination of the hydrogen atom concentration. This same method has been used by other workers[60,61].

iii) Chemical Reaction Product Analysis.

The reactions of certain compounds with hydrogen atoms have been found useful for determining the hydrogen atom concentrations.

The reaction of hydrogen atoms with ethyl chloride[62,63,64] produces a titratable product, HCl, as shown in (1-5).

$$H\cdot + C_2H_5Cl \longrightarrow C_2H_5\cdot + HCl \qquad (1\text{-}5)$$

It is suggested that the HCl produced at the temperature 125°C in this reaction represents from 35 to 40% of the concentration of atomic hydrogen[62].

Hydrogen atom concentrations have been estimated from the maximum destruction of HBr[65]. H atom concentrations have also been determined from the formation of HCN following the reactions with cyclic imines[66], formamide[67], and ethylenimine[63].

Volpi and Zocchi[68] suggested the determination of the atomic hydrogen concentration by chemical titration with excess ethylene. The stoichiometry of this reaction shows two hydrogen atoms consumed for each molecule of saturated hydrocarbons (CH_4, C_2H_6, C_3H_8) formed. More recently, Purnell et al.[60] compared the NOCl titration method with the ethylene reaction. They found that values determined by the ethylene method were greater by about 10%.

3. CHEMICAL REACTIONS OF ATOMIC HYDROGEN

(A) The Reaction with Paraffins

i) Methane

The kinetics of the reaction of H atoms with CH_4 have been studied by many workers during the past years. The reaction has been studied using most of the methods of gas-phase kinetics including: photochemical[69], flow discharge[70], flame[27,71], catalytic H-atom recombination[72], ESR[73] and inhibition-combustion studies[74,75,76].

Steacie[77] has reviewed values obtained prior to 1953, and arbitrarily selects an activation energy of about 12.5 kcal/mole with a steric factor of 0.1. Since then, numerous attempts have been made to measure the kinetic parameters for this reaction. The reported results fall into two distinct groups: (a) high activation energies (11 to 16 kcal/mole) with a correspondingly high pre-exponential factor, in the region 10^{14} $cc.mole^{-1}sec^{-1}$, and (b) low activation energies (4-8 kcal $mole^{-1}$) coupled with a low pre-exponential factor, in the region 10^{10}-10^{13} $cc.mole^{-1}sec^{-1}$. Table 1 presents sample data from various methods for various temperatures.

Walker et al.[76] have obtained the expression $k = (1.26 \pm 0.25) \times 10^{14}$ $\exp(-11{,}900 \pm 400/RT)$ $cc.mole^{-1}sec^{-1}$ from a critical review of the available data.

Most workers now agree on the following mechanism for the H + CH_4 reaction.

$$H\cdot + CH_4 \longrightarrow CH_3\cdot + H_2 \qquad (1\text{-}6)$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \qquad (1\text{-}7)$$

ii) Ethane

Numerous investigations of the kinetics of the reactions of H atoms

TABLE 1

Summary of the Published Arrhenius Parameters

for the Methane Reaction

Temp. (°K)	E (kcal $mole^{-1}$)	$Log_{10}A$ ($cc.mole^{-1}sec^{-1}$)	Method	Ref.
372-436	4.5	10.0	tungsten filament	72
620-738	7.8	13.0	photolysis	69[a]
673-763	15.1	14.52	H_2/O_2 ignition	74
1220-1790	11.5	14.30	flame	27
883	$k = 2.9 \times 10^{10}$		H_2/O_2 ignition	75
500-803	7.4	11.78	discharge	70
900	$k = 4.0 \times 10^{10}$		flame	71
773	$k = 6.3 \times 10^{10}$		H_2/O_2 ignition	76
372-773	11.9	14.1	H_2/O_2 ignition	76
426-743	11.8	13.84	ESR	73

(a) refers to D + CH_4 reaction.

with C_2H_6 have been made. The kinetic parameters for this reaction are listed in Table 2.

The activation energies presented in Table 2 vary from 6.8 to 14.1 kcal $mole^{-1}$ and the pre-exponential factor from 3.43×10^{12} to 5.78×10^{14} $cc.mole^{-1}sec^{-1}$. Baldwin and Melvin[85] reviewed the values prior to 1964. By combining three sets of values[21,28,85] over a wide temperature range (30°-1280°C), they found $\log_{10} A = 14.12 \pm 0.15$ $cc.mole^{-1}sec^{-1}$ and $E = 9.71 \pm 0.58$ kcal $mole^{-1}$. By the addition of C_2H_6 to slowly reacting mixtures of H_2 and O_2 at 500°C, Baldwin et al.[26] calculated a value of $k = 2.01 \times 10^{11}$ $cc.mole^{-1}sec^{-1}$. This value closely agrees with a value[85] of $k = 2.36 \times 10^{11}$ $cc.mole^{-1}sec^{-1}$ at 500°C obtained from the parameters they calculated previously for the temperature range 30°-1280°C. Recently, Azatyan et al.[87,88], using ESR and EPR methods, found activation energies and pre-exponential factors of E = 9.1, 9.3 kcal $mole^{-1}$ and $\log_{10}A$ = 13.61, 14.05 $cc.mole^{-1}sec^{-1}$, respectively, which agree resonably well with Baldwin's results[85].

All the kinetic parameters were determined on the basis that the initial step was (1-8) and that it was the rate controlling step.

$$C_2H_6 + H\cdot \longrightarrow C_2H_5\cdot + H_2 \qquad (1-8)$$

iii) Propane, n-Butane, i-Butane

The kinetics of the reactions of hydrogen atoms with C_3H_8, n-C_4H_{10} and i-C_4H_{10} have been extensively studied. A summary of the kinetic parameters of these reactions based on (1-9) as the primary step is given in Table 3. (RH represents a paraffin)

$$RH + H\cdot \longrightarrow R\cdot + H_2 \qquad (1-9)$$

TABLE 2

Summary of the Published Arrhenius Parameters for the Ethane Reaction

Temp. (°K)	E (kcal mole^{-1})	Log$_{10}$A (cc.mole^{-1}sec^{-1})	Method	Ref.
298	9.0 ± 0.2	-	discharge	78
353-436	6.8	12.53	tungsten filament	79
297-478	9.0	14.4	photolysis	21[a]
682-823	12.0	13.17	H_2/O_2 ignition	80
773-898	14 ± 1	14.76	H_2/O_2 ignition	81
683-823	12.2	14.52	H_2/O_2 ignition	82
993-1433	9.7 ± 2	14.1	flame	28
323-523	9.0	13.5	radiolysis	83
303-1553	9.9 ± 0.2	14.20 ± 0.1	H_2/O_2 ignition	84
304-1500	9.71 ± 0.58	14.12 ± 0.25	H_2/O_2 ignition	85
1025-1190	6.20	13.6	H_2/O_2 ignition	86
290-509	9.1	13.61	ESR	87
290-579	9.3	14.05	EPR	88

(a) refers to D + C_2H_6 reaction.

TABLE 3

Summary of the Published Arrhenius Parameters for C_3H_8, n-C_4H_{10} and i-C_4H_{10} Reactions

Temp. (°K)	E (kcal $mole^{-1}$)	$Log_{10}A$ (cc.$mole^{-1}sec^{-1}$)	Method	Ref.
		Propane		
298	8.0	0.1[b]	discharge	89[a]
300-500	7.2	14.5	photolysis	21[a]
683-823	8.5	13.43	H_2/O_2 ignition	80
773-898	8.3 ± 1	13.56	H_2/O_2 ignition	81
683-823	8.4	13.80	H_2/O_2 ignition	82
330-490	7.4	13.70	radiolysis	90
368-443	8.2	14.12	tungsten filament	91
301-793	7.83 ± 0.78	13.8 ± 0.37	H_2/O_2 ignition	92
853-953	7.8	13.73	H_2/O_2 ignition	93
300-752	8.35	14.16	H_2/O_2 ignition	94
		Normal Butane		
298	8.9	0.1[b]	discharge	89
298	7.9	0.1[b]	discharge	89[a]
300-500	7.1	14.5	photolysis	21[a]
323-523	6.7	13.3	radiolysis	83
343-443	7.1	13.82	tungsten filament	95
300-793	7.5 ± 0.5	13.9 ± 0.2	H_2/O_2 ignition	96
853-953	7.0	13.48	H_2/O_2 ignition	93
300-753	8.5	14.41	H_2/O_2 ignition	94

TABLE 3 (Continued)

Temp. (°K)	E (kcal $mole^{-1}$)	$Log_{10}A$ (cc.$mole^{-1}sec^{-1}$)	Method	Ref.
		iso - Butane		
298	9.3	0.1^b	discharge	97
300-500	6.3	14.5	photolysis	21^a
683-823	6.1	13.47	H_2/O_2 ignition	80
773-898	5.6 ± 1	12.89	H_2/O_2 ignition	81
683-823	5.1	12.76	H_2/O_2 ignition	82
323-523	5.1	13.1	radiolysis	83
300-793	6.8 ± 0.5	14.0 ± 0.2	H_2/O_2 ignition	96
300-753	7.25	14.12	H_2/O_2 ignition	94

(a) refers to D atom reactions.

(b) steric factor

iv) Other Paraffins

Previous to 1958, only a few studies were reported of the reactions of hydrogen atoms with n-C_5H_{12}[89], neo-C_5H_{12}[78] and n-C_6H_{14}[89,98]. This was probably because of the large number of products and possible side reactions present in these reactions. The reactions were so complicated that a reliable determination of the primary step was almost impossible at that time. Since 1958, there have been no investigations of the reaction of hydrogen atoms with paraffins containing more then 4 carbon atoms.

(B) The Reaction with Olefins

When atomic hydrogen reacts with olefinic hydrocarbons, excited alkyl radicals are formed. The subsequent unimolecular dissociation of these radicals has been the subject of extensive experimental and theoretical studies[99].

i) Ethylene

The kinetics and mechanism of the reaction of hydrogen atoms with ethylene have been extensively studied. Cvetanović[100] and Thrush[101] have reviewed the situation up to 1965, noting the conflicting results which have been obtained. It is generally agreed that the first step in this reaction is the addition of the H atom to form C_2H_5. The C_2H_5 radical so formed would be highly vibrationally excited and could contain up to 39.6 kcal mole^{-1} excess energy[99]. This radical may do one of two things: (1) it may decompose into the starting materials, (2) it may be deactivated by collisions and the resulting stabilized radical undergo further reaction. The following mechanism[51,60,102] for the H + C_2H_4 reaction has been accepted by most workers:

$$H\cdot + C_2H_4 \rightleftarrows C_2H_5^{\cdot *} \xrightarrow{M} C_2H_5^{\cdot} \qquad (1\text{-}10)$$

$$H\cdot + C_2H_5^{\cdot} \rightleftarrows C_2H_6^{**} \longrightarrow 2CH_3^{\cdot} \qquad (1\text{-}11)$$

$$H\cdot + CH_3^{\cdot} \rightleftarrows CH_4^{*} \xrightarrow{M} CH_4 \qquad (1\text{-}12)$$

$$CH_3^{\cdot} + CH_3^{\cdot} \rightleftarrows C_2H_6^{*} \xrightarrow{M} C_2H_6 \qquad (1\text{-}13)$$

$$CH_3^{\cdot} + C_2H_5^{\cdot} \longrightarrow C_3H_8 \qquad (1\text{-}14)$$

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow n\text{-}C_4H_{10} \qquad (1\text{-}15)$$

The kinetic data, determined by various workers, for the primary step in the H + C_2H_4 reaction are listed in the Tables 4, 5, 6. Since this reaction is found to be dependent upon experimental conditions (eg. pressure, concentration, reactants etc.), an attempt has been made to outline the conditions under which the values presented have been determined.

The rate constant determinations may be divided into two groups depending upon total pressure used: (a) high pressure conditions (above 5 torr) with $[C_2H_4] >> [H]$ at room temperature (Table 4), (b) k_1 as determined at low pressures (0.3 to 5 torr), various $[C_2H_4]/[H]$ ratios and room temperature (Table 5).

The activation energy and pre-exponential factor of the reaction (1-10) have been studied by various workers and their results are presented in Table 6. The two largest values (E = 6.6 and 7.2 kcal mole^{-1})[81,110], based on the rather indirect approach of determining the effect of small concentrations of C_2H_4 on the first explosion limit of the H_2 - 0_2 reaction, are considered to be much too large. The value E = 3.18 kcal·mole^{-1} was calculated by Baldwin et al.[111] based on a combination of the results of Yang[24] and Jennings[13].

The abstraction reaction of hydrogen atoms with C_2H_4

$$H\cdot + C_2H_4 \longrightarrow C_2H_3^{\cdot} + H_2 \qquad (1\text{-}16)$$

$$H\cdot + C_2H_3^{\cdot} \longrightarrow C_2H_2 + H_2 \qquad (1\text{-}17)$$

TABLE 4

Summary of the Published Rate Constants for the Ethylene Reaction at Room Temperature and High Pressure

$k \times 10^{-11}$ ($cc.mole^{-1} sec^{-1}$)	Pressure Range (torr)	Method	Ref.
6.0	435 ($n\text{-}C_4H_{10}$)	competitive	13
5-6[a]	∞ (He)	atomic fluoresence	45
5.30 ± 0.84	6.56(He)	mass spectrometric	40
6.00	75(He)	fluoresence	47
2.20[a]	∞ (He)	ESR	51
1.40[a]	∞ (Ar)	ESR	51
8.43	24.4(He)	mass spectrometric	104
1.5	16(Ar)	discharge	60
5.48 ± 0.54	700-1500(He)	atomic fluoresence	103
8.19 ± 1.15[b]	∞ (He)	atomic fluoresence	105
7.23 ± 0.60	500(He)	atomic fluoresence	106
1.63	high pressure	calorimetric	107
6.93	100(CO_2)	photolysis	19
2.5	> 305(C_2H_6)	competitive	108

(a) refers to the extrapolated values from low pressures (5 torr and 2 torr).

(b) refers to the extrapolated values from high pressure (500 torr).

TABLE 5

Summary of the Published Rate Constants for the Ethylene Reaction at Room Temperature and Low Pressure

$k \times 10^{-11}$ ($cc.mole^{-1}sec^{-1}$)	Conditions (torr)	(concentration)	Method	Ref.
1.81	0.3-0.6(H_2)	$[H] \sim [C_2H_4]$	Wrede gauge	109
1.93 ± 0.10	2.1(He)	$[H] < [C_2H_4]$	atomic fluoresence	45
0.88	1.6-3.1(Ar)	$[H] > [C_2H_4]$	ESR	50
2.29	2.3(He)	$[H] \ll [C_2H_4]$	mass spectrometric	104
1.99 ± 0.60	5(He)	$[H] \ll [C_2H_4]$	atomic fluoresence	105
1.46	2.16(He)	$[H] \gg [C_2H_4]$	atomic fluoresence	102
2.34	1.51(He)	$[H] \ll [C_2H_4]$	atomic fluoresence	102

TABLE 6

Summary of the Published Arrhenius Parameters for the Ethylene Reaction

Temp. (°K)	E ($kcal\ mole^{-1}$)	$Log_{10}A$ ($cc.mole^{-1}sec^{-1}$)	Method	Ref.
329-513	1.9	12.9	competitive	24
823-923	6.6	13.26	H_2/O_2 ignition	81
843-933	7.2	12.95	H_2/O_2 ignition	110
813	3.18	13.47	H_2/O_2 ignition	111
285-405	3.3	13.43	calorimetric	8
293-600	1.6 + 0.8	13.27	mass spectrometric	104
298,525	0.5		ESR	51
303-478	1.5 ± 0.1	12.9	photolysis	19

was suggested by Wartenberg and Schultze[112] in order to explain the formation of C_2H_2 found in their products. Klemenc and Patat[113] also found C_2H_2. In 1961, Jennings and Cvetanović[13] studied the ratio of the abstraction and addition reactions at room temperature by a competitive method and obtained the value of zero. This was recently reinvestigated[22] with similar results. Dzantiev and Shishkov[114] found the ratio of these reactions to be 0.25 when the H atoms were produced by photolysis of H_2S. They explained this high ratio by the presence of hot H atoms produced in the photolysis. Baldwin et al.[111] found no evidence that H atoms abstract H atoms from C_2H_4 at room temperature. They found the rate constant of the abstraction reaction to be $k = 2.5 \times 10^{11}$ $cc.mole^{-1}sec.^{-1}$ at 813°C, the activation energy to be $E = 9.8$ kcal $mole^{-1}$ on the assumption that $\log_{10}A = 14$ $cc.mole^{-1}sec.^{-1}$, and the value of the ratio of addition to abstraction to be 12.4 at 580°C.

ii) High Carbon Olefins

Prior to 1969, a number of measurements had been made of the relative rates[12,13,22,24,90,115,116] of these hydrogen atom-olefin reactions. With the exception of three independent photochemical studies by Cvetanović and co-workers, the values obtained vary considerably (Table 7). By using mercury photosensitized decomposition of n-butane and observing the decrease in the rate of production of hydrogen in the presence and absence of olefins, Cvetanović et al.[13] measured the rates of addition of H to olefins relative to the rate of abstraction of H from the $n\text{-}C_4H_{10}$. In another group of reactions, Cvetanović et al.[12] used mercury photosensitized decomposition of H_2 in the presence of small amounts of C_2H_4 or mixed with an added olefin. They obtained the rates from a comparison of the yields of n-butane in the two cases. The third method used by Cvetanović et al.[22] involved the photolysis of H_2S at 2490Å, while the relative rates were determined from a comparison of the yield of H_2 from H_2S alone and the yield of H_2 when H_2S was mixed with an added olefin[22]. Very good agreement was found for the values obtained in these experiments. The relative rate constants obtained by Cvetanović et al. have been confirmed by Niki et al.[41], who used a fast flow discharge system coupled to a time-of-flight mass spectrometer. Table 8 gives the absolute rate constants determined by Niki et al., as well as those obtained by a number of other workers.

Recently, Michael and co-workers[106] studied the kinetics for the reactions of hydrogen atoms with olefins: (a) by obtaining the absolute rates using a fast flow discharge system similar to that of Niki et al.[41], and (b) by measuring the rates relative to the well-characterised H + C_2H_2 reaction. They employed a steady-state photolysis apparatus and Lyman α photometry for the determination of H atoms. Their studies again confirmed the results of Cvetanović et al. and Niki et al. (See Tables 7 and 8).

Two early determinations of the activation energy for H atom addition to C_3H_6 have yielded values of 2.6[117] and 5.0[21] kcal mole^{-1}. The first of these was based on an assumed steric factor of 10^{-2} and the second was determined from rate measurements at two temperatures (298° and 478° K). In 1971, Braun et al.[118] gave the value of 1.2 kcal mole^{-1} for the temperature range 177°-473°K, under conditions where there was no interference from abstraction, non-terminal addition, or decomposition of excited propyl radicals. Their results can be compared to the value of 1.5 kcal mole^{-1} of Scheer and Klein[119] obtained for the temperature range 77°-90°K. At the low temperature of 77°K, Reid and Hill[120] gave a value for the rate constant

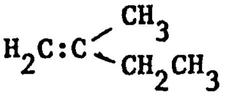
TABLE 7

Summary of the Published Relative Rates for High Carbon Olefin Reactions

Olefin/Reference	115, 116	24, 90	12, 13, 22	106
C_3H_6	1.00	1.00	1.00	1.00
C_4H_8-1			1.04	1.38 ± 0.43
C_5H_{10}-1			0.89	1.37 ± 0.43
iso-C_4H_8	0.48	9.52	2.52	3.60 ± 1.06
cis-C_4H_8-2	0.66	0.31	0.47	0.44 ± 0.11
trans-C_4H_8-2	0.52	0.35	0.59	0.57 ± 0.15
cis-C_5H_{10}-2			0.39	
trans-C_5H_{10}-2			0.44	
$(CH_3)_2C{:}CHCH_3$			1.03	
$(CH_3)_2C{:}C(CH_3)_2$	0.61	1.10	0.84	
1,3-C_4H_6		13.0	4.9	

TABLE 8

Summary of the Published Absolute Rate Constants (10^{11} cc.mole^{-1}sec^{-1}) for High Carbon Olefin Reactions

Olefin/Reference	41		107	47	121	8	118	122	106
C_3H_6	(4.6)[a]	6.2[b]	4.82		7.83		9.70		5.0
C_4H_8-1	8.3	8.3			9.04				6.8
C_5H_{10}-1									6.4
iso-C_4H_8	(4.2)	20		22.9		33.1			
cis-C_4H_8-2	4.8	4.1							3.9
tr-C_4H_8-2	5.4	4.6		6.02					4.3
$(CH_3)_2C{:}CHCH_3$	7.4	7.7							
$(CH_3)_2C{:}C(CH_3)_2$	7.0	8.6							
1,3-C_4H_6	(50)	32						17	
$CH_3HC{:}C(CH_3)_2$	7.8	9.2							
 $H_2C{:}C<^{CH_3}_{CH_2CH_3}$	(9.1)	21							

(a) in this column, the values in brackets are uncertain

(b) in this column, all the values refer to D atom reactions of 1.8×10^6 cc.mole^{-1}sec^{-1} for H-atom addition to C_3H_6. This value is in good agreement with the value of the lower rate limit of 2.0×10^6 cc.mole^{-1}sec^{-1} estimated by Scheer and Klein[119]. With the exception of work by Yang[24,90] (Table 7), no experimental determinations of activation energies of olefins other than C_3H_6 have been reported. As may be seen in Table 7, the values reported by Yang vary considerably from those of other workers. The reason for this is not immediately clear, but the noticeable deviation tends to throw some doubt on the work.

Cvetanović and co-workers[13,22] determined the ratio $k_{H\text{-abstraction}}/k_{H\text{-addition}}$ to be 0.082, 0.093, 0.032, and 0.015 for C_3H_6, $1\text{-}C_4H_8$, iso-C_4H_8, and $1,3\text{-}C_4H_6$, respectively. In these results, the amount of the abstraction reaction never exceeded 10% of the total reaction at room temperature.

The addition of a hydrogen atom to an olefin results in the formation of a vibrationally excited alkyl radical. This excited radical can dissociate, forming either the original H atom and olefin or a new radical and olefin. It may also undergo collisional stabilization. The reaction of H atoms with olefins can be described by reactions (1-18) to (1-20).

$$H\cdot + (\text{Olefin})_I \rightleftarrows R_1^{\cdot *} \qquad (1\text{-}18)$$

$$R_1^{\cdot *} \begin{array}{l} \longrightarrow R_2^{\cdot} + (\text{Olefin})_{II} \\ \xrightarrow[M]{} R_1^{\cdot} \end{array} \qquad (1\text{-}19)$$

$$H\cdot + (\text{Olefin})_I \longrightarrow H_2 + R_2^{\cdot} \qquad (1\text{-}20)$$

(C) The Reaction with Alkynes

i) Acetylene

Steacie[77] described several investigations of this reaction which were made prior to 1953. In particular, results obtained in flow systems indicate that acetylene is not consumed but that it merely promotes the recombination of hydrogen atoms. The various rate constants obtained to date for the reaction H + C_2H_2 are listed in Table 9. The values given by Wagner et al.[124] and Michael et al.[45] are considered to be most reliable. They studied the reaction over a wide pressure range and found a pressure dependence of the rate constant which has greatly assisted in establishing the mechanism of this reaction.

In 1967, Niki et al.[123] proposed the following reaction mechanism based on isotopic studies.

$$H + C_2H_2 \longrightarrow C_2H_3^{\cdot *} \qquad (1\text{-}21)$$

$$C_2H_3^{\cdot *} \xrightarrow{M} C_2H_3\cdot \qquad (1\text{-}22)$$

$$\dot{H} + C_2H_3^{\cdot} \longrightarrow C_2H_4^{*} \longrightarrow C_2H_2 + H_2 \qquad (1\text{-}23)$$

This mechanism has been confirmed recently by Wagner et al.[124] who found that, at high pressures (above 50 torr), most of the vibrationally excited vinyl radicals (excess energy $E \backsim 39$ kcal mole^{-1}) are deactivated to below the dissociation limit and can further react with H atoms. On the other hand, the vibrationally excited C_2H_4 in reaction (1-23) decomposes almost immediately and much higher pressures are required to stabilize this species.

The activation energy of the addition reaction H + C_2H_2 was first calculated by Le Roy and Dingle[125] over the temperature range 278°-372°K. Their values of $E = 1.5$ kcal mole^{-1} and $P = 4 \times 10^{-4}$ (steric factor) are in good agreement with those predicted by collision theory. From their studies over the temperature range 243°-473°K, Wagner et al.[124] found the expression $k_{1-21} = 2.3 \times 10^{12}$ exp(-2500/RT)cc.mole^{-1}sec^{-1} for the rate constant. They[126] also studied the reactions D + C_2H_2 and H + C_2D_2 over the temperature ranges 200°-469°K and 300°-470°K, respectively. They obtained the expressions

TABLE 9

Summary of the Published Rate Constants for the Acetylene Reaction at Room Temperature (units = 10^{10} cc.mole^{-1}sec^{-1})

Pressure/Reference (torr)	123	124[a]	45	3	125	37	109	68
0.5		0.35					8.1	
1.0	0.90	0.70	0.78					1.2
1.9		1.10	1.11					2.3
3.0		1.40	1.17					2.2
					0.81	1.10		
4.0		1.75						
4.7		2.00	1.24					
5.2			2.02					
8.6		2.35	3.90					
10.3		2.55	5.93					
15		2.90		5.0 ± 1.2[b]				
20		3.20						
30		3.35						
50		3.50						

(a) all values in this column were adopted from the Fig. 4 of Ref. 124.

(b) pressure range 1.0-15 torr.

$k = 3.1 \times 10^{13} \exp(-3700 \pm 200/RT)$ and $k = 2.0 \times 10^{13} \exp(-5300 \pm 500/RT)$ cc.mole^{-1}sec^{-1}, respectively, for each reaction.

ii) Methyl Acetylene

Methyl acetylene (C_3H_4) is the only other member of the alkyne group that has received attention. Thrush et al.[50] gave the rate constant $2.4 \pm 0.3 \times 10^{11}$ cc.mole^{-1}sec^{-1} for the H + C_3H_4 reaction at room temperature. They found that the rate constant was independent of pressure over the pressure range 0.9 to 2.4 torr. In 1970, Solomon et al.[127], using a fast flow discharge system coupled to a mass spectrometer, gave a value for the rate constant of approximately 10^{11} cc.mole^{-1}sec^{-1} at 283°K. The mechanism of the reaction is suggested to be similar to the H + C_2H_2 reaction and is given in steps (1-24) to (1-26).

$$H\cdot + C_3H_4 \rightleftarrows C_3H_5^{\cdot *} \qquad (1\text{-}24)$$

$$C_3H_5^{\cdot *} \xrightarrow{M} C_3H_5^{\cdot} \qquad (1\text{-}25)$$

$$H\cdot + C_3H_5^{\cdot} \longrightarrow H_2 + C_3H_4 \qquad (1\text{-}26)$$

(D) The Reaction with Halo-Hydrocarbons

i) Halogen-Substituted Paraffins

Work on these reactions has been reviewed thoroughly by Steacie[77], but few determinations of the kinetics for the various reactions have been made. In 1933, Chadwell and Titani[62] studied the reactions of hydrogen atoms with such saturated halohydrocarbons as CH_3F, CH_3Cl, CH_3Br, CH_3I, C_2H_5Cl and C_2H_5Br by product analysis. They produced their H atoms in a Wood's discharge flow system. Except for CH_3F, which was not found to react, they proposed a general reaction (1-27).

$$H\cdot + R_IX \longrightarrow HX + R_I^{\cdot} \qquad (1\text{-}27)$$

In the same year, Polanyi et al.[128] studied the reactions of atomic hydrogen with CH_3Cl, CH_3Br, CH_3I, C_2H_5I, CH_2Cl_2, $CHCl_3$ and CCl_4 by product analysis using a modified Wood's discharge tube system. In addition to reaction (1-27), they proposed the reaction (1-28) as also being important.

$$H\cdot + R_IX \longrightarrow H_2 + R_{II}X \qquad (1\text{-}28)$$

Both investigations gave values for the activation energies which are listed in Table 10.

Five years later, Vance and Bauman[129] investigated reaction (1-29).

$$H\cdot + CCl_4 \longrightarrow HCl + CCL_3^{\cdot} \qquad (1\text{-}29)$$

They determined the kinetic parameters by using a Wood's discharge flow system to produce H atoms and a calorimetric method to measure the atomic hydrogen concentration. They gave the activation energy and exponential factor as $E = 3.9$ kcal mole^{-1} and $\log_{10}A = 12.77$ cc.mole^{-1}sec^{-1} based on a steric factor of 7×10^{-3}. In 1965, Skinner and Ringrose[86] studied the reactions (1-30) and (1-31) by inhibition of the H_2-O_2 reaction at 970°-1300°K under shock-tube conditions.

$$H\cdot + CF_3Br \longrightarrow CF_3^{\cdot} + HBr \qquad (1\text{-}30)$$

$$H\cdot + 1,2\text{-}C_2F_4Br_2 \longrightarrow C_2F_4Br\cdot + HBr \qquad (1\text{-}31)$$

They gave the activation energies and exponential factors shown in Table 10. They proposed that the radical $C_2F_4Br.$ from reaction (1-31) can be attacked by hydrogen atoms as in (1-32).

$$H\cdot + C_2F_4Br\cdot \longrightarrow C_2F_4 + HBr \qquad (1\text{-}32)$$

They gave the kinetic parameters of the reaction (1-32) to be $E = 11.5$ kcal mole^{-1} and $\log_{10}A = 16.30$ cc.mole^{-1}sec^{-1}. It seems reasonable to suggest that the products of reaction (1-32) are produced by decomposition of vibrationally excited $C_2F_4BrH^*$.

Skinner and Ringrose[86] also obtained Arrhenius parameters for reaction (1-33) by studying the reverse reaction. The values are given in Table 10.

$$H\cdot + CF_3H \longrightarrow CF_3^{\cdot} + H_2 \qquad (1\text{-}33)$$

TABLE 10

Summary of the Published Arrhenius Parameters for the Halo-Hydrocarbon Reactions

Compound/Reference	62[a]	128[a]	131	86	54[c]	132	134	129
CH_3F	>9		3.91[a] 11.88[b]					
CH_3Cl	9	7.2					8.0[a] 14.49[b]	
CH_3Br	6.5	3.2			4.3[a] 13.73[b]		6.9[a] 14.55[b]	
CH_3I	<5	<4.5						
CF_4						43.7[a] 14.85[b]		
CF_3Br				17.5[a] 15.64[b]				
CCl_4		<3.3						3.9[a] 12.77[b]
$CHCl_3$		<4.3						
CH_2Cl_2		5.8						
C_2H_5Cl	8							
C_2H_5Br	6							
C_2H_5I		<4.5						
1,2-$C_2F_4Br_2$				14.5[a] 15.0[b]				
CF_3H				5.0[a] 12.70[b]				

(a) activation energy (kcal $mole^{-1}$).

(b) $log_{10}A$ (cc.$mole^{-1}sec^{-1}$).

(c) D atom reaction.

Clark and Tedder[130] studied the reactions of hydrogen atoms with the halo-methanes CCl_4, CCl_3Br, CCl_3D, CCl_3F, CCl_2HF and CCl_2HBr by product analysis using a discharge fast-flow system. They found that the first step in these reactions was the abstraction of a halogen atom as shown in (1-27). The resulting radical added H atoms to form a vibrationally excited molecule which was either stabilized or decomposed by elimination of HX. The elimination of the more stable HX was always favored. Table 11 gives their results for the relative rates of abstraction of different atoms from the same molecule.

TABLE 11

The relative rates of abstraction of different atoms from the same molecule.

Halomethane	Relative Rate Constant	Numerical Value
CCl_3F	k_F/k_{Cl}	0.21
CCl_3Br	k_{Br}/k_{Cl}	1.5
CCl_2HBr	k_{Br}/k_{Cl}	1.6
CCl_3D	k_D/k_{Cl}	3.3
CCl_2HBr	k_H/k_{Cl}	3.4

Parsanyan et al.[131] studied the reaction (1-34)

$$H\cdot + CH_3F \longrightarrow HF + CH_3^{\cdot} \qquad (1-34)$$

over the temperature range 858°-933°K using the flame method. The kinetic parameters obtained are given in Table 10. The values of the kinetic parameters (Table 10) for the reaction (1-35) were obtained by Kochubei

$$H^{\cdot} + CF_4 \longrightarrow HF + CF_3^{\cdot} \qquad (1-35)$$

and Moin[132] using a flow system over the temperature range 1323°-1523°K. Chadwell and Titani[62] found no reaction corresponding to (1-34) at room temperature and Dacey and Hodgins[133] found no reaction at 573°K as shown in (1-35).

Seidel[134] studied the reactions

$$H\cdot + CH_3Cl \longrightarrow HCl + CH_3^{\cdot} \qquad (1\text{-}36)$$

$$H\cdot + CH_3Br \longrightarrow HBr + CH_3^{\cdot} \qquad (1\text{-}37)$$

in crossed molecular beams at room temperature and gave the kinetic parameters shown in Table 10. Recently, Thrush et al.[54] studied the reaction

$$D\cdot + CH_3Br \longrightarrow DBr + CH_3^{\cdot} \qquad (1\text{-}38)$$

using a discharge flow system coupled with an electron paramagnetic resonance spectrometer over the temperature range 297°-480°K. They found that Seidel's value $k_{1-37} = 3.3 \times 10^9$ cc.mole^{-1}sec^{-1} at 300°K was an order of magnitude below their value $k = 3.20 \pm 0.5 \times 10^{10}$ at 297°K, possibly because Seidel's value was obtained with a long extrapolation and also because the activation energy refers only to relative translational energy. Thrush considered that the isotopic effect should not be greater than a factor of two, which would make Seidel's value still too high.

Scott and Jennings[14] investigated the mercury-photosensitized decomposition of C_2H_5F, 1,1-$C_2H_4F_2$ and 1,1,1-$C_2H_3F_3$. They proposed the reactions (1-39), (1-40) and (1-41), in each case using deuterium-labelling and the variation of product yields with light intensity

$$H\cdot + C_2H_5F \longrightarrow H_2 + CH_3CHF\cdot \qquad (1\text{-}39)$$

$$H\cdot + 1,1\text{-}C_2H_4F_2 \longrightarrow H_2 + CH_3CF_2^{\cdot} \qquad (1\text{-}40)$$

$$H\cdot + 1,1,1\text{-}C_2H_3F_3 \longrightarrow H_2 + CH_2CF_3^{\cdot} \qquad (1\text{-}41)$$

The major products in each case arose from radical combination and disproportionation. They also found that after the abstraction of an H atom, the resulting radical usually added an H atom to form a vibrationally excited molecule which decomposed by elimination of HF rather than stabilize by collision.

Table 10 summarizes the various kinetic parameters obtained for the haloparaffin reactions. Because of rather large discrepancies and a general lack of information, comparison of the values is difficult.

ii) Halo-Substituted Ethylenes

Little attention has been given to the reaction of hydrogen atoms with halogen-substituted ethylenes. In an early investigation, Melville and Robb[11] obtained a collision efficiency of 0.3×10^{-4} and $< 10^{-4}$ for the reaction of hydrogen atoms with tetrafluoroethene and tetrachloroethene respectively, by using the molybdenum oxide method.

In 1968, Rennert and Wijnen[18] studied the reaction of hydrogen atoms with C_2H_3Cl by photolyzing HI in the presence of C_2H_3Cl. The following reactions were suggested:

$$H\cdot + C_2H_3Cl \longrightarrow C_2H_4Cl\cdot^* \qquad (1\text{-}42)$$

$$H\cdot + C_2H_3Cl \longrightarrow C_2H_2Cl\cdot + H_2 \qquad (1\text{-}43)$$

$$H\cdot + C_2H_3Cl \longrightarrow C_2H_3^{\cdot} + HCl \qquad (1\text{-}44)$$

They also found the following ratios of rate constants, $\frac{k_{43}}{k_{42}} = 2.15$ and $\frac{k_{44}}{k_{42}} = 1.47$. Recently, Tanner and Jamieson[135] investigated the kinetics of the reaction of hydrogen atoms with C_2H_3Cl by using a Wood's discharge tube over the temperature range 305°-767°K. They gave the specific reaction rates for HCl production to be $3.6 \times 10^{11} \exp(-2750/RT)$ cc.mole^{-1}sec^{-1} and for C_2H_4 plus C_2H_6 production to be $1.8 \times 10^{11} \exp(-2800/RT)$. They found that the maximum yields of HCl at both 601° and 767°K exceeded the flow rates of atomic hydrogen, indicating that the reaction had limited chain characteristics.

Teng and Jones[136,137] studied the products formed in the reactions of hydrogen atoms with C_2F_4 and C_2HF_3 using a Wood's discharge tube. The determination of the reaction mechanism was complicated by the large number and types of products formed. Scott and Jennings[15] studied the products formed by the addition of hydrogen atoms to C_2H_3F, 1,1-$C_2H_2F_2$ and 1,1,2-C_2HF_3 using the mercury-photosensitization method. Hydrogen atoms have been shown to add largely or exclusively to the less fluorinated carbon of these fluoro-ethylenes. The major reaction products are formed by combination and disproportionation reactions of the resulting radicals. Less important products are formed by addition of H atoms to the original radicals forming vibrationally excited molecules which stabilize by collision or decompose by elimination of HF.

More recently, Penzhorn and Sandoval[17] studied the addition and abstraction reactions of thermal hydrogen atoms with fluorinated ethylenes using a photolysis method. They found that the relative rates of addition are cis-$C_2F_2H_2$:C_2FH_3: C_2H_4: trans-$C_2F_2H_2$: 1,1-$C_2F_2H_2$: C_2F_3H: C_2F_4 as 1.00: 1.12: 1.43: 1.67: 2.08: 2.36: 2.42, while those for abstraction are C_2FH_3: C_2F_3H; cis-$C_2F_2H_2$: trans-$C_2F_2H_2$: 1,1-$C_2F_2H_2$ as 1.00: 1.78: 1.94: 3.61: 6.60. They suggested the steps (1-45) to(1-47) as the mechanism for these reactions. In each case, they assumed that both k_{45} and $k_{46} \gg k_{47}$.

$$H\cdot + C_2F_xH_y \longrightarrow C_2F_xH^{\bullet}_{y+1} \tag{1-45}$$

$$H\cdot + C_2F_xH_y \longrightarrow C_2F_xH^{\bullet}_{y-1} + H_2 \tag{1-46}$$

$$H\cdot + C_2F_xH_y \longrightarrow C_2F_{x-1}H^{\bullet}_y + HF \tag{1-47}$$

A review of the literature reveals that, except for the work of Jamieson et al.[135], there are almost no measurements of the absolute rate constants or kinetic parameters of the reactions of hydrogen atoms with halogen-substituted ethylenes.

4. THE PRESENT INVESTIGATION

An examination of the literature reveals that although some studies have been made of the hydrogen atom reactions with the fluoroethylenes by photosensitization in static systems[15,17], little work has been done on these reactions in flow system[136].

The present investigation involved the study of the three reactions: $H + C_2H_4$, $H + C_2H_3F$, $H + 1,1\text{-}C_2H_2F_2$ for three temperatures under identical conditions. Computer techniques were applied, using known rate constants where possible, in order to build up and test mechanisms for the reactions. By this study, it was possible to obtain values for those rate constants not previously known and to determine activation energies for each step in each reaction mechanism.

CHAPTER II

EXPERIMENTAL

1. MATERIALS

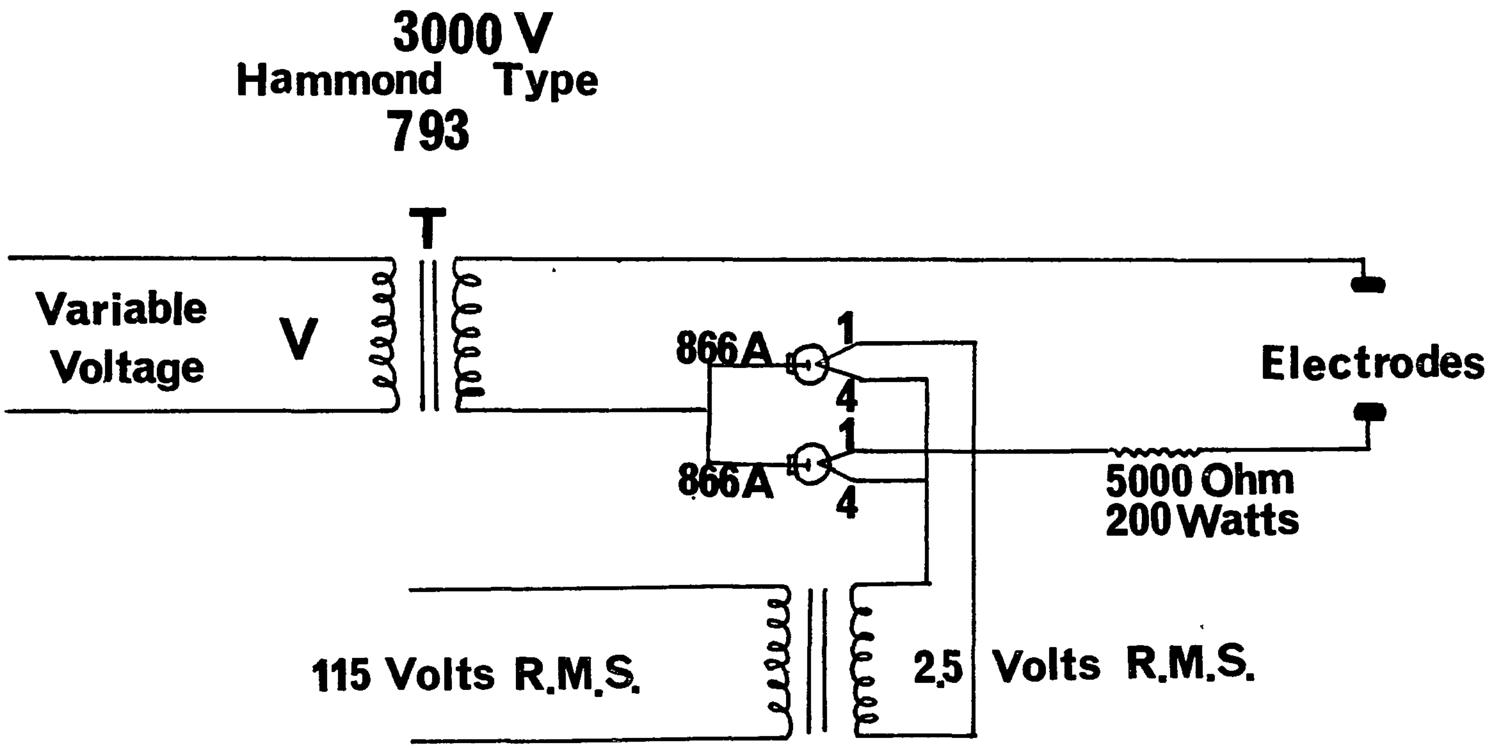
Hydrogen and helium were supplied by Canadian Liquid Air Limited. Hydrogen was purified by passing through a Fisher Scientific Co. Deoxo unit. Helium was purified by passing through a gas purifier containing molecular sieve 5A. Methane, ethane, ethylene, propane, n-butane, propylene, vinyl fluoride, 1,1-difluoroethylene and acetylene were obtained from Matheson Co. of Canada Limited. Purification was made by bulb-to-bulb distillation, discarding the first and last third of each distillation. Negligibly small amounts of impurities were detected in the purified gases. The ethyl chloride was supplied by Ingram and Bell Limited. Syrupy orthophosphoric acid was obtained from Mallinckrodt Chemical Works Limited. Squalane was obtained from Chromatographic Specialties Limited. Silica gel (mesh size 28-200) was obtained from W. Grace Chemical Limited.

2. DISCHARGE SYSTEM

The electrical circuit for the d.c. discharge is shown in Figure 1. The voltage from a powerstat variable transformer, T, as indicated on the voltmeter, V, was applied to the primary of a 3000 volt Hammond transformer. The alternating current was rectified by two half wave rectifier tubes (866-A) connected in parallel. The d.c. current produced was supplied to the discharge tube through a 5000 ohm, 200 watt resistor. With 74 volts across the primary of the transformer, and 1.1-1.2 torr of hydrogen, a stable discharge and a stable production of hydrogen atoms were obtained.

Figure 1

Electrical Circuit for D.C. Discharge

3000 V
Hammond Type
793
T
Variable
Voltage
V
866A
1
4
866A
1
4
Electrodes
5000 Ohm
200 Watts
115 Volts R.M.S.
2.5 Volts R.M.S.

3. APPARATUS

(A) Reaction System

The fast-flow discharge system used in this work was a typical Wood-Bonhoeffer discharge tube system similar to that used for the production of active nitrogen by Winkler and co-workers[138]. A diagram of the apparatus is shown in Figure 2.

Hydrogen from a cylinder was passed through a Deoxo unit and admitted to the reaction system through an adjustable manostat, M, containing dibutyl phthalate. The level of the liquid could be varied in order to give a constant pressure of hydrogen despite fluctuation in atmospheric pressure. From the manostat, M, the hydrogen passed through a furnace, F, and liquid nitrogen trap, T_p. The furnace and liquid nitrogen trap were provided for further purification of the hydrogen. A calibrated capillary flowmeter F_1 was used to control the hydrogen flow rate. The actual flow rate was determined from the rate of evacuation of the known volume, V_1 (1120.1 cc.). From the flowmeter, F_1, the hydrogen passed into both ends of the discharge tube made of Pyrex glass tubing, 35 cm long and 22 mm o.d., and containing an aluminum electrode at each end.

As mentioned earlier, hydrogen atoms can be produced by electrical discharge in hydrogen gas. It was first shown by Wood[2] that hydrogen atoms could be pumped out of a hydrogen glow discharge and carried for considerable distances before they recombine. He found, that in order for the experiment to be successful, it was essential that the walls of the reaction tube be "poisoned" in order to slow down the recombination of the atoms. This could be accomplished by admitting a trace of water vapor to the hydrogen or by coating the wall with a poison such as phosphoric acid.

Chadwell and Titani[62] found that the addition of traces of water to the hydrogen can introduce serious errors, due to the reactivity of the O atoms and OH radicals produced. Larkin and Thrush[139] also found that the molecular oxygen formed can catalyze hydrogen atom removal as well as react with any free radicals produced.

Therefore, it appeared that a wall poison was most suitable. Thus, the present apparatus was coated with syrupy-phosphoric acid from just below the electrodes to beyond the exit of the reaction vessel, V.

The reaction vessel, V, was made of Pyrex tubing, 65 cm long and 25mm o.d. with a 40/50 ground joint at the bottom to permit the introduction of the wall poison. A reaction jet, J, was placed in the center of the gas stream, 19 cm below the inlet from the discharge tube. This jet was a bulb with four holes spaced at equal distances around its circumference. This design has been proven best for reactant gas introduction (see diagrams reference 140). A constriction was provided above the reaction jet to prevent any back diffusion of the reactants into the discharge tube. The pressure was measured with a tilting McLeod gauge connected at S_m.

In order to vary the reaction temperature, the reaction vessel was surrounded by a furnace. A Chromel-Alumel thermocouple was used for temperature measurement and the E.M.F. produced was measured by a Leeds and Northrup 7645 Potentionmeter. The thermocouple was attached to the surface of the reaction vessel adjacent to the reaction jet. Three temperatures, 30°, 230°, and 330°C were used in this work.

An exit tube which connected the reaction vessel with two traps, T_1 and T_2, was located just above the ground joint in the main reaction vessel.

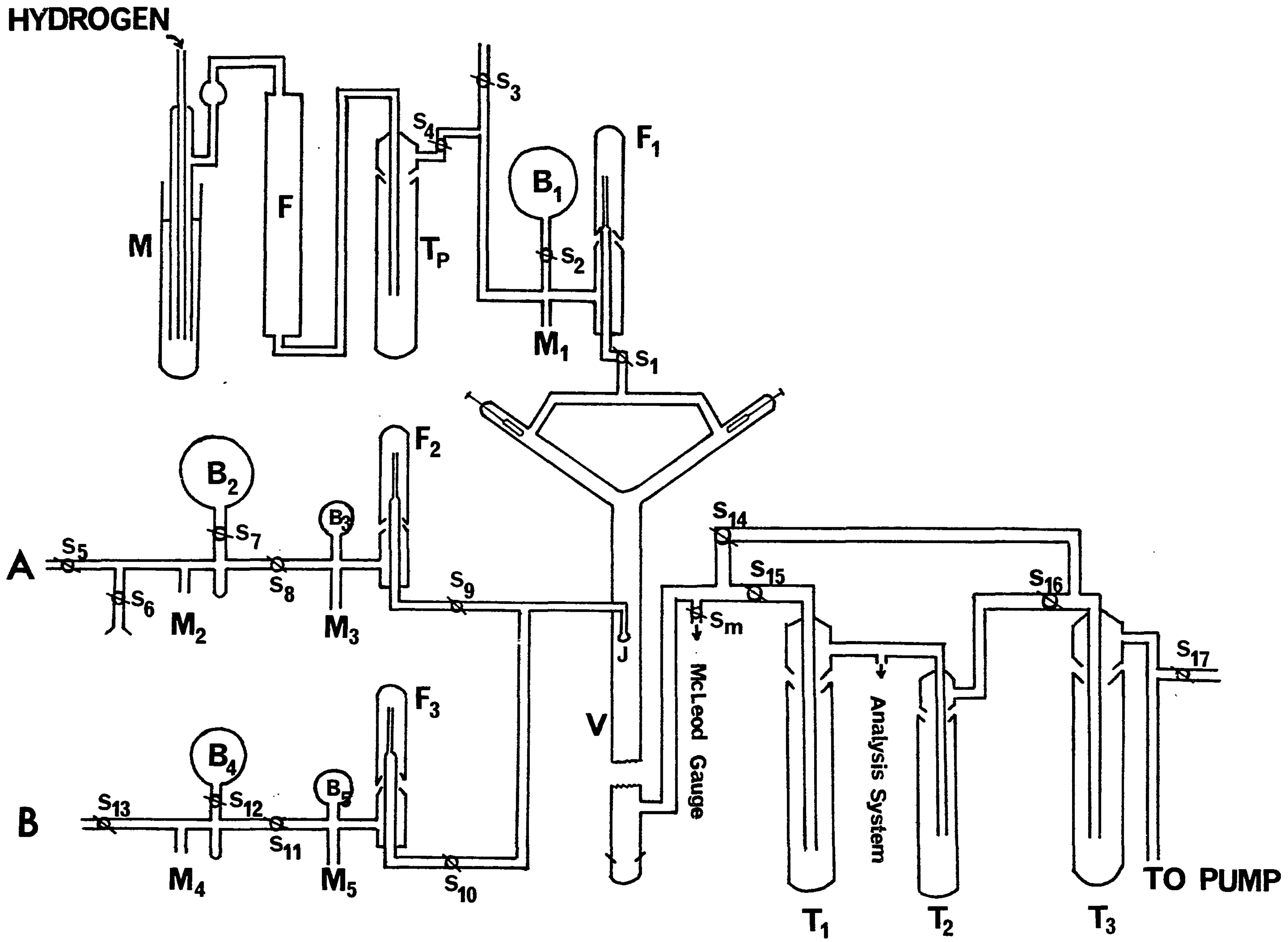
The traps were normally immersed in liquid nitrogen in order to trap the reaction products. In order to trap the methane produced in the reaction, the second trap, T_2, was lined with silica gel supported on silicone grease. The third trap, T_3, was installed to protect the vacuum pump and was always surrounded by liquid nitrogen. In order to allow equilibrium flow conditions to be reached before trapping of the products occurred, an alternate flow line was provided around the two traps, T_1 and T_2, through stopcock, S_{14}. Thus, only those products produced during the desired reaction time were trapped. Reaction products trapped in traps, T_1 and T_2, could be distilled directly into the analysis system (see Figures 2 and 3).

Two gas flow control systems, A and B, similar to that for hydrogen, were used to admit the reactant to the reaction vessel. The reactant entered the reaction jet by stopcocks, S_9 and S_{10}. The capillary size in the flow meters, F_2 and F_3, was adjusted in order that one system provided high flow rates of reactant while the other provided low flow rates. Each flow system consisted of a known volume, B_2 or B_4 (1097.7 or 596.17 cc.), a ballast volume, B_3 or B_5 (approximately 120 cc.), a capillary flowmeter, F_2 or F_3, and two manometers, M_2 and M_3, or M_4 and M_5. The known volume, B_2 or B_4, contained the reactants, as did the ballast volume. The pressure of the reactants involved in the reaction was kept constant by manipulating the scratched stopcock, S_8 or S_{11}. All three flow systems were connected to the vacuum pump through the stopcocks, S_3, S_5 and S_{13}, by an auxillary line (not shown in the figure).

The pump, a two stage Cenco Hypervac 23, gave an ultimate vacuum of 2 microns.

Figure 2

Diagram of Reaction System


HYDROGEN
M
F
T_P
S_4
S_3
B_1
S_2
M_1
F_1
S_1
A
S_5
S_6
M_2
B_2
S_7
S_8
B_3
M_3
F_2
S_9
J
V
B
S_{13}
M_4
B_4
S_{12}
S_{11}
B_5
M_5
F_3
S_{10}
S_{14}
S_{15}
S_m
McLeod Gauge
S_{16}
Analysis System
S_{17}
T_1
T_2
T_3
TO PUMP

(B) Analysis System

The analysis system consisted of a gas chromatograph, an associated gas sample introduction system and a sample collection system. A schematic diagram of the apparatus is shown in Figure 3.

i) Gas Chromatograph (Figure 4)

The gas chromatograph, a Hewlett-Packard 5750 Research Gas Chromatograph, was designed to take full advantage of a dual column, multi-detector, programmable, highly automated system to provide the analyst with maximum versatility, sensitivity, reproducibility, and ease of operation. A simple block diagram of this chromatograph is shown in Figure 4. The chromatograph contained two columns, two detectors and a programmable temperature control system. The chromatograph was fitted with both dual thermal conductivity and dual flame ionization detectors, the thermal conductivity detector being used for this work. Two equally-dimensioned columns were filled with identical packing and the carrier gas flows were balanced so that the bleed signals were equal and increased at the same rate with temperature. The column used for all measurements in this work was similar to that of Pritchard et al.[141]. It consisted of a 1/4 inch copper tube 24 feet in length and packed with 3% squalane on silica gel.

ii) Sample Introduction System (Figures 3 and 5, A, B, C)

The sample introduction system was built from two Varian six way linear gas sampling valves (identified as I and II in Figure 5). These valves were connected in such a way as to maintain a constant flow of helium regardless of the position of either valve. By proper positioning of the two valves, either calibration gas samples from the standard volume or samples of reaction mixtures from the collection loop may be introduced into the gas chromatograph. Included in the sample introduction

Figure 3

Schematic Diagram of Analysis Apparatus

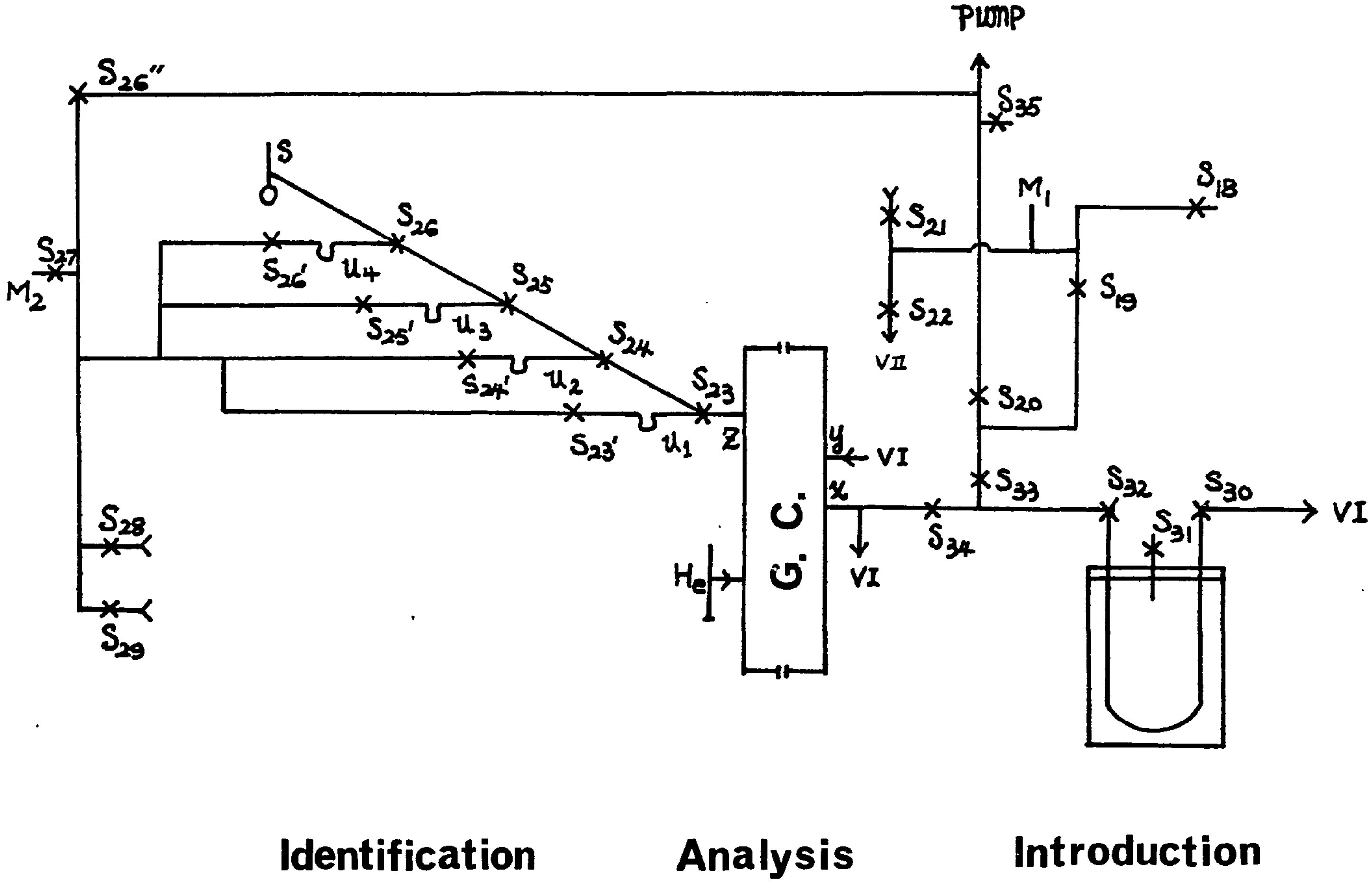

PUMP
S26''
S35
S
S26
M1
S18
S21
S27
M2
S26'
u4
S25
S22
S19
S25'
u3
S24
VII
S24'
u2
S23
S20
S23'
u1
Z
y
VI
x
S33
S32
S30
VI
S28
S34
S31
He
G. C.
VI
S29
Identification
Analysis
Introduction

Figure 4

Block Diagram of Hewlett-Packard 5750

Research Gas Chromatograph

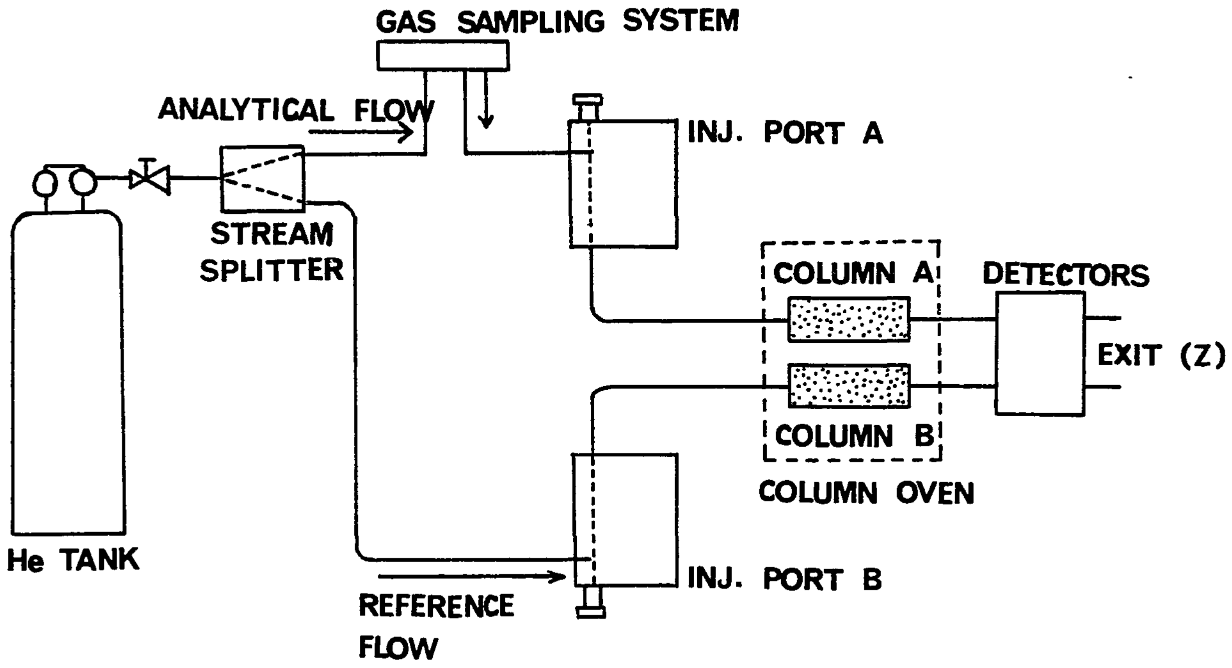

GAS SAMPLING SYSTEM
ANALYTICAL FLOW
INJ. PORT A
STREAM
SPLITTER
COLUMN A
DETECTORS
EXIT (Z)
COLUMN B
COLUMN OVEN
He TANK
INJ. PORT B
REFERENCE
FLOW

Figure 5

Diagram of Sample Introduction System

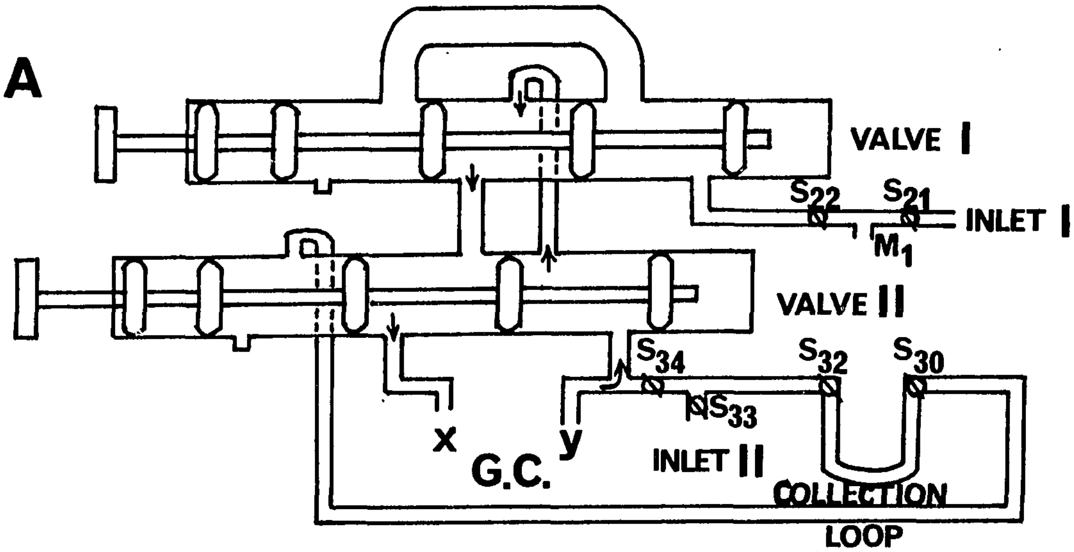
Inlet I - to admit calibration gases to standard volume.

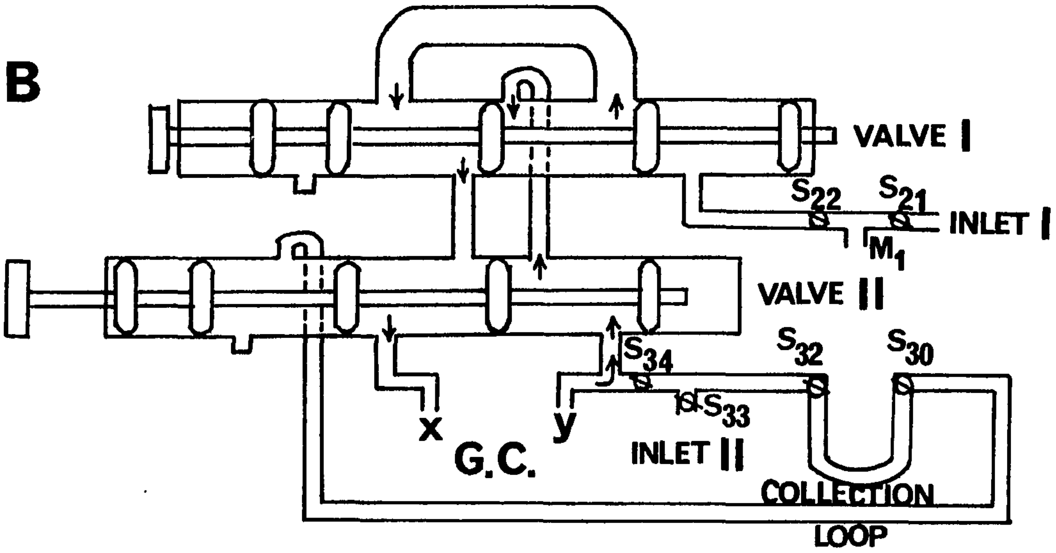
Inlet II - to admit samples from reaction to collection loop.

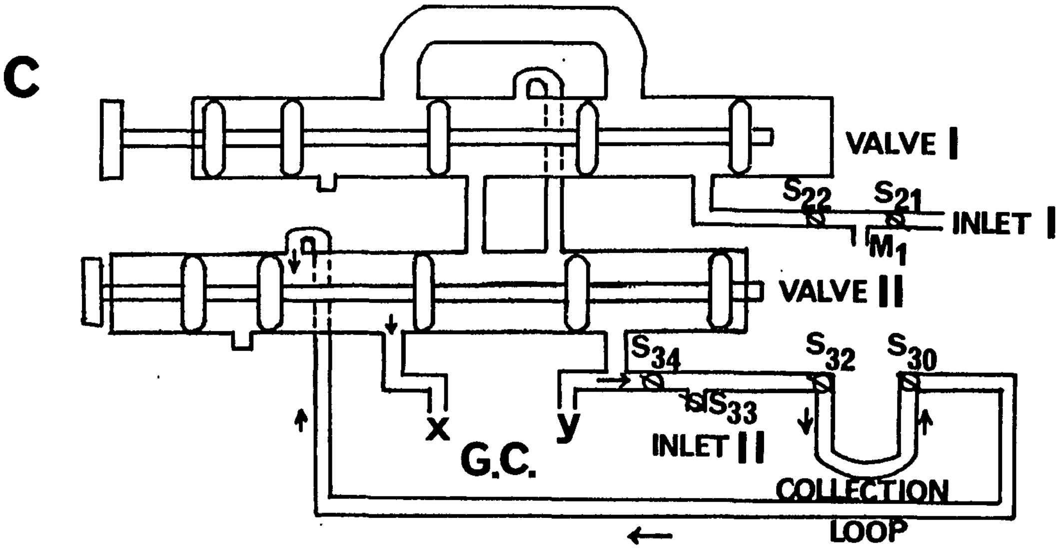
5A - Preparation stage - samples may be admitted to collection loop or standard volume while a continuous flow of He is maintained.

5B - Action stage I - admission of calibration gas from sample volume to gas chromatograph.

5C - Action stage II - admission of reaction sample from collection loop to gas chromatograph.


A
VALVE I
S22
S21
INLET I
M1
VALVE II
S34
S32
S30
S33
x
y
G.C.
INLET II
COLLECTION
LOOP


B
VALVE I
S22
S21
INLET I
M1
VALVE II
S34
S32
S30
S33
x
y
G.C.
INLET II
COLLECTION
LOOP


C
VALVE I
S22
S21
INLET I
M1
VALVE II
S34
S32
S30
S33
x
y
G.C.
INLET II
COLLECTION
LOOP

system are five on-off (flip-flop) Hoke valves, S_{22}, S_{30}, S_{32}, S_{33}, S_{34}, one glass stopcock, S_{21}, and a mirror backed manometer, M_1. Inlet I (Figure 5) was connected to either vacuum pump (S_{19} and S_{20}, Figure 3) or to a source of calibration gas. Inlet II was connected to either a vacuum pump (S_{20}, Figure 3) or to the reaction system (S_{19} and S_{18}, Figure 3).

The normal position of the two valves I and II is shown in Figure 5A. Helium from the gas chromatograph entered at Y and exited to the gas chromatograph at X as indicated by arrows. The positions of X and Y in relation to the gas chromatographic flow are shown in Figures 3 and 4.

With the valves positioned as in Figure 5A, samples could be admitted to the standard volume or to the collection loop. In order to admit a calibration gas to the standard volume, the volume was evacuated through valve, S_{22}, and stopcock, S_{21}, and the chosen gas admitted through stopcock, S_{21}, and valve, S_{22}, to the desired pressure as measured on manometer, M_1. After introduction of the calibration sample to the standard volume, the sample was injected into the gas chromatograph by closing (i.e. pushing in) valve I as shown in Figure 5B, the arrows again showing the flow of gas. In order to collect samples from the reaction vessel, stopcock, S_{19}, and Hoke valves, S_{33} and S_{32}, were opened, valves, S_{34} and S_{30}, were closed. The collection loop was first evacuated through stopcock, S_{20}, and then connected directly to the reaction vessel by stopcock, S_{18} (Figure 3). The reaction products in traps, T_1 and T_2 (Figure 2), were distilled (via S_{18}, S_{19}, S_{33}, and S_{32}) directly into the collection loop. The collection loop was made from 1/4" stainless steel which could be immersed in a dewar of liquid nitrogen. This dewar was sealed by a rubber stopper and connected to a vacuum pump through stopcock, S_{31}. This allowed evacuation above the liquid nitrogen to ∽ 15mm, corresponding to a loop temperature of ∽ -220°C. At this temperature collection of CH_4 was complete. When distillation from the reaction system was complete valves, S_{32} and S_{33}, were closed and the loop allowed to come to room temperature. The gas in this loop was then injected into the gas chromatograph by closing valve II (Figure 5C) and opening valves, S_{34}, S_{32} and S_{30}, simultaneously.

iii) Sample Collection System (Figure 3)

In order to facilitate identification of specific peaks, the exit of the gas chromatograph (Z) was connected to a series of U-tubes, U_1, U_2, U_3 and U_4 (Figure 3). Up to four products could be collected during any set of experiments simply by varying the flow of He through the various U tubes immersed in liquid nitrogen. The excess helium was expelled to the atmosphere through stopcock, S_{28} or S_{29}. After sufficient sample was collected, it was distilled through stopcock, S_{28} or S_{29}, into an I.R. cell or mass spectrometer sample bulb. The various U-tubes were evacuated before distillation through stopcock, S_{26}, and the pressure measured on manometer, M_2. I.R. spectra were taken on a Perkin-Elmer 237-B grating instrument, while mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-110B or 21-103 Mass Spectrometer.

The sample collection chain ended in a bubble flowmeter, S, which provided a measurement of helium flow.

4. EXPERIMENTAL METHOD

(A) Reaction Procedure

At the beginning of each reaction run, the entire reaction system was evacuated to high vacuum and a check was made to insure that the system was leak tight. Hydrogen was introduced through the discharge tube by adjusting the manostat M to the proper position. The discharge was operated for about a half hour (primary voltage of 74 volts) in order to obtain a constant production of hydrogen atoms. During this pre-run time, the temperature of the reaction vessel was adjusted to the desired reaction temperature and the reactant, C_2H_4, C_2H_3F or $C_2H_2F_2$, was introduced through the stopcock, S_5 or S_{13} (Figure 2), into the chosen reactant control system. Reactant flow system A was used either to control high flow rate reactants or to admit C_2H_4 or C_2H_5Cl to determine the concentration of H atoms. The ethyl chloride was admitted through stopcock, S_6, from a small bulb surrounded by an ice-water mixture. Flow system B was fitted with a suitable capillary for low flow rates of reactant. During the pre-reaction period, a removable furnace jacket was placed around trap, T_2, in order to prevent any gas from being absorbed by the silica gel lining. Following this pre-reaction period, the heater jacket was removed from trap, T_2, and liquid nitrogen dewars placed around the traps. With the flow by-passing traps, T_1 and T_2, through stopcock, S_{14}, the reaction was started by opening stopcock, S_9 or S_{10}. The reactant pressure in the ballast volume, B_3 or B_5, was kept constant by manipulation of a scratched stopcock, S_8 or S_{11}. After several minutes, stopcock, S_{16}, was opened. This was followed by simultaneous opening of stopcock, S_{15}, and closing of stopcock, S_{14}. When the desired reaction time was reached, stopcock, S_{14}, was opened and S_{15} closed simultaneously. Stopcocks, S_9 or S_{10}, and S_8 or S_{11}, were closed and the discharge and hydrogen flow turned off immediately. The system was evacuated and stopcocks, S_{14} and S_{16}, were closed. The liquid nitrogen dewars were removed and the heater jacket, at a temperature of 200°C, was placed around trap, T_2, to de-gas the silica gel[142]. The gases were then distilled via S_{18}, S_{19}, S_{33} and S_{32}, into the collection loop (Figure 3).

(B) Analysis Procedure

The entire analysis system was evacuated to 1 micron or better as indicated on the McLeod gauge. The gas chromatograph oven temperature was adjusted to 140°C and the helium flow rate to 66.6 ml per min. The distillation of the sample into the collection loop and its introduction into the gas chromatograph have been described earlier. It was found that it took about one hour to complete distillation from traps T_1 and T_2.

Calibration of the gas chromatograph was made by peak height measurements of pure samples admitted through the standard volume loop on valve I. (Described earlier).

The flow rate of hydrogen atoms was determined from the reaction with C_2H_4 and the reaction with C_2H_5Cl. The products, CH_4, C_2H_6, C_3H_8 and n-C_4H_{10}, of the reaction H + C_2H_4, were analyzed by gas chromatography. The product HCl of the reaction H + C_2H_5Cl was determined by titration against standardized NaOH.

The inner and outer parts of a 34/45 joint were used to make the collection tube for the HCl. The inner portion was sealed off forming a small round bottom flask while the outer portion was connected to a stopcock and B_{10} joint. The B_{10} joint could be connected to the apparatus at

S_{21} (Figure 3). The tube, which contained 100 cc. of de-ionized distilled water, was pumped down to high vacuum and the water in the tube was frozen by immersing the tube in liquid nitrogen. HCl was distilled from traps, T_1 and T_2, through stopcock, S_{18}, and condensed on the frozen water in the titration tube. Upon completion of the distillation, the tube was removed and warmed to room temperature and the solution titrated in the lower portion of the tube (inner portion of joint). A full explanation of the determination of the concentration of atomic hydrogen will be discussed later.

CHAPTER III

RESULTS

1. QUALITATIVE RESULTS

(A) H Atom-C_2H_4, -C_2H_3F, and -1,1-$C_2H_2F_2$ Reactions

Over the temperature range 303°-603°K, the reactions of hydrogen atoms with the three compounds, C_2H_4, C_2H_3F and 1,1-$C_2H_2F_2$, gave the products shown below.

$H + C_2H_4$	$H + C_2H_3F$	$H +$ 1,1-$C_2H_2F_2$
CH_4	CH_4	CH_4
C_2H_6	C_2H_6	C_2H_6
C_3H_8	C_3H_8	C_3H_8
n-C_4H_{10}	n-C_4H_{10}	n-C_4H_{10}
	C_2H_4	C_2H_4
	C_3H_6	C_3H_6
	C_2H_2	C_2H_2
	HF	HF
		C_2H_3F

Except for HF, all the products were separated by gas chromatography on a 24 foot silica-gel squalane column. Identification of each product was confirmed by I.R. and mass spectroscopy. Although HF was detected by mass spectroscopy as a product of the latter two reactions, it was not quantitatively analyzed. This was because of the possibility of reaction, and subsequent loss, of the HF on the glass walls of the reaction system. It was also noted that the product trap, T_1, became etched after several reaction runs.

Table 12 shows the absolute and relative retention times for the reactants and products of these three reactions. Since all the trapped gases from each run were injected into the gas chromatograph at one time, only short run times (10 seconds) were used so that the gas chromatograph was not overloaded by excessive amounts of collected products. The results show that the errors arising from trapping for such short periods were always less than 5%.

(B) H Atom-C_2H_5Cl and H Atom-C_2H_4 Reactions for the Determination of Hydrogen Atom Flow Rates

The hydrogen atom flow rate was determined by reaction with ethyl chloride giving a titratable product HCl. The products from several H atom-C_2H_5Cl runs were injected into the gas chromatograph showing that the products, CH_4, C_2H_6, C_3H_8 and C_2H_4, were formed in the reaction. HCl and possible chlorocarbon-products could not be separated by the column.

The hydrogen atom flow rate was also determined from the products, CH_4, C_2H_6, C_3H_8 and n-C_4H_{10}, in the reaction with excess C_2H_4.

TABLE 12

Absolute and Relative Retention Times for Reactants and Products

Column: 24 ft., 1/4 in. copper tubing packed with silica-gel coated with squalane.

Carrier flow (He): 66.6 ml per min.

Filament current: 150 milliamperes

Column temperature: 140°C

Thermalconductivity oven temperature: 255°C

Compound	Absolute Retention time (min.)	Relative* Retention time
CH_4	7.2	1.20
C_2H_6	14.5	2.42
C_2H_4	19.6	3.27
1,1-$C_2H_2F_2$	20.5	3.42
C_3H_8	33.1	5.52
C_2H_2	34.1	5.68
C_2H_3F	37.1	6.18
C_3H_6	46.5	7.75
n-C_4H_{10}	59.0	9.83

*All values normalized to air = 6.0 min.

2. QUANTITATIVE RESULTS

The gas chromatograph was calibrated for each individual reactant and product of the three reactions studied. This was accomplished by injecting accurately known quantities of each gas into the gas chromatograph. Quantitative measurements were made by comparing sample peak heights to calibration curves. Examples of the calibration curves used for comparison are shown in Figures A1-A5 (Appendix A). These plots show peak height (cm.) versus amount of gas injected (μmole). Good linear plots were obtained for each gas and the calibrations are considered accurate to ± 5%.

The experimentally determined flow rates were compared to expected flow rates calculated from a proposed mechanism of the reaction. This calculation was accomplished with the aid of a computer program which integrated numerically the simultaneous differential equations derived from the mechanism. The program used a modified 4th order Runge-Kutta-Gill process to integrate the equations. From the initial flow rate of hydrogen atoms (F_H) and the initial flow rate of reactant (F_R) at $t = 0$, the program calculated the amounts of products formed up to the time when 99.9% of either of the two reactants was used. It is only necessary to supply values for the rate constants corresponding to each step in the mechanism. However, it must be assumed that no radical concentration gradients, for any of the reacting species, occur in the system.

For convenience, all calculations were made using flow rate units rather than concentration units. This results in the unit, μmole^{-1}, for the second order rate constant. In order to obtain the normal units, cc.mole^{-1} sec^{-1}, a conversion factor obtained by multiplying the linear flow rate (L) by the area of reaction vessel (A) was used. In the H atom-C_2H_4 reaction at 303°K, where L = 375 cm.sec^{-1} and A = 4.91 cm^2, 1 μmole·sec^{-1} equaled 5.43×10^{-10} mole·ml^{-1}. Unimolecular rate constants are unaffected by this change of units, sec^{-1}, remaining appropriate. Using these units, calculated product flow rates were given directly in μmole·sec^{-1} and were thus immediately comparable with the experimental results. The computer calculations were performed on the CDC 6400 Computer.

(A) H Atom-C_2H_4 Reaction

In agreement with previous workers[60,77,143,144], the products CH_4, C_2H_6, C_3H_8 and n-C_4H_{10} were found at each of the three temperatures studied. The molecular hydrogen flow rate was 90.90 μmole·sec^{-1}. The ethylene flow rates varied from 0.84 to 17.00 μmole·sec^{-1}. The total pressure was 1.20 torr for all runs. The maximum linear flow rate of this reaction was calculated to be 375.3, 623.0 and 746.9 cm.sec^{-1} at 303°, 503° and 603°K, respectively. Computer calculations show that the maximum reaction times were 6.71, 5.87 and 5.87 msec., at 303°, 503° and 603°K, respectively. These times correspond to distances of 2.52, 3.66 and 4.38 cm. below the reactant inlet jet of the reaction vessel, all of which are well short of the distance from the inlet jet to the exit tube.

Figures 6, 7 and 8 illustrate the variation of the flow rates of the individual products as a function of the initial ethylene flow rate at 303°, 503° and 603°K, respectively. In each figure, the experimental results are indicated by various symbols while results determined by numerical integration of the simultaneous differential equations derived from the mechanism (Discussion Section 1) are illustrated by solid lines.

Figure 6

Hydrogen atom - ethylene reaction, flow rate of products at 303°K. ■, CH_4; ○, C_2H_6; ●, C_3H_8.

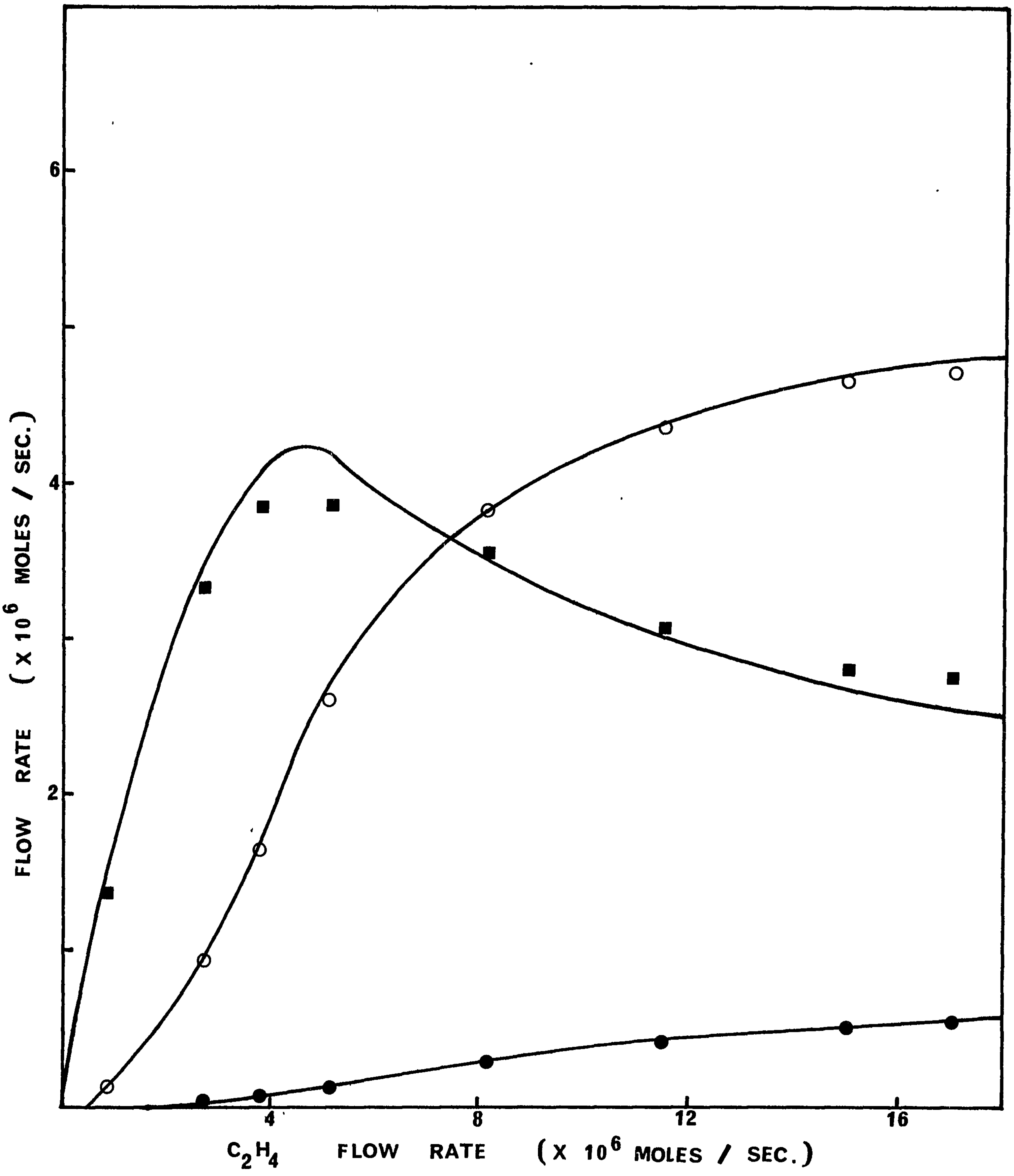

FLOW RATE (X 10^6 MOLES / SEC.)
6
4
2
4
8
12
16
C2H4 FLOW RATE (X 10^6 MOLES / SEC.)

Figure 7

Hydrogen atom - ethylene reaction, flow rate of products at 503°K. ■, CH_4; ○, C_2H_6; ●, C_3H_8.

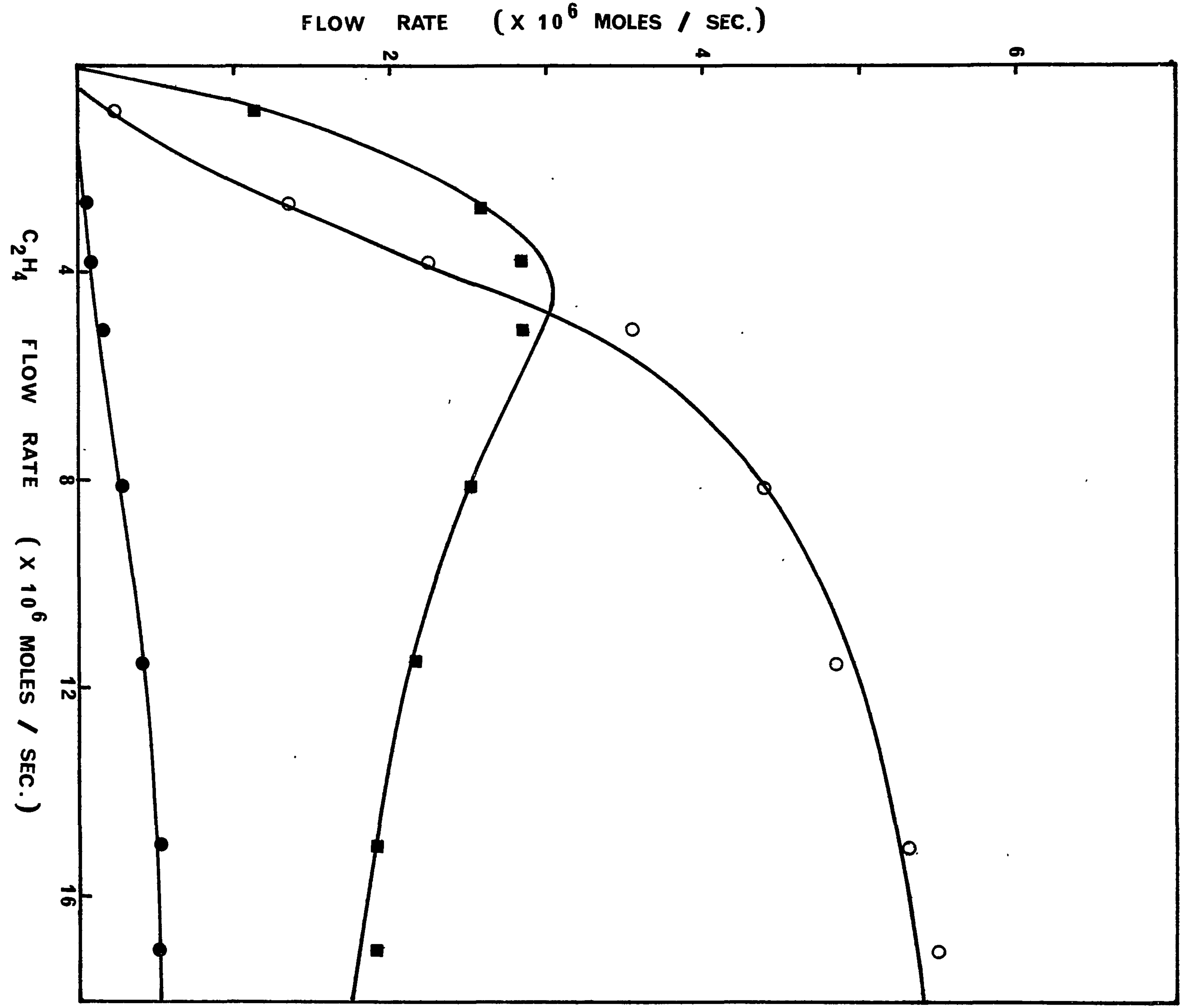
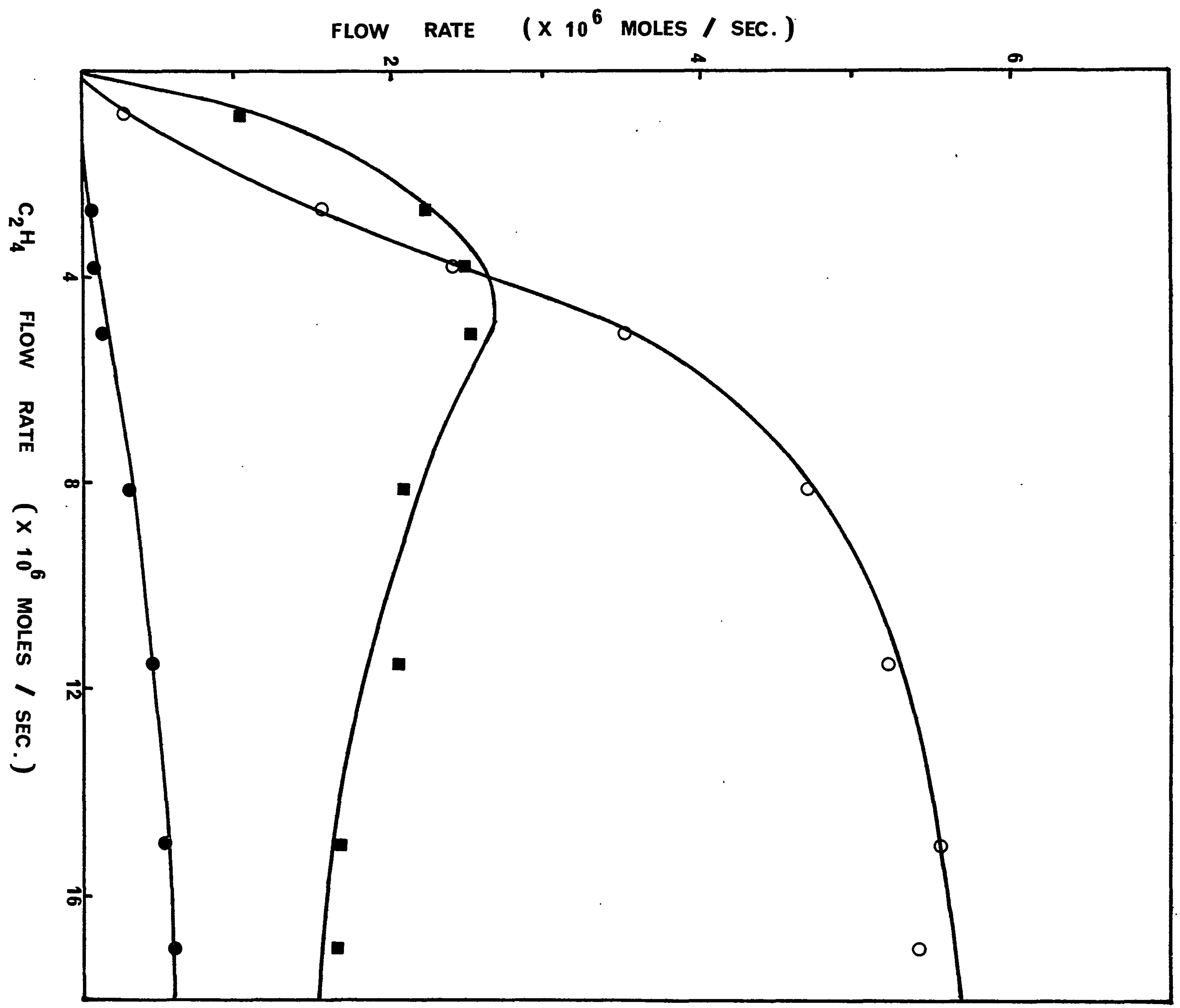

FLOW RATE (X 10^6 MOLES / SEC.)
2
4
6
C_2H_4 FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16

Figure 8

Hydrogen atom - ethylene reaction, flow rate of products at 603°K. ■, CH_4; ○, C_2H_6; ●, C_3H_8.


FLOW RATE (X 10^6 MOLES / SEC.)
2
4
6
C_2H_4 FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16

The yield of n-C_4H_{10} was too small to be illustrated on the graphs. However, the actual and calculated yields are given in Appendix B, Tables B1 to B6.

The results of a series of experiments made at these temperatures are summarized in Appendix B, Tables B1, B2 and B3. These tables show that the stoichiometric ratio (H/C_2H_4) from excess hydrogen atoms to excess ethylene varies from 3.73 to 2.33 at 303°K, from 3.41 to 2.18 at 503°K and from 3.32 to 2.14 at 603°K. When the hydrogen atoms are much in excess, the stoichiometric ratio should approach 4.0 (i.e., one ethylene to four H atoms) and all ethylene is converted to methane. When the ethylene is much in excess, the stoichiometric ratio should approach 2.0 and all the ethylene is converted to C_2H_6, C_3H_8 and n-C_4H_8.

The calculated data for all the products of the reaction are summarized in Appendix B, Tables B4, B5 and B6. The rate constants, k_6 to k_{12}, giving the best agreement between experimental and calculated results, are given in Table 13. Figures 6, 7 and 8 and Tables B1 to B6 show excellent agreement between the experimental and calculated results. The activation energies and frequency factors for each of the steps (6) to (12) of the mechanism (Discussion Section 1) are also given in Table 13. These factors were determined by performing a least-squares fit to the Arrhenius equation $k = A \exp(-E/RT)$.

(B) H Atom-C_2H_3F Reaction

The products CH_4, C_2H_6, C_3H_8 and n-C_4H_{10} of the H atom-C_2H_3F reaction were in agreement with the products of the H atom-C_2H_4 reaction. Additional products found in this reaction were: C_2H_4, C_3H_6 and C_2H_2. The yield of n-C_4H_{10} was too small for quantitative measurement (i.e., much less than 1% yield). The molecular hydrogen flow rate was 85.00 $\mu mole \cdot sec^{-1}$. The hydrogen

TABLE 13

Kinetic Parameters of the H Atom - C_2H_4 Reaction

Reaction	Temp. (°K)	Log_{10} k (cc·mole^{-1}sec^{-1})	Log_{10} A (cc·mole^{-1}sec^{-1})	E (kcal mole^{-1})
(6)	303	11.35		
H· + C_2H_4 =	503	11.60	12.03	0.95
$C_2H_5\cdot$	603	11.70		
(7)	303	13.41		
H· + $C_2H_5\cdot$ =	503	13.69	14.12	0.99
$2CH_3\cdot$	603	13.77		
(8)	303	12.07		
H· + $CH_3\cdot$ =	503	12.08	12.09	0.03
CH_4	603	12.08		
(9)	303	13.09		
$CH_3\cdot$ + $CH_3\cdot$ =	503	13.24	13.48	0.54
C_2H_6	603	13.28		
(10)	303	13.17		
$CH_3\cdot$ + $C_2H_5\cdot$ =	503	13.24	13.36	0.26
C_3H_8	603	13.26		
(11)	303	12.74		
$C_2H_5\cdot$ + $C_2H_5\cdot$ =	503	12.81	12.90	0.22
n-C_4H_{10}	603	12.82		
(12)*	303	1.00		
H· 1st. order wall Rx. =	503	1.23	1.50	0.69
1/2 H_2	603	1.23		

*Here k has units of sec^{-1}.

atom flow rate, determined by either the H atom-C_2H_4 reaction or the H atom -C_2H_5Cl reaction method, was 13.70 μmole·sec^{-1}. The vinyl fluoride flow rate varied over the range 0.79 to 16.70 μmole·sec^{-1}. The total pressure was 1.12 torr. The maximum linear flow rates for this reaction were: 373.1, 619.4 and 742.5 cm.sec^{-1} at 303°, 503° and 603°K, respectively. The maximum reaction times were determined to be 17.7, 15.3 and 15.3 msec., at 303°, 503° and 603°K, respectively. These reaction times correspond to 6.60, 9.50 and 11.39 cm, respectively, below the reaction vessel inlet jet.

Figures 9, 10 and 11 show the variation of the flow rates of the individual products as a function of the initial vinyl fluoride flow rates at 303°, 503° and 603°K, respectively. The measured flow rates are indicated by symbols, while flow rates calculated by the computer program are represented by solid lines. The results of a series of experiments made at the three temperatures are summarized in Appendix B, Tables B7, B8 and B9. The computer calculated data for the three temperatures are also summarized in Appendix B, Tables B10, B11 and B12. The rate constants, k_4 to k_{15}, giving the best agreement between experimental and calculated results, are given in Table 14. The activation energies and frequency factors for each of the mechanism steps (4) to (15) are also given in Table 14.

The mechanism given in Discussion (Section 2) was used to calculate yields of products. Steps (6) to (12) of the mechanism are the same as those for the ethylene reaction and the identical rate constants k_6 to k_{12} were used in the H + C_2H_3F reaction. The product flow rates determined by the computer are given in Tables B10, B11 and B12.

Figure 9

Hydrogen atom - vinyl fluoride reaction, flow rate of products at 303°K. ■, CH_4; ▲, C_2H_4; ○, C_2H_6; □, C_2H_2; △, C_3H_6; ●, C_3H_8.

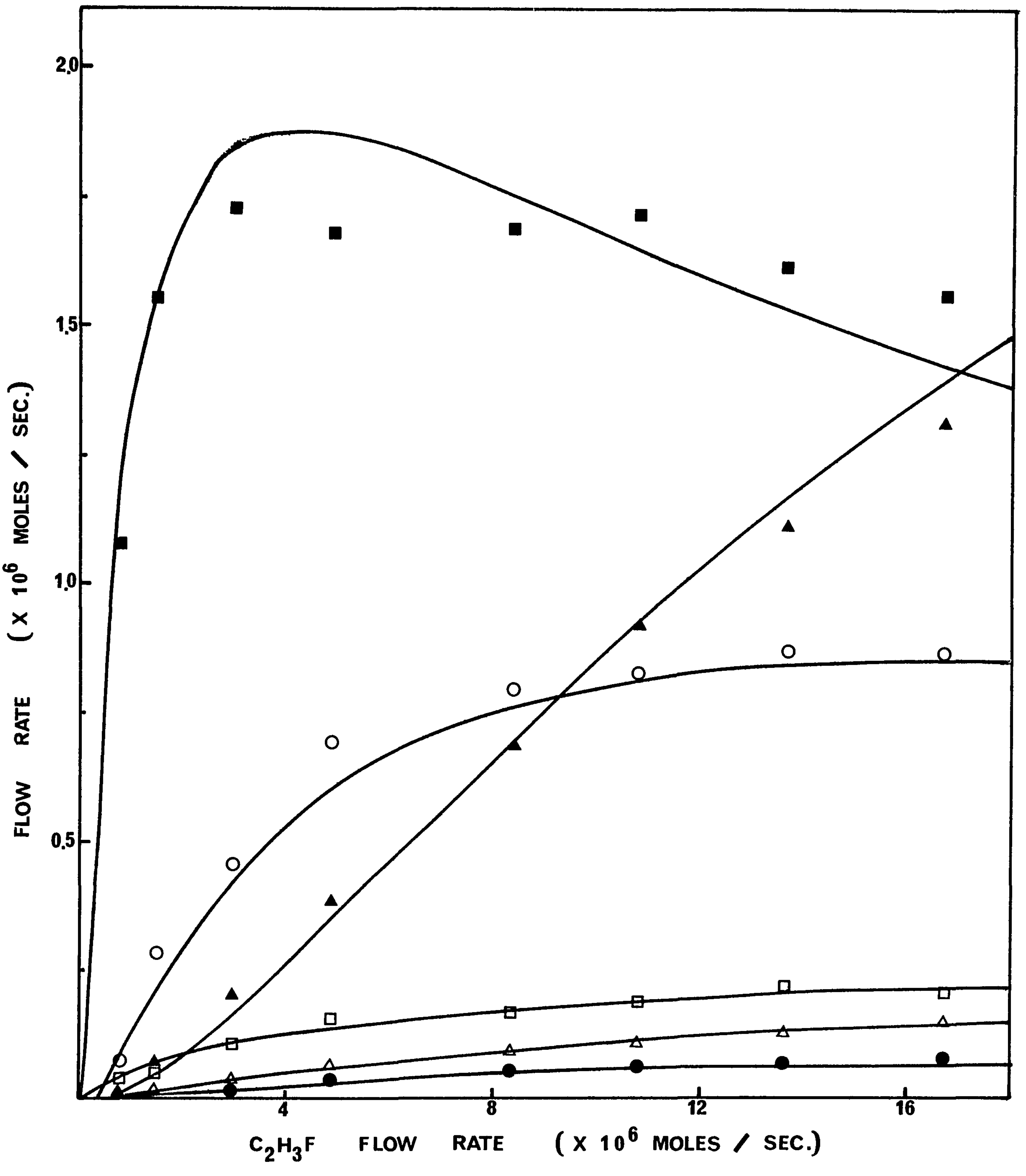
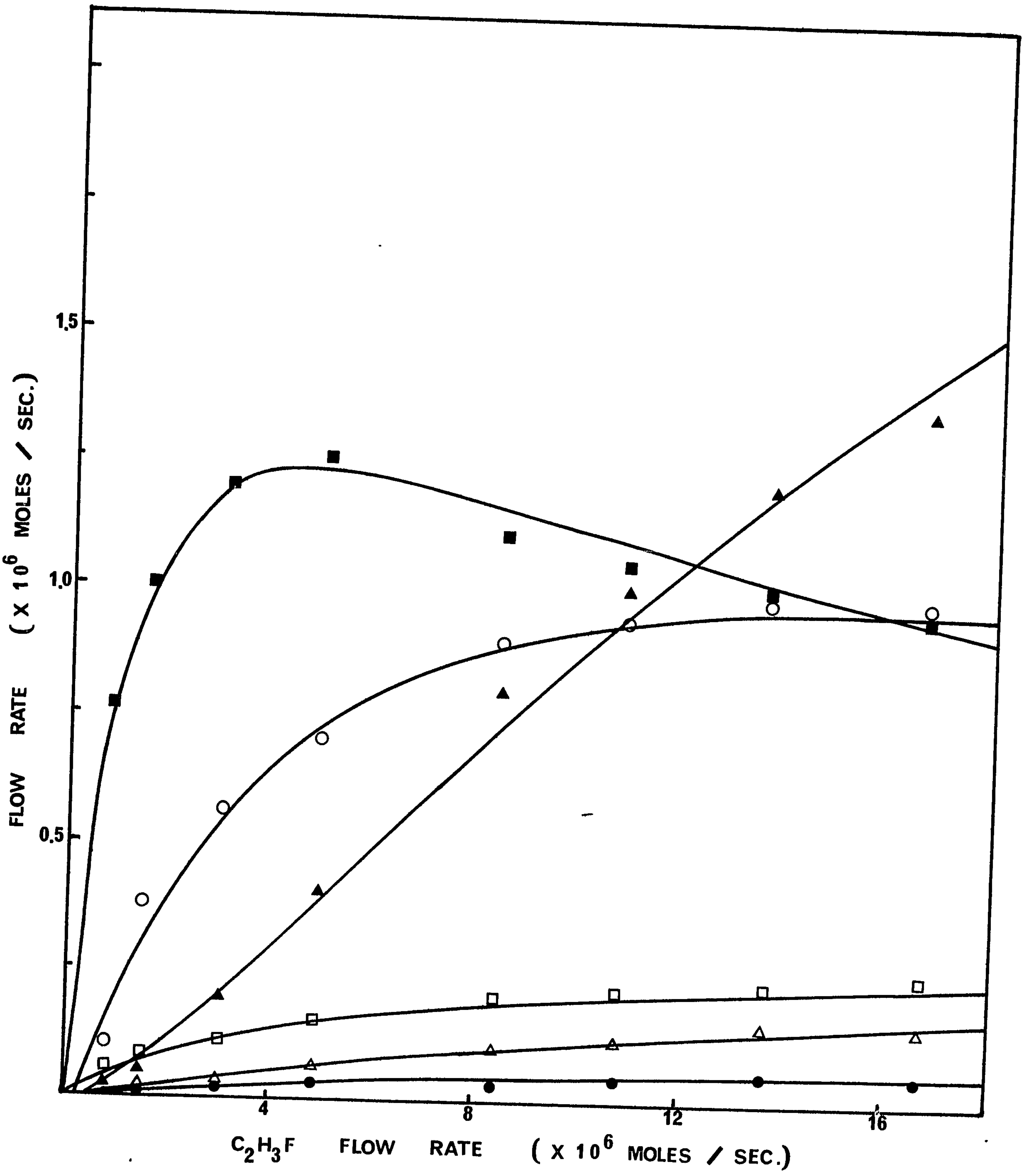

2.0
1.5
1.0
0.5
FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16
C2H3F FLOW RATE (X 10^6 MOLES / SEC.)

Figure 10

Hydrogen atom - vinyl fluoride reaction, flow rate of products at 503°K. ■, CH_4; ▲, C_2H_4; ○, C_2H_6; □, C_2H_2; △, C_3H_6; ●, C_3H_8.



1.5
1.0
0.5
FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16
C_2H_3F FLOW RATE (X 10^6 MOLES / SEC.)

Figure 11

Hydrogen atom - vinyl fluoride reaction, flow rate of products at 603°K. ■, CH_4; ▲, C_2H_4; ○, C_2H_6; □, C_2H_2; △, C_3H_6; ●, C_3H_8.

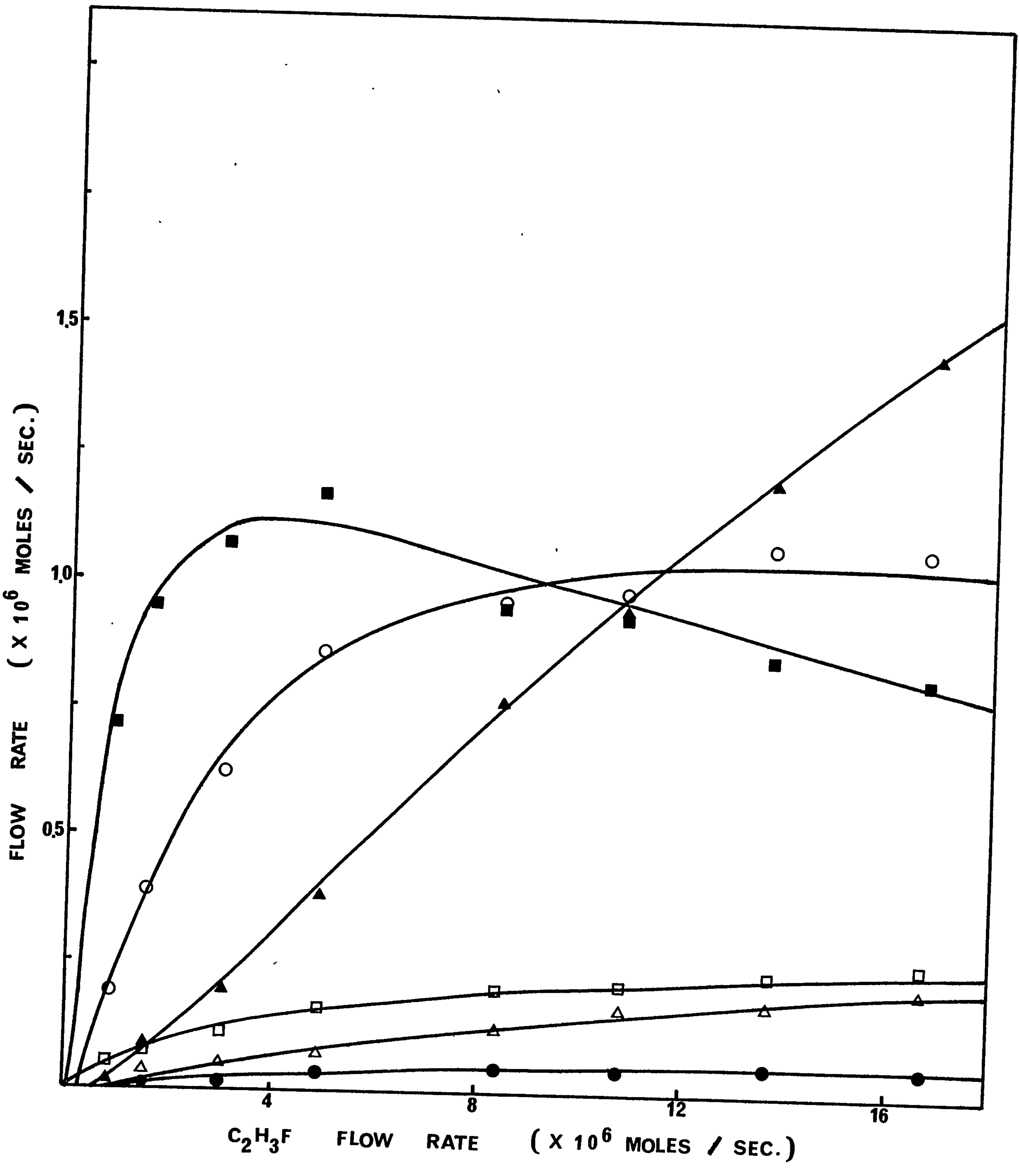

1.5
1.0
0.5
FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16
C2H3F FLOW RATE (X 10^6 MOLES / SEC.)

TABLE 14

Kinetic Parameters of the H Atom - C_2H_3F Reaction

Reaction	Temp. (°K)	$\log_{10}$ k (cc·mole^{-1}sec^{-1})	$\log_{10}$ A (cc·mole^{-1}sec^{-1})	E (kcal mole^{-1})
(4)	303	10.44		
H· + C_2H_3F =	503	10.76	11.23	1.09
C_2H_4F·	603	10.83		
(5)	303	13.38		
H· + C_2H_4F· =	503	13.66	14.10	1.00
C_2H_4 + HF	603	13.74		
(6) - (12)	Same as the H atom - C_2H_4 reaction			
(13)	303	9.27		
H· + C_2H_3F =	503	9.60	10.14	1.22
C_2H_2F· + H_2	603	9.71		
(14)	303	13.07		
H· + C_2H_2F· =	503	13.33	13.74	0.93
C_2H_2 + HF	603	13.40		
(15)	303	13.31		
CH_3· + C_2H_4F· =	503	13.58	13.98	0.94
C_3H_6 + HF	603	13.64		

Figures 9, 10 and 11 and Appendix B, Tables B7 to B12, show good agreement between experimental and calculated results.

(C) H Atom-1,1-$C_2H_2F_2$ Reaction

The products CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, C_2H_4, C_3H_6, C_2H_2 and HF of the H atom-1,1-$C_2H_2F_2$ reaction were in agreement with the products of the H atom-C_2H_3F reaction. An additional product C_2H_3F was found in the H atom-1,1-$C_2H_2F_2$ reaction. The yields of C_3H_8 and n-C_4H_{10} were too small for quantitative measurement (i.e., much less than 1% yield). The molecular hydrogen flow rate was 90.90 μmole·sec^{-1} and the hydrogen atom flow rate was 16.75 μmole·sec^{-1}, as determined by the H atom-C_2H_4 reaction method. The 1,1-difluoroethylene flow rate varied over the range 1.20 to 17.20 μmole·sec^{-1}. The total pressure was 1.20 torr. The maximum linear flow rates were 373.5, 620.1 and 743.3 cm.sec.$^{-1}$ at 303°, 503° and 603°K, respectively. The maximum reaction times were determined as 33.3, 26.7 and 26.7 msec. at 303°, 503° and 603°K, respectively, which corresponded to complete reaction at 12.43, 16.53 and 19.81 cm. below the reaction vessel inlet jet.

Figures 12, 13 and 14 illustrate the variation of the flow rates of individual products as a function of the initial 1,1-$C_2H_2F_2$ flow rate at 303°, 503° and 603°K, respectively. In each figure, the measured flow rates are indicated by symbols, while flow rates calculated by computer are represented by solid lines. The results of a series of experiments made at the three temperatures are summarized in Appendix B, Tables B13, B14 and B15. The computer calculated data are also summarized in Appendix B, Tables B16, B17 and B18. The rate constants, k_1 to k_{15}, giving the best agreement between experimental and calculated results, are given in Table 15. The activation energies and frequency factors for each of the steps (1) to

Figure 12

Hydrogen atom - 1,1-difluoroethylene reaction, flow rate of products at 303°K. ▽, C_2H_3F; □, C_2H_2; ■, CH_4; ▲, C_2H_4; ○, C_2H_6.

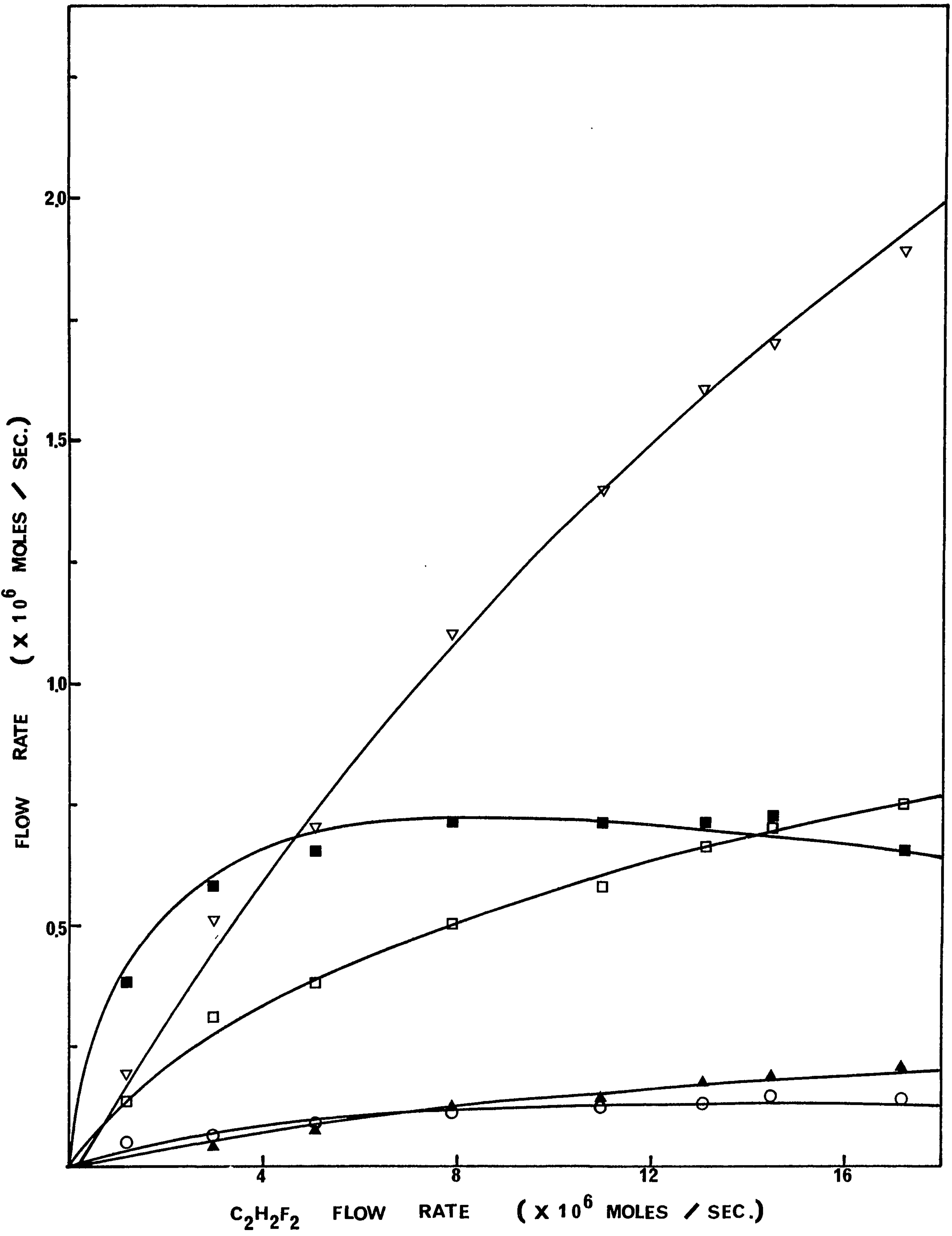

2,0
1,5
1,0
0,5
FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16
C2H2F2 FLOW RATE (X 10^6 MOLES / SEC.)

Figure 13

Hydrogen atom - 1,1-difluoroethylene reaction, flow rate of products at 503°K. ▽, C_2H_3F; □, C_2H_2; ■, CH_4; ▲, C_2H_4; ○, C_2H_6.

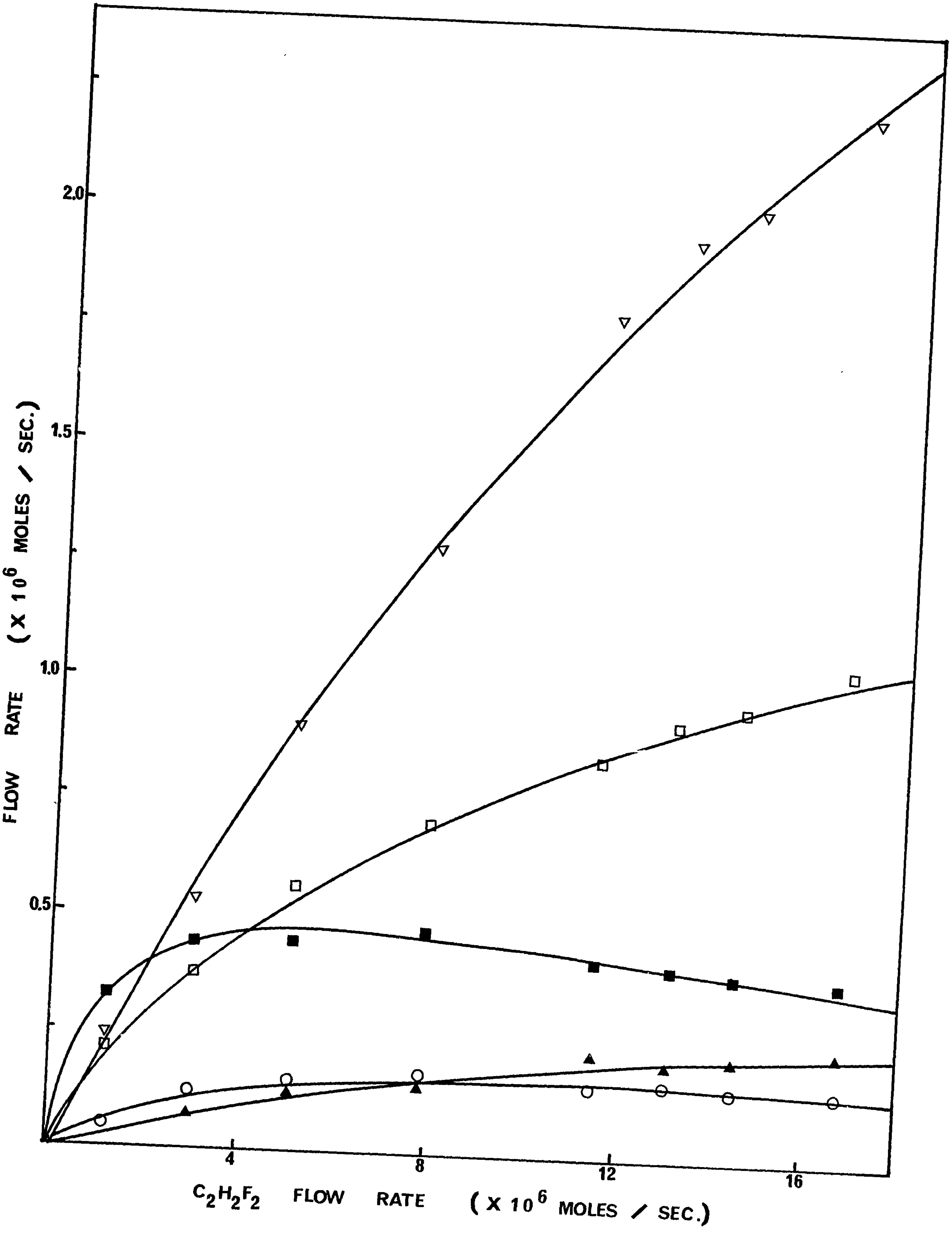

FLOW RATE (X 10^6 MOLES / SEC.)
2.0
1.5
1.0
0.5
4
8
12
16
$C_2H_2F_2$ FLOW RATE (X 10^6 MOLES / SEC.)

Figure 14

Hydrogen atom - 1,1-difluoroethylene reaction, flow rate of products at 603°K. ▽, C_2H_3F; □, C_2H_2; ■, CH_4; ▲, C_2H_4; ○, C_2H_6.

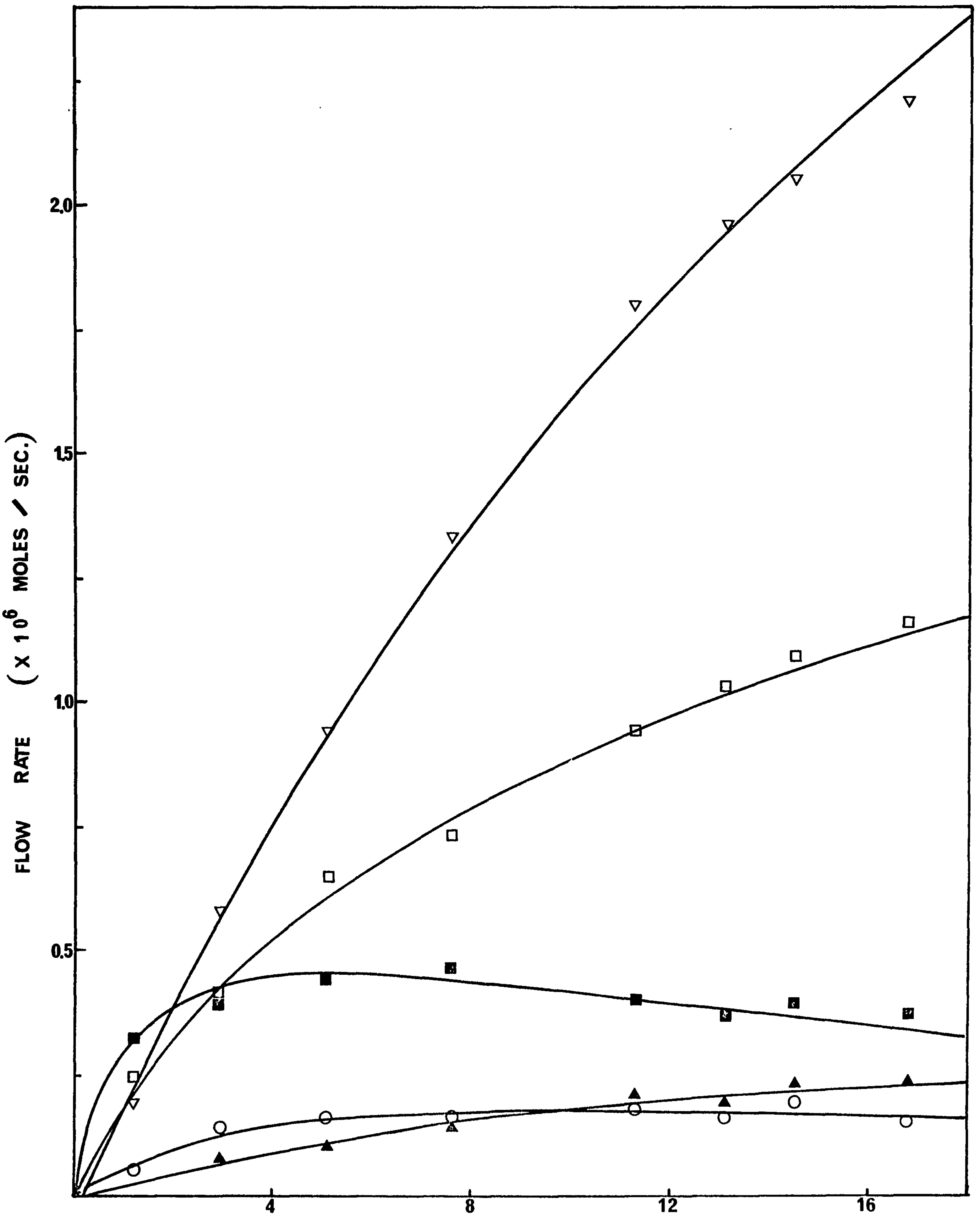

2,0
1,5
1,0
0,5
FLOW RATE (X 10^6 MOLES / SEC.)
4
8
12
16
C2H2F2 FLOW RATE (X 10^6 MOLES / SEC.)

TABLE 15

Kinetic Parameters of the H Atom -1,1-$C_2H_2F_2$

Reaction	Temp. (°K)	$\log_{10}$ k (cc·mole^{-1} sec^{-1})	$\log_{10}$ A (cc·mole^{-1} sec^{-1})	E (kcal mole^{-1})
(1)	303	9.89		
$H\cdot + C_2H_2F_2$ =	503	10.37	11.07	1.63
$C_2H_3F_2^{\cdot}$	603	10.47		
(2)	303	13.38		
$H\cdot + C_2H_3F_2^{\cdot}$ =	503	13.66	14.10	1.00
C_2H_3F + HF	603	13.74		
(3)	303	9.31		
$H\cdot + C_2H_2F_2$ =	503	9.90	10.79	2.05
$C_2H_2F\cdot$ + HF	603	10.04		

(4) - (15) As given for the H atom - C_2H_3F reaction.

(15) of the mechanism are also given in Table 15.

The mechanism given in Discussion (Section 3) was used to calculate the yields of products. Steps (4) to (15) of the mechanism are the same as those for the H + C_2H_3F reaction. The yields calculated by the computer are given in Appendix B, Tables B16, B17 and B18.

Figures 12, 13 and 14, and Appendix B, Tables B13 to B18, show good agreement between experimental and calculated results.

(D) H Atom Flow Rate Measurement

i) H Atom-C_2H_4 Reaction Method

Volpi and Zocchi[68] suggested the determination of the hydrogen atom flow rate by reaction with excess ethylene. They stated that the stoichiometry of this reaction is two hydrogen atoms consumed for each molecule of saturated hydrocarbons formed. More recently, Purnell et al.[60], using the C_2H_4 method, determined a value of the hydrogen atom flow rate which compared favourably with that found by the H + NOCl optical titration technique.

The total yield of saturated products, $F_{sat.}$, of the H atom-C_2H_4 reaction should obey the equation:

$$F_{CH_4} + F_{C_2H_6} + F_{C_3H_8} + F_{n-C_4H_{10}} = 0.5 \times F_H$$

This equation is based on the well-established mechanism for this reaction (Discussion Section 1). By using this equation, a value of 13.70 μmole·sec^{-1} was obtained for the hydrogen atom flow rate, (Table 16).

Under the slightly different conditions used in the H atom-C_2H_4 and H atom-1,1-$C_2H_2F_2$ reactions, the hydrogen atom flow rate was found to be 16.75 μmole·sec^{-1}, (Table 17).

Figure 15 shows a typical plot of $F_{sat.}$ as a function of $F_{C_2H_4}$. It is

TABLE 16

F_H from the Yield of $F_{sat.}$ in the H Atom-C_2H_4 Reaction

F_H = 85.00 x 10^{-6} mole·sec^{-1}, Temperature = 303 ± 2°K

F = Flow rate (mole·sec^{-1}) x 10^{-6}

$F_{C_2H_4}$		$F_{products}$			$F_{sat.}$	F_H
Input	Reacted	CH_4	C_2H_6	C_3H_8		
17.8	6.00	2.60	3.90	0.52	7.02	14.04
17.9	6.20	2.47	3.83	0.43	6.73	13.46
17.5	6.00	2.60	3.85	0.35	6.80	13.60
					Average =	13.70

TABLE 17

F_H from the Yield of $F_{sat.}$ in the H Atom-C_2H_4 Reaction

F_{H_2} = 90.90 x 10^{-6} mole·sec^{-1}, Temperature = 303 ± 2°K

F = Flow rate (mole·sec^{-1}) x 10^{6}

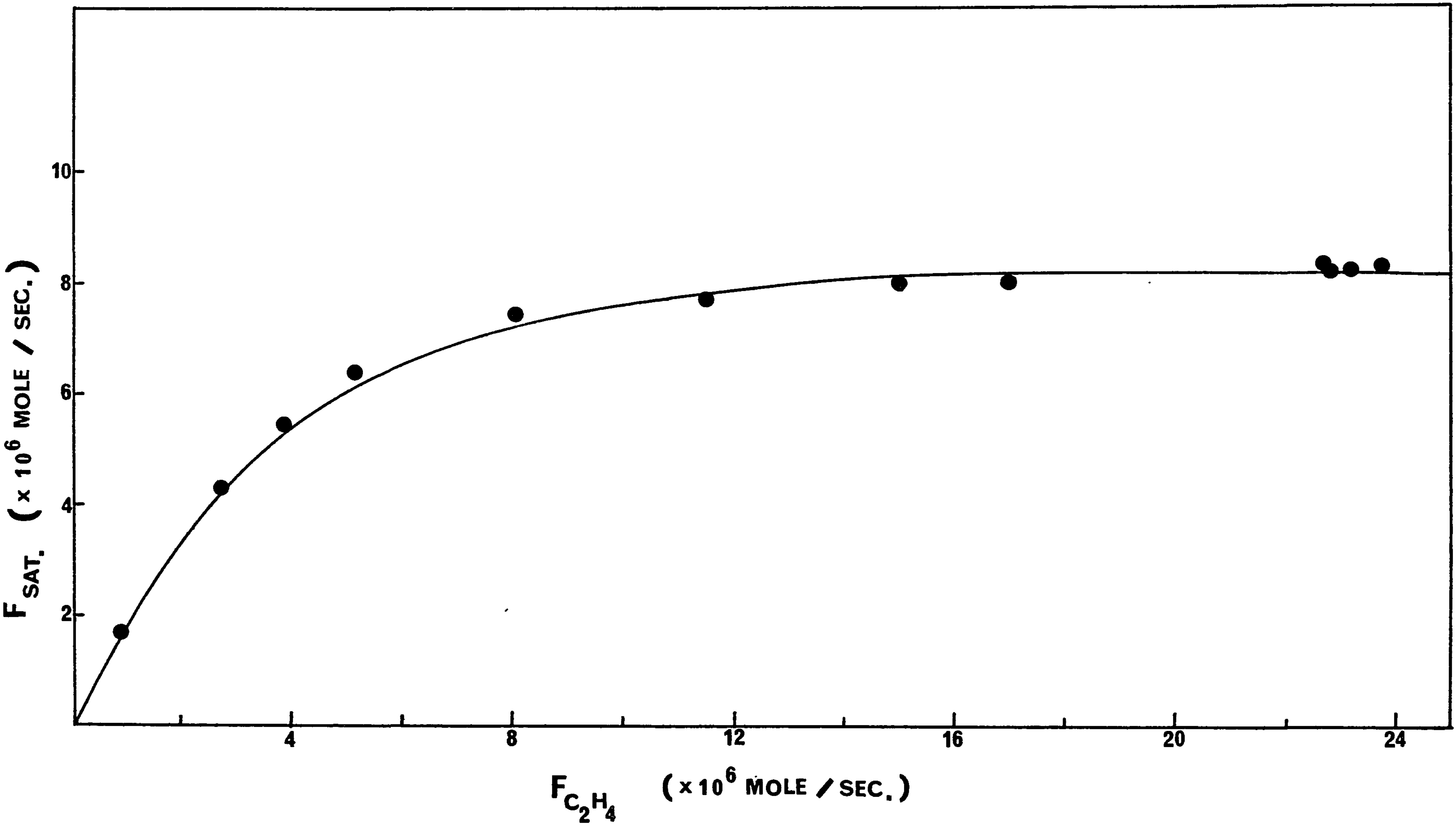
$F_{C_2H_4}$		$F_{products}$				$F_{sat.}$	F_H
Input	Reacted	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}		
22.70[a]	7.28	2.40	5.50	0.48	0.03	8.41	16.82
22.80[b]	7.10	2.37	5.40	0.54	0.04	8.35	16.70
23.20[a]	7.50	2.44	5.40	0.48	0.02	8.34	16.68
23.70[b]	7.20	2.55	5.30	0.52	0.03	8.40	16.80
						Average =	16.75

(a) Titration for the F_H in the H atom-1,1-$C_2H_2F_2$ reaction.

(b) Titration for the F_H in the H atom-C_2H_4 reaction.

Figure 15

Hydrogen atom - ethylene reaction, total flow rate of the combined products at 303°K.


$F_{SAT.}$ (× 10^6 MOLE / SEC.)
10
8
6
4
2
4
8
12
16
20
24
$F_{C_2H_4}$ (× 10^6 MOLE / SEC.)

evident that $F_{sat.}$ increases with increasing $F_{C_2H_4}$ until a limiting value is reached. In this plot, a limiting value of 8.37 μmole·sec^{-1} corresponding to an hydrogen atom flow rate of 16.75 μmole·sec^{-1} is observed.

ii) H Atom-C_2H_5Cl Reaction Method

Chadwell and Titani[62] found that CH_4, C_2H_6, C_3H_8, HCl and C_2H_4 were the products of the H atom-C_2H_5Cl reaction. They also found that about 35 to 40 percent reaction occurred at temperatures in the neighborhood of 398°K. Later, Winkler and Jamieson[63] suggested this reaction as a method to determine the hydrogen atom flow rate on the basis of the amounts of the titratable product, HCl.

This method has been used to determine the hydrogen atom flow rate in the H atom-C_2H_3F reaction. Table 18 shows the results obtained from the H atom-C_2H_4Cl reaction at 303°, 503° and 603°K. The experimental conditions are the same as those shown in Table 16 where the flow rate of H atoms was found to be 13.70 μmole·sec^{-1}.

TABLE 18

F_H from the Yield of HCl in the Reaction, H Atom-C_2H_5Cl

$F_{H_2} = 85.00 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

Temperature (°K)	F_{HCl}	F_H	% Reaction
303 ± 2	4.40	13.70	32.1
503 ± 2	5.71	13.70	41.7
603 ± 2	6.77	13.70	49.4

Comparison of the yield of HCl with the value 13.70 μmole·sec^{-1} shows that about 32.1, 41.7 and 49.4 percent reaction occurred at 303°, 503° and 603°K, respectively. This result is in agreement with the 35% to 40% reaction at the temperature 398°K obtained by Chadwell and Titani[62]. The products of several runs of the H atom-C_2H_5Cl reaction were injected into the gas chromatograph giving the following results: CH_4 (76%), C_2H_6 (8%), C_2H_4 (15%) and C_3H_8 (1%). The ratio, CH_4 yield/C_2-compound yield, was 3.3 which was in good agreement with the ratio 3.4 of Chadwell and Titani.

CHAPTER IV

DISCUSSION

1. H ATOM-C_2H_4 REACTION

The following mechanism for the H atom-C_2H_4 reaction is similar to mechanisms proposed by many workers[50,51,60,102,143] and has been used to obtain the calculated results shown in Figures 6 to 8 and Appendix B, Tables B4 to B6.

$$H\cdot + \overbrace{C_2H_4 \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} C_2H_5^{\cdot\,*} \xrightarrow[M]{k_{6'}} C_2H_5^{\cdot}}^{k_{6eff.}} \qquad (6)$$

$$H\cdot + \overbrace{C_2H_5^{\cdot} \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} C_2H_6^{**} \xrightarrow{k_{7'}} 2CH_3^{\cdot}}^{k_{7eff.}} \qquad (7)$$

$$H\cdot + \overbrace{CH_3^{\cdot} \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} CH_4^{*} \xrightarrow[M]{k_{8'}} CH_4}^{k_{8eff.}} \qquad (8)$$

$$CH_3^{\cdot} + \overbrace{CH_3^{\cdot} \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} C_2H_6^{*} \xrightarrow[M]{k_{9'}} C_2H_6}^{k_{9eff.}} \qquad (9)$$

$$CH_3^{\cdot} + C_2H_5^{\cdot} \xrightarrow{k_{10}} C_3H_8 \qquad (10)$$

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \xrightarrow{k_{11}} n\text{-}C_4H_{10} \qquad (11)$$

$$H\cdot \xrightarrow[\text{first order Wall Rx}]{k_{12}} 1/2\ H_2 \qquad (12)$$

The rate constants, k_6 to k_{12}, over the temperature range 303° to 603°K, which give the best agreement between experimental and calculated results, are given in Table 13. The activation energies and frequency factors for each of the reaction steps (6) to (12) are also given in Table 13.

The kinetics of the H atom-C_2H_4 reaction can be studied under two very different sets of experimental conditions: (a) in the presence of a large excess of C_2H_4 and high pressures, (b) in the presence of low C_2H_4 concentration and low pressures. Under the first set of conditions, the subsequent reaction of C_2H_5 radicals with hydrogen atoms can be ignored and only the initial step of the reaction need be considered. For the second set of conditions, the mechanism of the subsequent steps and the final stable products of the reaction must be considered. Low C_2H_4 concentration and low pressures were used in this work.

The kinetics of the initial step (6) have been studied many times under both sets of conditions. However, only Purnell et al.[60] have obtained rate constants for all steps postulated in the mechanism of this reaction. Their measurements were made only at room temperature and no calculation of activation energies was possible.

The most detailed analytical information available on this reaction consists of work by Toby and Schiff[143] (1956) who reported mass spectrometric analysis of the products from the reaction of deuterium atoms with C_2H_4, and work by Purnell et al.[60] (1970) who used gas chromatographic analysis to determine the products of the H atom-C_2H_4 reaction. Both studies were performed in a discharge flow system and gave methane and ethane as the main products. Minor amounts of propane and n-butane were also formed.

The reactions of the alkyl radicals CH_3 and C_2H_5 with molecular hydrogen, paraffins, and C_2H_4, and also the reactions of hydrogen atoms with paraffins are much slower than the steps (7-11) of the H + C_2H_4 reaction[145, 146,147]. Therefore, these reactions have been ignored in the present work.

As mentioned earlier, the computer program must be supplied with values for rate constants, k_6 to k_{12}. These rate constants were chosen from literature values and then varied (usually within the range of published values) until agreement between calculated and experimental results was reached. Each step of the mechanism of the reaction H + C_2H_4 will now be discussed. Sections (1A) to (1G).

(1A) $k_{6eff.}$

The published values of $k_{6eff.}$ were found to be within the approximate limits 1 x 10^{11} to 8 x 10^{11} $cc.mole^{-1}sec^{-1}$ at room temperature. (See Tables 4 and 5). The value of $k_{6eff.}$ = 2.21 x 10^{11} $cc.mole^{-1}sec^{-1}$, found in this work, lies within the range of published values and is in good agreement with the values found under similar experimental conditions.

The pressure dependence of $k_{6eff.}$ has been established by many workers[40,47,51,60,103,105,106]. Therefore, it is not reasonable to compare values of k_6 obtained using different pressure conditions.

With the exception of the two values 6.6 kcal/mole[88] and 7.2 kcal/mole[110], which are considered to be too high because of the occurrence of an abstraction reaction, the published activation energy values lie within the range 0.5 to 3.3 kcal $mole^{-1}$ (Table 6). All of these values have been based on the occurrence of only the primary step (6). The value, E_6 = 0.95 kcal $mole^{-1}$, found in this work, lies within the range of the published values.

It appears that the recently published values of E_6 tend towards the lower value. For example, Penzhorn and Darwent[19] found a value of 1.5 ± 0.1 over the temperature range 303° to 478°K. Westenberg and deHaas[51] studied the reaction at the temperatures 297° and 525°K and calculated E_6 to be about 0.5 kcal $mole^{-1}$.

(1B) $k_{7eff.}$

When the hydrogen atom flow rate is greater than that of the initial ethylene flow rate, the ethyl radicals are removed by step (7) since $k_{7eff.}$ is much greater than $k_{6eff.}$. The vibrationally excited $C_2H_6^{**}$ (step (7)), which has 97.5 kcal mole^{-1} excess energy[99], could decompose to two methyl radicals or to an ethyl radical. The decomposition to the two CH_3 radicals requires 10 kcal mole^{-1} less energy than decomposition to the C_2H_5 radical[99] and, therefore, should be the dominant process.

Michael et al.[102] studied the reaction $H + C_2H_4$. Since no C_2H_5 radicals were observed, they assumed that the $CH_3^{\cdot}$ formation rate from step (7) was very fast. The present value of $k_{7eff.} = 2.58 \times 10^{13}$ cc.mole^{-1}sec^{-1} is in reasonable agreement with the only published value of $k_{7eff.} = 5.0 \times 10^{13}$ cc.mole^{-1}sec^{-1} at room temperature[60]. Step (7) has a small activation energy of 0.99 kcal mole^{-1}.

(1C) $k_{8eff.}$

When $[C_2H_4] < [H]$, the methyl radical reacts mainly with H to produce CH_4, step (8). However, when $[C_2H_4] > [H]$, the methyl radical has a greater chance of reacting with other radicals to form other hydrocarbons, steps (9 and 10). In the latter case, the CH_4 concentration decreases. This is shown in both the calculated and experimental results. (Figures 5 to 8 and Tables B1 to B6).

The vibrationally excited CH_4^* formed in step (5) has 102 kcal mole^{-1} excess energy[99]. This step has been found to be pressure dependent[60]. Brown et al.[148] estimated $k_{8eff.} = 2.2 \times 10^{12}$ cc.mole^{-1}sec^{-1} (1.6 torr of Ar). Room temperature values of $k_{8eff.}$ were reported by Purnell et al.[60] as 2.3×10^{12} cc.mole^{-1}sec^{-1} (8 torr of Ar) and by Tal'roze et al.[149] as $(1.0 \pm 0.3) \times 10^{12}$ cc.mole^{-1}sec^{-1} (6.7 torr of He). The present room temperature value of 1.17 x 10^{12} cc.mole^{-1}sec^{-1} (1.2 torr of H_2) is in reasonable agreement with these previously reported results. The negligibly small value of E_8 = 0.03 kcal mole^{-1} found in this work is considered reasonable for such an atom-radical reaction.

(1D) $k_{9eff.}$

The reaction step (9) represents the formation of C_2H_6 by methyl radical recombination. In this reaction, excited ethane with about 87.4 kcal mole^{-1} excess energy[99] is formed. Since the excited ethane from this step has less energy than ethane from step (7), it would be expected to stabilize more readily and, therefore, should be the dominate mode of ethane production. Reaction (9) has been extensively studied and has been found to be pressure dependent[77,150]. Most of the earlier workers[151,152,153,154,155] gave $k_{9eff.}$ = 2.0-2.4 x 10^{13} cc.mole^{-1}sec^{-1} for the temperature range 398°-448°K and under high pressure conditions.

High pressure rate constants for $k_{9eff.}$ have been recently reported by Van Den Berg et al.[156] and Basco et al.[157]. They measured the CH_3 radical concentration by kinetic spectroscopy and obtained values of $k_{9eff.}$ = 2.43 x 10^{13} (293°K) and 2.60 x 10^{13} cc.mole^{-1}sec^{-1} (298°K).

The value of $k_{9eff.}$ = 1.22 x 10^{13} cc.mole^{-1}sec^{-1} at 303°K found in this work is in agreement with previous workers. It is also in good agreement with a recent theoretically calculated value[150] of 1.3 x 10^{13} cc.mole^{-1}sec^{-1} at 293°K. Furthermore, the value of E_9 = 0.54 kcal mole^{-1} is in reasonable agreement with the published value of 0.70 kcal/mole[151,152].

(1E) k_{10}

The formation of C_3H_8 (step 10) is due to the combination of CH_3 and C_2H_5 radicals. The disproportionation reaction of CH_3 and C_2H_5 resulting in the formation of CH_4 and C_2H_4 has also been suggested[158]. However, the ratio of the rates of disproportionation to rates of combination were found by many workers[159,160,161,162] to be in the range 0.036-0.04. Different free radical sources and temperatures were used. Therefore, the disproportionation reaction has been considered negligible in this work.

Heller[163] used the values $k_{9eff.} = 2.2 \times 10^{13}$ and $k_{11} = 2.0 \times 10^{13}$ $cc.mole^{-1}sec^{-1}$ (373°K) from the work of Shepp et al.[164] in order to calculate k_{10}. They used the formula $k_{10} = 2\ (k_{9eff.} \times k_{11})^{1/2}$. This formula has been proven valid by many workers[158,159,161,162]. The value of $k_{10} = 1.48 \times 10^{13}$ $cc.mole^{-1}sec^{-1}$ (303°K) in this work can be compared to the value of $4.2 \pm 0.5 \times 10^{13}$ $cc.mole^{-1}sec^{-1}$ (373°K) obtained by Heller. The accuracy of Heller's value of k_{10} is essentially dependent on the reliability of $k_{9eff.}$ and k_{11}.

(1F) k_{11}

The formation of $n\text{-}C_4H_{10}$ is dependent upon the combination of two ethyl radicals as in step (11). The ratio of the rates of disproportionation to combination reaction for two ethyl radicals was found by many workers[158,161,164,165,166,167] to be in the range of 0.12-0.14. Because of the small value of the ratio $k_{disprop.}/k_{comb.}$, the disproportionation reaction has been neglected in this work. Comparison of Shepp's value[164] of $k_{11} = 1.5 \pm 1 \times 10^{13}$ $cc.mole^{-1}sec^{-1}$ (323°K) with the value of $k_{11} = 5.33 \times 10^{12}$ $cc.mole^{-1}sec^{-1}$ (303°K), found in this work, shows reasonable agreement. Thynne[168] has suggested that Shepp's value of $E_{11} = 2$ kcal $mole^{-1}$ is too high for radical-radical combination. Thus, the small value for $E_{11} = 0.02$ kcal $mole^{-1}$, found in this work, would seem to be more reasonable.

The yields of C_3H_8 and n-C_4H_{10} are small (less than 8% of the total yield) compared to those of C_2H_6 and CH_4. Therefore, the rate constants k_{10} and k_{11} are less accurate than $k_{8eff.}$ and $k_{9eff.}$. Despite this, the rate constants $k_{9eff.}$, k_{10}, and k_{11} give a reasonable fit to the relation $k_{10} = 2(k_{9eff.} \times k_{11})^{1/2}$.

(1G) k_{12}

The rate constant, k_{12}, is dependent upon the type of poisoning used in the system. Without reaction step (12) in the mechanism, the calculated results cannot be made to fit the experimental data. Omission of step (12) causes the calculated maximum in the methane yield to be too high and thus the shape of the methane production curve does not follow the actual result. The value, $k_{12} = 10\ sec^{-1}$ (303°K), used here, compares favourably with measurements of other workers. A number of results obtained by using various poisons have been published. Drifilm[8,106] (a mixture of dimethyldichlorosilane and trichloromethylsilane[169]) as a "poison" gave values of $k_{12} = 14\text{-}30\ sec^{-1}$. Metaphosphoric acid[127,143,170] gave values of $k_{12} = 3.8\text{-}4.5\ sec^{-1}$. Hydrofluoric acid[171] or Teflon-coated[172] vessels gave values of $k_{12} = 0.21\ sec^{-1}$.

The following reactions are two other possibilities for the removal of hydrogen atoms:

$$H\cdot + H\cdot + H_2 \longrightarrow H_2 + H_2 \qquad (a)$$

$$H\cdot + H\cdot + H\cdot \longrightarrow H_2 + H\cdot \qquad (b)$$

These reactions have been studied by a number of workers[139,171,172] and have been found to be much slower than the reactions (6) to (12). Therefore, they have been neglected in this study.

It has been shown that room temperature rate constants found in this work for each of the steps (6-12) of the H atom-C_2H_4 reaction are in reasonable agreement with published values. The present temperature coefficient studies have provided information not previously available for the elementary reactions (i.e., subsequent steps in the H atom-C_2H_4 reaction).

2. H ATOM-C_2H_3F REACTION

The original purpose of studying the H atom-C_2H_4 reaction was to assist in the elucidation of the H atom-C_2H_3F reaction mechanism. Examination of the product yields of both reactions have indicated a great similarity in the products. Therefore, it is proposed that the H atom-C_2H_4 reaction mechanism forms an important part of the H atom-C_2H_3F reaction mechanism. The following sequence of reactions (4-15) is thus proposed for the H atom-C_2H_3F reaction.

$$H\cdot + C_2H_3F \overbrace{\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_2H_4F\cdot^{*} \xrightarrow[M]{k_{4'}}}^{k_{4eff.}} C_2H_4F\cdot \tag{4}$$

$$H\cdot + C_2H_4F\cdot \overbrace{\underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} C_2H_5F^{**} \xrightarrow{k_{5'}}}^{k_{5eff.}} C_2H_4 + HF \tag{5}$$

$$H\cdot + C_2H_4 \quad \text{(as presented in Section 1)} \qquad (6)-(12)$$

$$H\cdot + C_2H_3F \xrightarrow{k_{13}} C_2H_2F\cdot + H_2 \tag{13}$$

$$H\cdot + C_2H_2F\cdot \overbrace{\underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} C_2H_3F^{**} \xrightarrow{k_{14'}}}^{k_{14eff.}} C_2H_2 + HF \tag{14}$$

$$CH_3^{\cdot} + C_2H_4F\cdot \overbrace{\underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} \text{iso-}C_3H_7F^{**} \xrightarrow{k_{15'}}}^{k_{15eff.}} C_3H_6 + HF \tag{15}$$

This mechanism has been found to give excellent agreement between the calculated and the experimental amounts of products formed over the range 303°-603°K. It can be seen in Figures 9 to 11 that the overall shapes of the calculated lines (i.e., solid lines) are in almost perfect agreement with experimental data. Since these shapes are a direct consequence of the mechanism, they provide powerful evidence of its validity.

In the computer calculation, the values of $k_{6eff.}$ to k_{12} have been set identical to those determined for the H atom-C_2H_4 reaction. The rate constants, $k_{4eff.}$, $k_{5eff.}$, k_{13}, $k_{14eff.}$, and $k_{15eff.}$, were varied to give the best fit to the experimental data. The rate constants, $k_{4eff.}$ to $k_{15eff.}$, the activation energies, and the frequency factors over the temperature range 303° to 603°K for each of the reaction steps (4) to (15) are given in Table 14. The kinetic parameters for each of the steps of the reaction will now be discussed. Sections (2A) to (2F).

(2A) $k_{4eff.}$

Hydrogen atom addition to vinyl fluoride at the least fluorinated carbon, step (4), was proposed by Scott and Jennings[15] and Penzhorn and Sandoval[17]. This has been found to be the case in the present work. The effect of introducing a fluorine atom into an unsaturated system has been discussed by Clark et al.[173]. Because of the high electronegativity of fluorine, it attracts σ-electrons (i.e., negative inductive effect, $-I_{\sigma}$) and polarizes the C-F bond so that the C-F bond dipole attracts other electrons in the CH_2CHF molecule towards the substituted carbon atom. On the other hand, the substituted carbon atom is part of a π-electron system where the fully occupied 2p orbitals of the fluorine atom have π-symmetry and the electrons in these orbitals repel the π-electrons, giving rise to a $+ I_{\pi}$ effect. The combined result of the $-I_{\sigma}$ and $+ I_{\pi}$ effects leads to a reduction in the electron density of the substituted carbon atom and a deactivation of the double bond. The H atom attacks the carbon with the higher electron density (the least fluorinated) and it would be expected that the rate of reaction of H atoms with C_2H_3F

would be less than with C_2H_4, and that there would be a further decrease in reactivity with 1,1-$C_2H_2F_2$. This behaviour, observed by other workers[174-179], holds true in this work.

If the primary step in the H + C_2H_3F reaction is similar to that of the H + C_2H_4 reaction, the addition of a hydrogen atom to C_2H_3F results in the formation of a vibrationally excited radical, $C_2H_4F^*$, as in step (4). This excited radical can dissociate, forming an H atom and C_2H_3F, step (-4), or it can undergo collisional stabilization, step (4'). The following values were obtained: $k_{4eff.} = 2.77 \times 10^{10}$ cc.mole^{-1}sec^{-1} (303°K) and $E_4 = 1.09$ kcal mole^{-1}. On the basis of the arguments presented above, these values seem reasonable when compared to $k_{6eff.} = 2.21 \times 10^{11}$ cc.mole^{-1}sec^{-1} and $E_6 = 0.95$ for the addition reaction H + C_2H_4.

(2B) $k_{5eff.}$

When the C_2H_4F radical formed in step (4) reacts with a hydrogen atom, it gives "hot" fluoroethane, $C_2H_5F^{**}$, which contains approximately 98 kcal mole^{-1} excess energy. This is based on Coomber and Whittle's[180] value of D (CH_3CHF-H) = 98 kcal mole^{-1}. This "hot" $C_2H_5F^{**}$ could decompose by step (5'): the elimination of HF across the C-C bond, or by step (-5): the elimination of an H atom. Since the activation energy for elimination of HF, in the range 58 to 62 kcal/mole[181-184], is much less than the activation energy for elimination of an H atom, the HF elimination (step 5') is the most probable step.

Because of the strength of the C-F bond (D(C_2H_5-F) = 106 kcal mole^{-1})[185], elimination of an F atom from $C_2H_5F^{**}$ has been considered unlikely. Collisional deactivation of $C_2H_5F^{**}$ by a third body has been neglected because of the absence of C_2H_5F in the reaction products and because of the high ratio of elimination of HF to collisional stabilization for $C_2H_5F^{**}$ ($k_{elim.}/k_{stab.} > 38$) [186-188]. The cleavage of the C-C bond from $C_2H_5F^{**}$ has not been considered because of the absence of fluoromethane in the products. If cleavage occurs, the formation of CH_3F would be expected as in Steps (16) and (17).

$$C_2H_5F^{**} \longrightarrow CH_3\cdot + CH_2F\cdot \qquad (16)$$

$$H + CH_2F\cdot \longrightarrow CH_3F \qquad (17)$$

Based upon observation of products produced in the mercury-photosensitized decomposition of C_2H_5F, Scott and Jennings[14] stated that recombination, reaction (18), and disproportionation, reaction (19), are important steps for C_2H_4F radicals.

$$2\ C_2H_4F\cdot \longrightarrow C_4H_8F_2 \qquad (18)$$

$$2\ C_2H_4F\cdot \longrightarrow C_2H_5F + C_2H_3F \qquad (19)$$

Since neither $C_4H_8F_2$ nor C_2H_5F have been found as products for the hydrogen atom-rich condition present in this work, steps (18) and (19) have been neglected.

The rate constant $k_{5eff.} = 2.4 \times 10^{13}$ cc.mole^{-1}sec^{-1} (303°K) and the activation energy $E = 1.00$ kcal mole^{-1} are reasonable for this reaction and are, in fact, close to the values for the similar reaction (7) in the H + C_2H_4 mechanism.

(2C) $k_{6eff.}$ to k_{12}

Elimination of HF from $C_2H_5F^{**}$ **gives C_2H_4 which would be expected to** react with H atoms in a manner similar to that discussed previously. The products, CH_4, C_2H_6, C_3H_8 and n-C_4H_{10}, found in the H atom-C_2H_4 reaction, have also been found in the vinyl fluoride reaction. The yield of these four products in the H + C_2H_3F reaction has been satisfactorily explained by using the same kinetic parameters in steps (6) to (12) as were used for the

H atom-C_2H_4 reaction. Under similar experimental conditions, the calculated stoichiometric values for the H atom-C_2H_4 reaction within the H atom- C_2H_3F reaction and the stoichiometric values for the direct H atom- C_2H_4 reaction were in good agreement.

(2D) k_{13}

Penzhorn and Sandoval[17] found that hydrogen atoms might be expected to abstract either a fluorine atom or a hydrogen atom from C_2H_3F. The rate of abstraction of an F atom was much slower than the rate of abstraction of an H atom. This can be explained by: (a) the C-F bond ($D(CH_2CH\text{-}F) = 111 \pm 3$ kcal $mole^{-1}$)[189,190] is stronger than the C-H bond ($D(C_2H_3\text{-}H) = 104$ kcal $mole^{-1}$)[191] and (b) the resulting CH_2CF radical is much more stable than the CH_2CH radical because of the large negative inductive effect of the F atom.

The rate constant for step (13) was found to be $k_{13} = 1.85 \times 10^9$ $cc.mole^{-1}sec^{-1}$ (303°K), which is 14.9 times smaller than the rate for the addition reaction, step (4). This trend was found earlier by Penzhorn and Sandoval[17]. The activation energy of this step, $E_{13} = 1.22$ kcal $mole^{-1}$, was found to be greater than that of the addition reaction.

(2E) $k_{14eff.}$

Two additional products, C_2H_2 and C_3H_6, were found in the vinyl fluoride reaction. C_2H_2 arises via step (14) where the C_2H_2F radical from step (13) reacts with a hydrogen atom to give "hot" $C_2H_3F^{**}$. This $C_2H_3F^{**}$ would be expected to contain about 104 kcal $mole^{-1}$ escess energy. This hot radical could stabilize or decompose into either C_2H_2 and HF, step (14'), or into the original C_2H_2F radical and an H atom, step (-14).

Since the ratio of the rate of elimination of HF yielding C_2H_2 to that of stabilization by third body collision was found to be very high ($k_{elim.}$/

$k_{stab.} \approx 45)$[192], the stabilization of $C_2H_3F^{**}$ by collision was not considered significant. The activation energy for elimination of HF from $C_2H_3F^{**}$, step (14'), was found to be in the range of 70 to 81 kcal mole^{-1} by Simmie et al.[190] and by Cadman et al.[193]. This is much below the activation energy for elimination of H_2 from $C_2H_3F^{**}$. Thus, the elimination of HF yielding C_2H_2 is considered the most likely step for reaction (14).

The possibility of radical recombination (steps (20a) and (20b))

$$2C_2H_2F\cdot \Longleftrightarrow C_4H_4F_2^{**} \begin{array}{ll} \longrightarrow HF + C_4H_3F & (20a) \\ \xrightarrow[M]{} C_4H_4F_2 & (20b) \end{array}$$

was not considered since neither C_4H_3F nor $C_4H_4F_2$ was detected as a product in this work.

The rate constant of step (14) was found to be $k_{14eff.} = 1.17 \times 10^{13}$ cc.mole^{-1}sec^{-1} (303°K) and the activation energy was found to be $E = 0.93$ kcal mole^{-1}.

(2F) $k_{15eff.}$

C_3H_6 arises via the reaction of CH_3 and C_2H_4F radicals, step (15). This reaction gives the "hot" species, iso-$C_3H_7F^{**}$ which could stabilize or decompose into either C_3H_6 and HF, step (15'), or into the original CH_3 and C_2H_4F radicals, step (-15). Trotman-Dickenson et al.[186] found that for iso-$C_3H_7F^{**}$, elimination of HF was greatly favoured over stabilization ($k_{elim.}/k_{stab.} = 20 \pm 5$). No iso-$C_3H_7F$ was detected. Thus, HF elimination is the dominant step. Cadman et al.[184] found the activation energy for elimination of HF from iso-$C_3H_7F^{**}$ to be 53.9 kcal mole^{-1}.

The rate constant of step (15), $k_{15\text{eff.}} = 2.03 \times 10^{13}$ cc.mole^{-1}sec^{-1} (303°K), was found to be greater than that of step (14). The activation energy of step (15) was found to be $E_{15} = 0.94$ kcal mole^{-1}.

3. H ATOM-1,1-$C_2H_2F_2$ REACTION

As mentioned earlier, there is great similarity in product yields for both the H + C_2H_3F and H + 1,1-$C_2H_2F_2$ reactions. It is considered that the reaction H + C_2H_3F could form an important part of the H + 1,1-C_2H_2F reaction mechanism. The following sequence of reactions (1) to (15) is proposed for the H atom-1,1-$C_2H_2F_2$ reaction. The complete mechanism (i.e., steps 1-15) is presented in Appendix C.

$$\overbrace{H\cdot + CH_2CF_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CF_2^{\cdot\,*} \xrightarrow[M]{k_{1'}} CH_3CF_2^{\cdot}}^{k_{1eff.}} \qquad (1)$$

$$\overbrace{H^{\cdot} + CH_3CF_2^{\cdot} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH_3CF_2H^{**} \xrightarrow{k_{2'}} C_2H_3F + HF}^{k_{2eff.}} \qquad (2)$$

$$H\cdot + CH_2CF_2 \xrightarrow{k_3} CH_2CF\cdot + HF \qquad (3)$$

$$H\cdot + C_2H_3F \qquad \text{(as presented in Section 2)} \qquad (4)\text{-}(15)$$

In order to test this mechanism, values of k_4 to k_{15} were set identical to the values chosen for the H atom-C_2H_3F reaction, and $k_{1eff.}$, $k_{2eff.}$ and k_3 were varied to give the best fit to the experimental data over the temperature range 303° to 603°K. Figures 12 to 14 show that the calculated data (solid lines) are in excellent agreement with the experimental data, indicating that the mechanism is satisfactory for explaining the H + 1,1-$C_2H_2F_2$ reaction.

The rate constants $k_{1eff.}$ to $k_{15eff.}$, the activation energies, and the frequency factors over the temperature range 303° to 603°K for each of the reaction steps (1) to (15) are given in Table 15. The kinetic parameters for each of the steps of the reaction will now be discussed. Sections (3A) to (3D).

(3A) k_{1eff}.

A hydrogen atom adds to CH_2CF_2 at the nonfluorinated carbon giving a vibrationally excited $CH_3CF_2^*$ radical, step (1). This excited radical can dissociate forming an H atom and $C_2H_2F_2$, step (-1), or it can undergo collisional stabilization, step (1').

As mentioned earlier in Section 2, the reactivity for addition of H atoms to C_2H_4, C_2H_3F and 1,1-$C_2H_2F_2$ should show a decreasing trend because of the inductive effects, $-I_\sigma$ and $+ I_\pi$, of the substituted F atoms. Table 19, showing the relative rates for the addition of a number of atoms and radicals to various fluoroethylenes, summarizes the work of several investigations[17,174-179]. This table shows a decrease of reactivity when going from C_2H_4 to 1,1-$C_2H_2F_2$ for all cases except the reactions of H atoms studied by Penzhorn and Sandoval[17]. This is in agreement with the effects of $-I_\sigma$ and $+ I_\pi$ discussed previously. Although there are minor disagreements in the values for the last two compounds listed in the table, the general trend shows an increase in the relative rates. In some cases, the reactivity of C_2F_4 is even greater than that of C_2H_4.

Moss and Jennings[194] have also found that this behaviour parallels that observed in reactions with partly fluorinated propylenes and butenes. Moss[176] considered that the $+ I_\pi$ effect offsets the $-I_\sigma$ effect when three or four F atoms are attached to the double bonded carbon atoms so that the π-electron density is similar for both the non-fluorinated and the fluorinated carbon atoms of C_2HF_3 and C_2F_4. On the other hand, Trotman-Dickenson et al.[174]

TABLE 19

Relative Rates of the Addition of Atoms and Radicals to Fluoroethylenes

	H		H	H	O	S	CH_2	CCl_3		CF_3
Olefin	(303°K)	(503°K)	(298°K)	(298°K)	(298°K)	(290°K)	(298°K)	(298°K)	(437°K)	(437°K)
$CH_2 = CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$CH_2 = CHF$	0.13	0.14	0.51	0.78	0.38	0.42	0.60	0.68	0.71	0.47
$CH_2 = CF_2$	0.04	0.06	0.42	1.45	0.22	0.10	0.33	0.12	0.25	<0.47
$CHF = CF_2$			0.07	1.65	0.57	0.07	0.16	0.05	0.27	
$CF_2 = CF_2$			0.09	1.70	1.60	0.09	0.10	0.23	1.21	0.12
Reference	This work		177	17	176	179	174	175		178

stated that the reactivities of the double bonds decrease with the substitution of each successive F atom because of the $-I_\sigma$ effect. However, their results are the only ones which show a general decrease throughout the series. Further study of H + C_2HF_3 and H + C_2F_4 would be worthwhile for comparison of the kinetic parameters of these reactions with others in the table.

Tedder and Walton[175] found that the activation energies for addition of CCl_3 radicals to C_2H_4, C_2H_3F and 1,1-$C_2H_2F_2$ were 3.2, 3.3 and 4.6 kcal mole^{-1}, respectively. The trend of increasing activation energies for the series C_2H_4-$C_2H_2F_2$ is in good agreement with the trend found in this work (i.e., 0.95, 1.09 and 1.63 kcal mole^{-1}) for the addition of H atoms to C_2H_4, C_2H_3F and 1,1-$C_2H_2F_2$, respectively.

(3B) k_{2eff}.

The CH_3CF_2 radical, formed in step (1), reacts with a hydrogen atom to give a "hot" species, $CH_3CF_2H^{**}$, which can stabilize or decompose into either C_2H_3F and HF, step (2'), or into a CH_3CF_2 radical and an H atom, step (-2). Trotman-Dickenson et al.[186] found that the ratio of the rate of elimination of HF yielding C_2H_3F to that of stabilization by third body collision was very high ($k_{elim.}/k_{stab.} = 20.4$). For this reason, the stabilization of $CH_3CF_2H^{**}$ was not considered significant. The activation energy for elimination of HF from $CH_3CF_2H^{**}$ was found to be in the range 61.9 to 66.6 kcal/mole[183,190]. Therefore, the hot species, $CH_3CF_2H^{**}$, with $\backsim$ 101 kcal mole^{-1} excess energy, has sufficient energy to eliminate HF, step (2'). It is less likely that the excess energy will cause a C-H bond (D = 101 kcal/mole[180]) or C-F bond (D = 110 kcal/mole[115]) to break.

The combination of two CH_3CF_2 radicals as shown in reactions (21a) and (21b) was not considered to be important since the products $C_4H_5F_3$ and $C_4H_6F_4$ were absent.

$$2\ CH_3CF_2\cdot \rightleftharpoons C_4H_6F_4^{**} \begin{cases} \longrightarrow HF + C_4H_5F_3 & (21a) \\ \xrightarrow[M]{} C_4H_6F_4 & (21b) \end{cases}$$

(3C) k_3

Except for high temperature investigations, the abstraction reaction of an H atom in the H atom-C_2H_4 reaction has not been considered by the many investigators[13,22,111]. The present work proposes that an H atom abstracts an H atom from the fluorinated carbon in the H atom-C_2H_3F reaction. This was considered likely because of the large negative inductive effect of the fluorine resulting in a weakening of the C-H bond on the same carbon. After abstraction of H in the H + C_2H_3F reaction, C_2H_2 is formed. Step (14).

C_2H_2 was also found as a product of the H atom -1,1-$C_2H_2F_2$ reaction, but the yield was too great to be explained by using only step (14) as in the H atom-C_3H_3F reaction. Therefore, an additional type of abstraction reaction is considered to have occurred. It is possible to propose that either an H atom or an F atom may be abstracted. As shown below, only the F atom abstraction results in the formation of C_2H_2.

If F atom abstraction occurs, the mechanism would be

$$H\cdot + CH_2CF_2 \longrightarrow CH_2CF\cdot + HF \qquad (3)$$

$$H\cdot + CH_2CF\cdot \rightleftharpoons CH_2CHF^{**} \longrightarrow C_2H_2 + HF \qquad (14).$$

There are three reasons why F atom abstraction is proposed in the mechanism:

(a) D (CH_2CF-F) is probably about 111 kcal mole^{-1} (based on the value D (CH_2CH-F) = 111 ± 3 kcal/mole[190]) and D (H-F) = 135 ± 0.2 kcal/mole[196]. Therefore, reaction (3) is exothermic.

(b) The radical CH_2CF in reaction (3) is considered stabilized by the negative inductive effect of the F atom on the fluorinated carbon.

(c) The computer calculation of the C_2H_2 yield follows the experimental yield exactly, when based upon the proposed F atom abstraction, **Reaction,** (3) and (14).

If H atom abstraction occurs, the mechanism would be

$$H\cdot + CH_2CF_2 \longrightarrow CF_2CH\cdot + H_2 \qquad (22)$$

$$H\cdot + CF_2CH\cdot \rightleftharpoons CF_2CH_2^{**} \longrightarrow C_2HF + HF \qquad (23).$$

There are three reasons why the H atom abstraction reaction is not expected to occur:

(a) No C_2HF was found as a product.

(b) In step (22), a C-H bond is broken and an H-H bond formed. In C_2H_4, D (CH_2CH-H) = 104 kcal/mole[191]. If a β-deactivation effect results from the presence of fluorine, the D (C-H) in CH_2CF_2 should be greater than 104 kcal mole^{-1} (based on the evidence of Coomber and Whittle[180] that D(CH_3CHF-H) ≃ 98 and D (CF_3CH_2-H) ≃ 110 kcal mole^{-1}). Therefore, since D (H-H) = 103 kcal/mole[202] for H_2, the reaction (22) would be expected to be endothermic.

(c) From studies of abstraction reactions in the series CH_3CH_3, CH_3CH_2F, CH_3CHF_2 and CH_3CF_3, Whittle et al.[180,197] proposed that: (i) C_α-H is slightly activated by F atom (relative to C_2H_6) and (ii) C_β-H is strongly deactivated, (again relative to C_2H_6). They suggested that the deactivation of C_β-H by F atoms is partly caused by a polar effect and partly by an increase in the strength of the C_β-H bond. This β-deactivation effect was also found by other workers[15,198-201]. Thus, the abstraction of a hydrogen atom from CH_2CF_2 should be less possible then hydrogen atom abstraction from C_2H_4 which has not been found to occur.

(3D) k_4 to k_{15}

Elimination of HF from $CH_3CHF_2^{**}$ gives C_2H_3F, step (2), which would be expected to react with H atoms in a manner similar to that discussed previously. (Section 2). The products, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, C_2H_4, C_3H_6 and C_2H_2, found in the H atom-C_2H_3F reaction are also found in the 1,1-$C_2H_2F_2$ reaction. The yield of these products is satisfactorily explained by using the same kinetic parameters in steps (4) to (15) as were used for the H atom-C_2H_3F reaction.

As mentioned earlier, the trend of the rates of hydrogen atom addition reactions is: $H + C_2H_4 > H + C_2H_3F > H + 1,1\text{-}C_2H_2F_2$ and the trend of hydrogen atom abstraction reactions is: $H + 1,1\text{-}C_2H_2F_2 > H + C_2H_3F > H + C_2H_4$. The results of this work also show the ratios of rates of abstraction to rates of addition for the reactions $H + C_2H_4$, $H + C_2H_3F$ and $H + 1,1\text{-}C_2H_2F_2$ at three temperatures, 303°, 503° and 603°K, to be 0; 0.067, 0.070, 0.075; and 0.262, 0.339, 0.375, respectively.

Furthermore, it has been found that F atom abstraction occurs only in the $H + CH_2CF_2$ reaction. The ratios of the rates of H atom abstraction in $H + C_2H_3F$ to F atom abstraction in $H + CH_2CF_2$ were calculated to be 1.10, 1.99 and 2.14 for the temperatures, 303°, 503° and 603°K, respectively.

4. PREDICTION OF THE MECHANISMS FOR THE H + C_2HF_3 AND H + C_2F_4 REACTIONS

(4A) H Atom-C_2HF_3 Reaction

Since 1,1-$C_2H_2F_2$ was the major product of the H + C_2HF_3 reaction[137], and since the other products, C_2H_3F, C_2H_4, C_2H_2, C_2H_6 and HF, found in this reaction, were also found in the H atom-1,1-$C_2H_2F_2$ reaction, it is reasonable to predict that the H + 1,1-$C_2H_2F_2$ reaction forms an important part of the H + C_2HF_3 reaction mechanism. The following sequence of reactions is proposed for this reaction:

$$\mathrm{H\cdot + CHFCF_2 \rightleftharpoons CH_2FCF_2^{\cdot\,*} \xrightarrow[M]{} CH_2FCF_2^{\cdot}} \qquad (24)$$

$$\mathrm{H\cdot + CH_2FCF_2^{\cdot} \rightleftharpoons CH_2FCF_2H^{**} \longrightarrow CH_2CF_2 + HF} \qquad (25)$$

$$\mathrm{H\cdot + CH_2CF_2} \quad \text{(same as presented in Section 3) (1)-(15)}$$

The proposed reaction (24) is similar to the addition reactions of hydrogen atoms to 1,1-$C_2H_2F_2$ or to C_2H_3F, while reaction (25) is similar to the HF elimination reactions from the vibrationally excited fluorinated molecules, $CH_3CHF_2^{**}$ or $CH_3CH_2F^{**}$, in the H + 1,1-$C_2H_2F_2$ or H + C_2H_3F reactions.

An additional product, CH_2FCF_3, was detected in very small yields. The first possibility for the formation of this minor product is the addition of HF to $CHFCF_2$ as in reaction (26).

$$\mathrm{HF + CHFCF_2 \longrightarrow CH_2FCF_3} \qquad (26)$$

Moore[203] has found that the addition of HF to C_2H_3F has a very high activation energy (17 ± 2 kcal $mole^{-1}$). It is suggested that reaction (26) would also have a high activation energy. Therefore, reaction (26) is not considered significant.

The second possibility for the formation of CH_2FCF_3 is the formation and stabilization of the $CH_2FCF_3^{**}$ as given in reactions (27) to (29). Reaction (30) might also be expected to occur.

$$CH_2FCF_2H^{**} \longrightarrow CH_2FCFH\cdot + F\cdot \qquad (27)$$

$$F\cdot + CH_2FCF_2\cdot \rightleftharpoons CH_2FCF_3^{**} \longrightarrow CHFCF_2 + HF \qquad (28)$$

$$CH_2FCF_3^{**} \xrightarrow[M]{} CH_2FCF_3 \qquad (29)$$

$$CH_2FCF_3^{**} \longrightarrow CH_2F\cdot + CF_3\cdot \qquad (30)$$

If the "hot" $CH_2FCF_2H^{**}$ (from step (25)) has enough excess energy to break the C-F bond as in step (27), the resulting F atom might react with the radical CH_2FCF_2 (from step (24)) to give another "hot" molecule, $CH_2FCF_3^{**}$. This hot species could either eliminate HF to give $CHFCF_2$ as a product, step (28), or stabilize by collision to give CH_2FCF_3, step (29), or break the C-C bond to give CF_3 and CH_2F radicals, step (30). The small yield of CH_2FCF_3 may be the result of either one or both of the following:

(a) The rate constants for reactions (29) and (30) are less than the rate constant for reaction (28). (b) The rate of formation of F atoms, step (27) is slower than the rate of elimination of HF, step (25).

Since no formation of products from $CF_3\cdot$ radical reactions was observed, the rate of reaction of step (30) must be slower than (29). In any case, the yield of CH_2FCF_3 was so small (less than 1% total yield) that reactions (27) to (30) are not of great importance in the reaction H + C_2HF_3. However, it is possible that they play an important role in the H + C_2F_4 reaction where the yield of $C_2F_4H_2$ was $\sim$ 14% of the total yield.

(4B) H Atom-C_2F_4 Reaction

Except for C_2HF_3 as a major product and CF_3H as a minor product, the products, 1,1-$C_2H_2F_2$, C_2H_3F, C_2H_4, C_2H_2, C_2H_6, HF and CH_2FCF_3, found in the H atom-C_2F_4 reaction, are also found in H atom-C_2HF_3 reaction[137]. Therefore, the following sequence of reactions is proposed as a possible mechanism.

$$H\cdot + C_2F_4 \rightleftharpoons CF_2CF_2H\cdot^{*} \xrightarrow[M]{} CF_2CF_2H\cdot \tag{31}$$

$$H\cdot + CF_2CF_2H\cdot \rightleftharpoons CF_2HCF_2H^{**} \longrightarrow CFHCF_2 + HF \tag{32}$$

$$CF_2HCF_2H^{**} \longrightarrow CF_2HCFH\cdot + F\cdot \tag{33}$$

$$CF_3 + H\cdot \longrightarrow CF_3H \tag{34}$$

$H + CF_2CFH$ (same as presented in Section (4A))

(1) to (15), (24), (25) and (27) to (30)

The major product C_2HF_3 comes from reactions (31) and (32) which are similar to those proposed for the addition reactions of hydrogen atoms to the other fluorinated ethylenes. Two possible reactions, (27) and (33), act as sources of F atoms. This accounts for the increased yield of CH_2FCF_3, reaction (29).

It was observed that when the temperature was increased, the yield of CH_2FCF_3 decreased (i.e., 303° -14% yield, 503° -3% yield and 603°K -less than 1% yield). It is suggested that less collisional stabilization (29) occurs as the temperature increases, thus leading to a decreased yield of CH_2FCF_3.

CF_3H was detected as a very small product (much less than 1%). This product could result from the reaction of hydrogen atoms with CF_3 radicals originating from reaction (30).

The above assumptions have been proposed on the basis of previous product analysis[137] obtained by using a different flow system and different conditions from those used in the present work. Therefore, a complete re-investigation of the H + C_2HF_3 and H + C_2F_4 reactions might be considered worthwhile. If this could be done, the kinetic parameters of the H + 1,1-$C_2H_2F_2$ reaction could be applied to the H + C_2HF_3 and H + C_2F_4 reactions, by repeating the computer simulation method used in this work. This would allow testing of the proposed steps in order to determine their validity as part of the mechanisms of these reactions.

CHAPTER V

CONTRIBUTIONS TO KNOWLEDGE

A knowledge of the nature and distribution of the products of a reaction is an essential prerequisite for the proposal and discussion of a detailed mechanism. With this thought in mind, the H atom fluoro-ethylene reactions and the proposed mechanisms have been thoroughly investigated and then tested by using the technique of computer simulation. This simulation technique is an excellent method for testing a mechanism provided that some knowledge of rate constants for basic reactions is available. In this case, the H atom-C_2H_4 reaction was used as a starting point.

As previously stated, few of the H atom fluoro-ethylene reactions have been studied and no absolute rates have been determined for these reactions up to the present time. This work fills in this gap in the knowledge of these reactions.

Determination of the kinetic parameters for various radical-radical and atom-radical reactions has been a side product of this study. Many of these reactions had not been studied previously.

The effect of partial fluorine atom substitution on the C_2H_4 reactivity, as in the case of C_2H_3F and 1,1-$C_2H_2F_2$, has been discussed and once the full series of fluoro-substituted ethylenes has been studied, it will be possible to discuss the total effect of fluorine atom-substitution both on addition and abstraction reactions. Further work could be done on a similar series for other halogenated-ethylenes (i.e., chloro-, bromo- or iodo-ethylene), since it appears from a literature review that little work has been done on this series. A comparison of the various series would also be useful.

APPENDIX A

Gas Chromatography Calibration Curves

Figure Al

Calibration Curves for CH_4 and C_2H_6

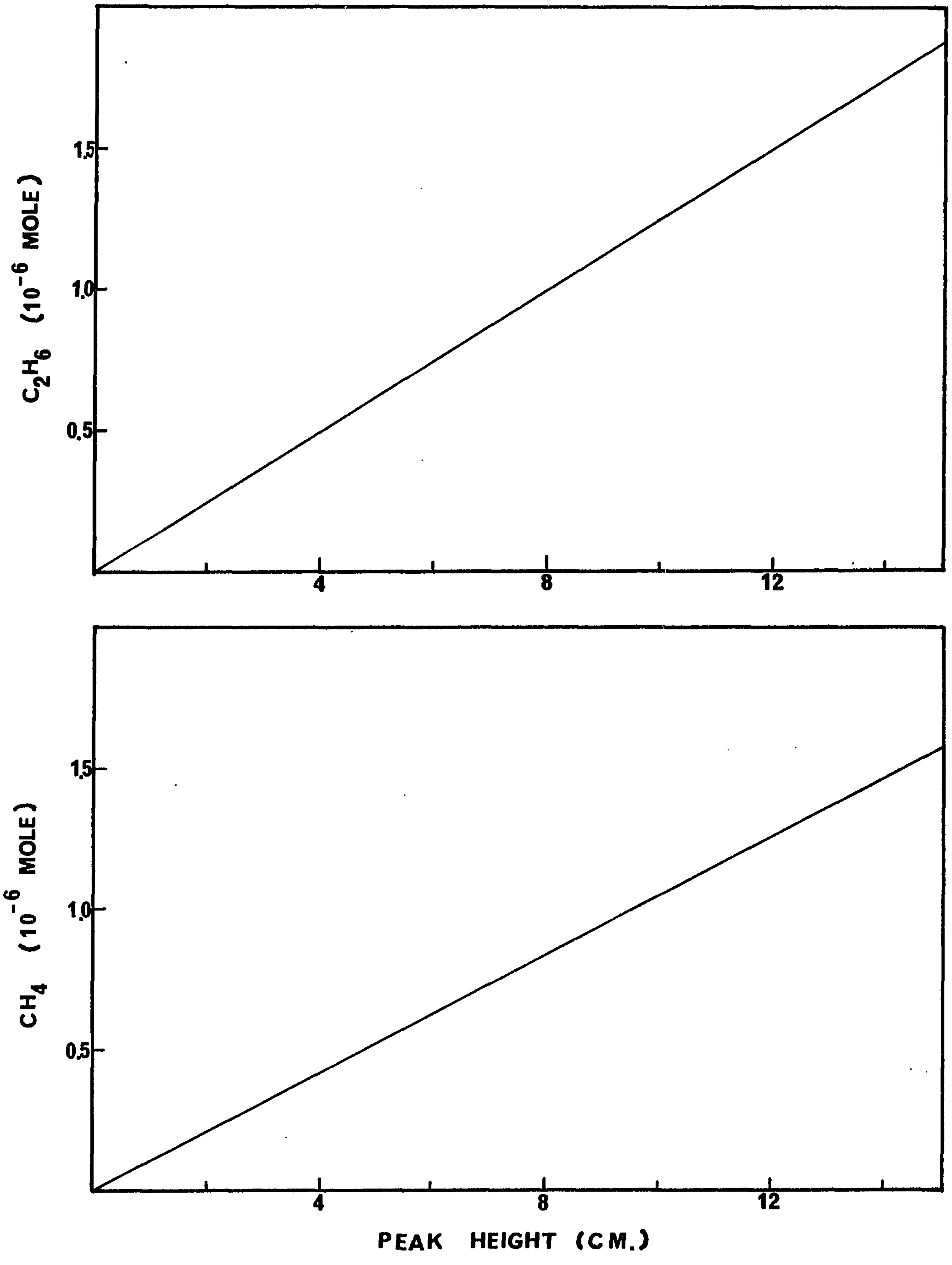
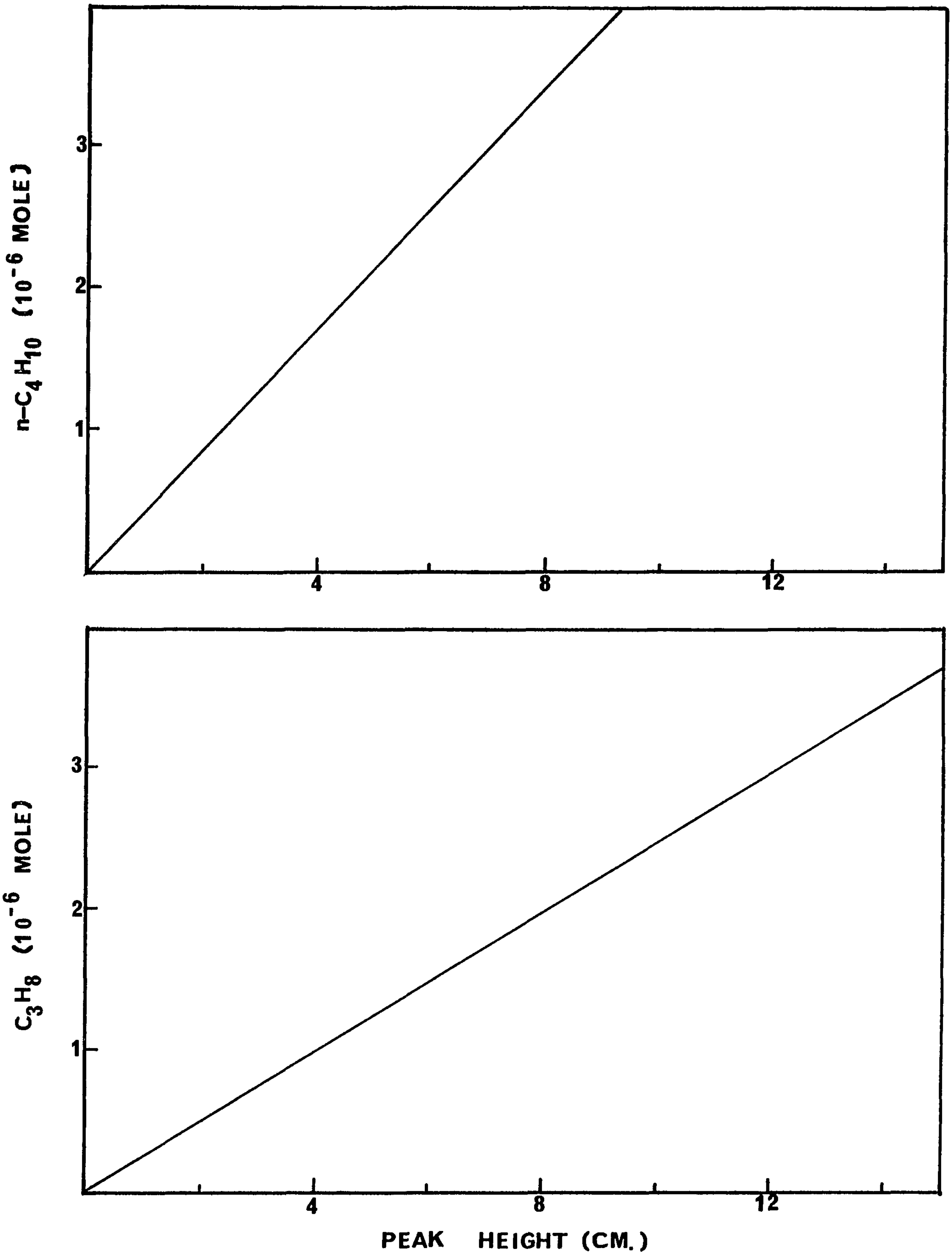

C_2H_6 (10^{-6} MOLE)
1.5
1.0
0.5
4
8
12
CH_4 (10^{-6} MOLE)
1.5
1.0
0.5
4
8
12
PEAK HEIGHT (CM.)

Figure A2

Calibration Curves for C_3H_8 and n-C_4H_{10}



$n\text{-}C_4H_{10}$ (10^{-6} MOLE)
1
2
3
4
8
12
C_3H_8 (10^{-6} MOLE)
1
2
3
4
8
12
PEAK HEIGHT (CM.)

Figure A3

Calibration Curves for C_2H_4 and C_3H_6

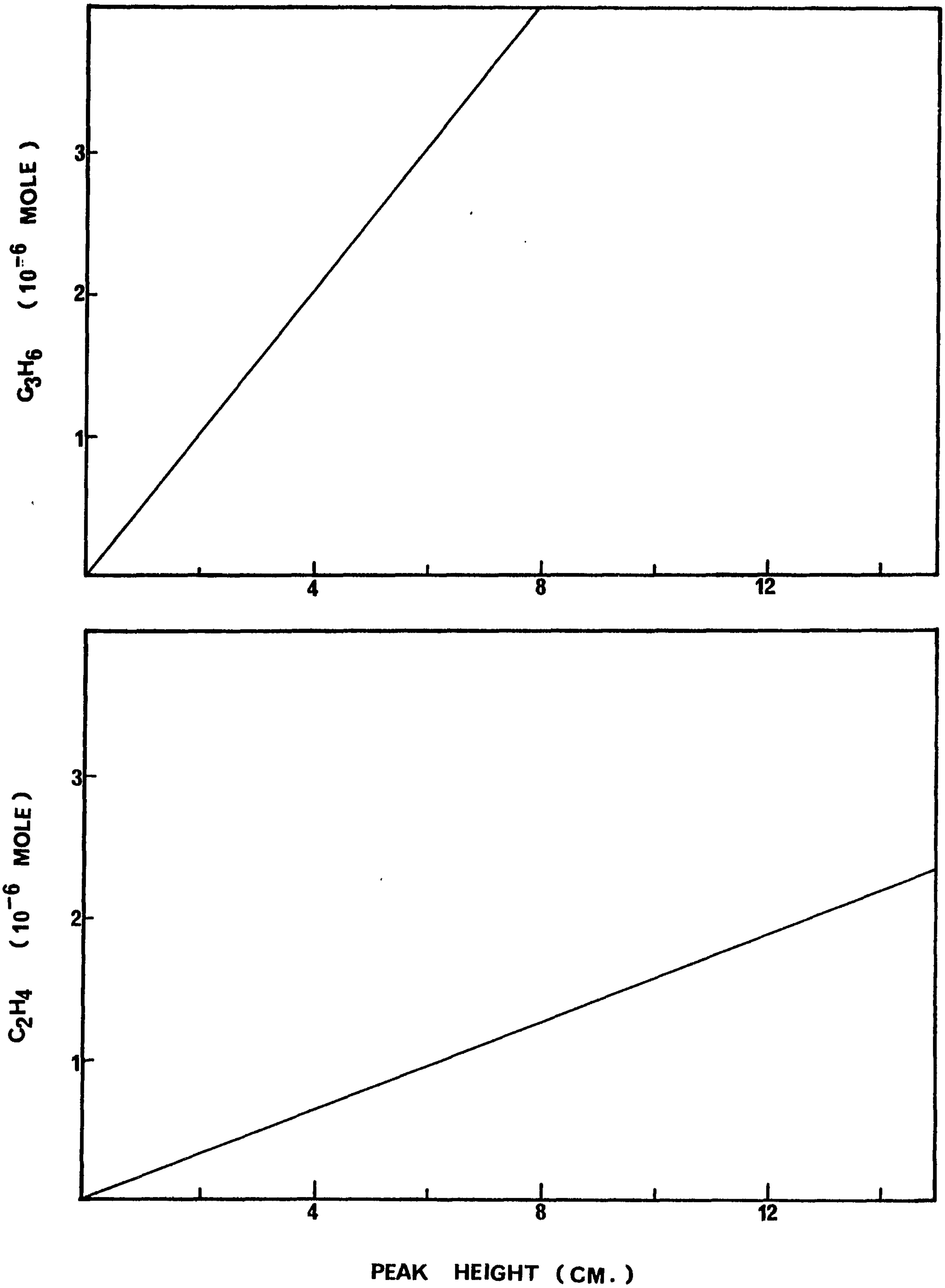

C_3H_6 (10^{-6} MOLE)
1
2
3
4
8
12
C_2H_4 (10^{-6} MOLE)
1
2
3
4
8
12
PEAK HEIGHT (CM.)

Figure A4

Calibration Curves for C_2H_2 and C_2H_3F

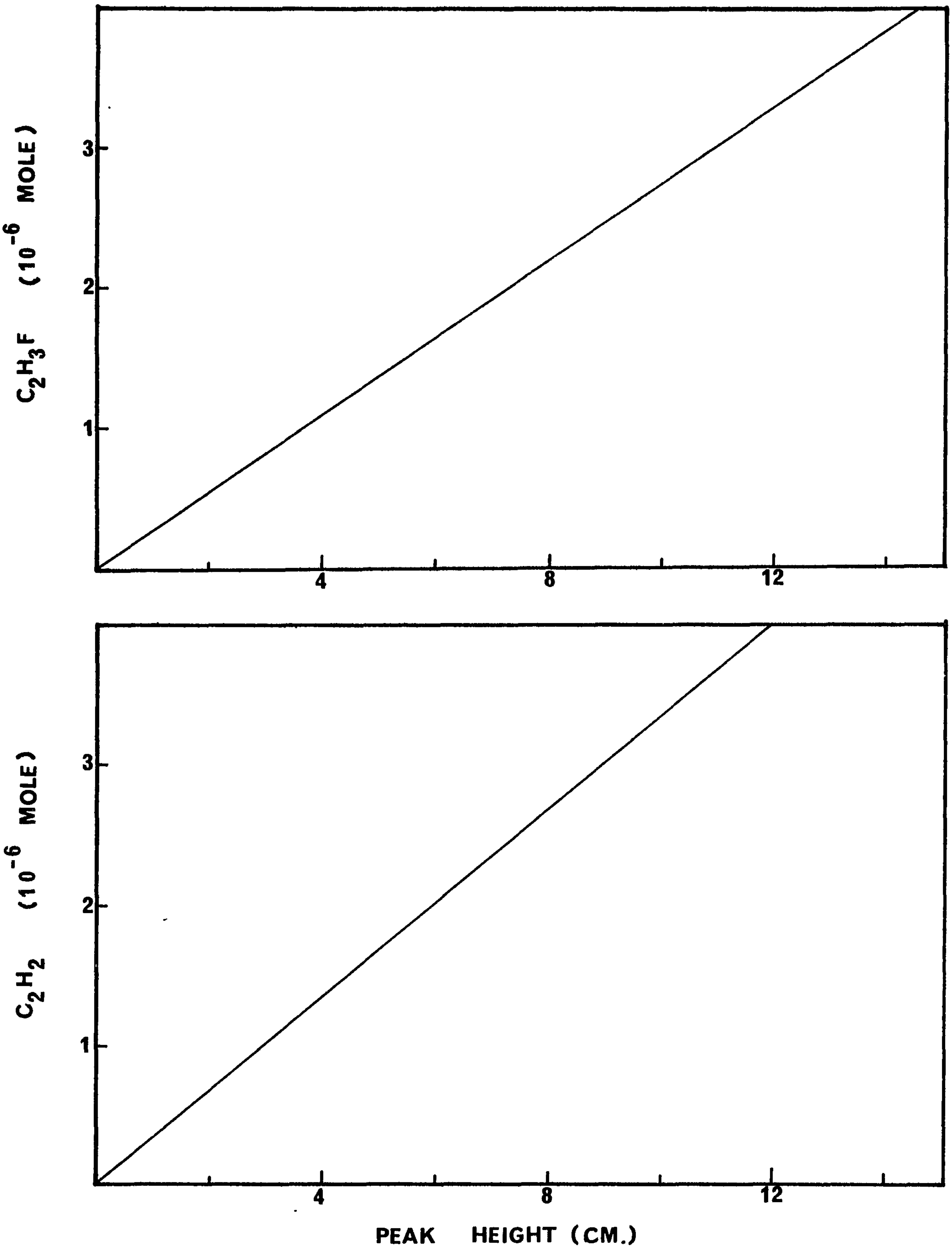
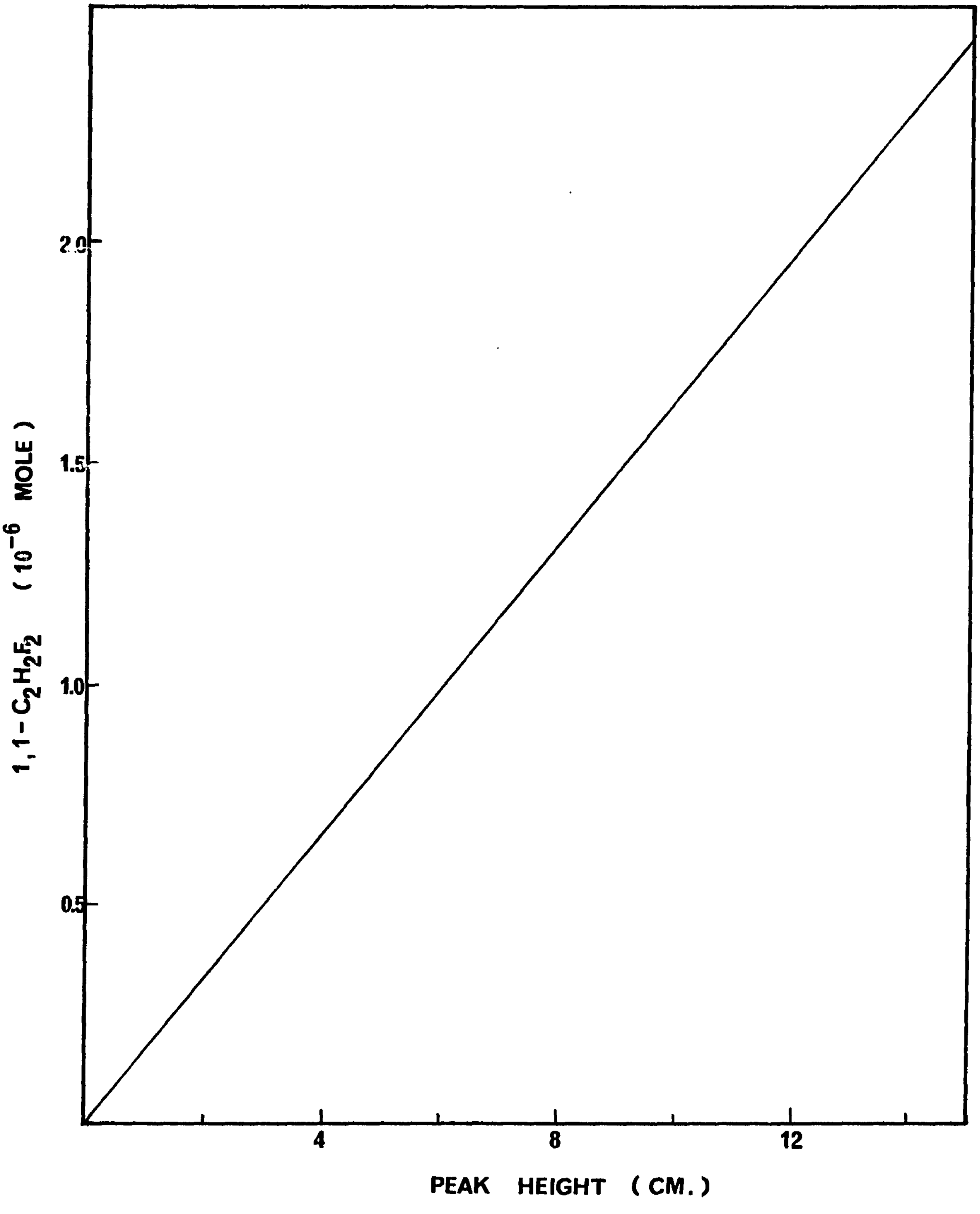

C_2H_3F (10^{-6} MOLE)
1
2
3
4
8
12
C_2H_2 (10^{-6} MOLE)
1
2
3
4
8
12
PEAK HEIGHT (CM.)

Figure A5

Calibration Curve for 1,1-$C_2H_2F_2$


2.0
1.5
1.0
0.5
$1,1-C_2H_2F_2$ (10^{-6} MOLE)
4
8
12
PEAK HEIGHT (CM.)

APPENDIX B

Summary of Experimental and Calculated Data

TABLE B1

Reaction Products Formed at Various $F_{C_2H_4}$

Temperature = 303 ± 2°K

F_H = 16.75 x 10^{-6} mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_4}$		$F_{products}$				Stoichiometry	Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}		
0.84	0.84	1.45	0.13	--	--	3.73	101
2.70	2.70	3.30	0.95	0.03	--	3.23	98
3.84	3.84	3.85	1.65	0.06	--	3.03	95
5.10	4.82	3.85	2.60	0.12	--	2.79	98
8.10	6.10	3.53	3.82	0.28	--	2.57	98
11.50	6.50	3.06	4.35	0.40	0.02	2.42	100
15.00	7.00	2.80	4.65	0.51	0.04	2.35	97
17.00	7.00	2.75	4.70	0.55	0.04	2.33	99

(Dotted line indicates negligible yield of product)

TABLE B2

Reaction Products Formed at Various $F_{C_2H_4}$

Temperature = 503 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_4}$		$F_{products}$				Stoichiometry	Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$		
0.84	0.84	1.10	0.23	--	--	3.41	93
2.70	2.70	2.58	1.35	0.03	--	3.00	99
3.84	3.82	2.83	2.25	0.06	--	2.75	98
5.10	4.77	2.85	3.55	0.15	--	2.52	109
8.10	6.10	2.50	4.40	0.28	--	2.41	100
11.50	6.70	2.16	4.85	0.41	0.02	2.26	98
15.00	7.00	1.91	5.30	0.47	0.03	2.20	100
17.00	7.00	1.90	5.50	0.55	0.03	2.18	105

(Dotted line indicates negligible yield of product)

TABLE B3

Reaction Products Formed at Various $F_{C_2H_4}$

Temperature = 603 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_4}$		$F_{products}$				Stoichiometry	Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}		
0.84	0.84	1.05	0.27	--	--	3.32	95
2.70	2.70	2.23	1.55	0.04	--	2.91	97
3.84	3.82	2.47	2.43	0.06	--	2.69	97
5.10	4.78	2.52	3.50	0.12	--	2.49	103
8.10	6.10	2.06	4.70	0.29	--	2.29	101
11.50	6.75	2.02	5.20	0.41	0.02	2.23	102
15.00	7.00	1.65	5.55	0.51	0.03	2.15	103
17.00	7.40	1.65	5.40	0.55	0.03	2.14	96

(Dotted line indicates negligible yield of product)

TABLE B4

Computer Calculated Yields of Reaction Products at Various $F_{C_2H_4}$

Temperature = 303 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_4}$		$F_{products}$				Stoichiometry	Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$		
0.84	0.84	1.42	0.12	--	--	3.71	100
2.70	2.70	3.46	0.91	0.04	--	3.27	100
3.84	3.84	4.17	1.63	0.08	--	3.07	100
5.10	4.97	4.25	2.60	0.16	--	2.83	100
8.10	5.99	3.59	3.65	0.34	0.01	2.55	100
11.50	6.56	3.12	4.18	0.50	0.02	2.40	100
15.00	6.93	2.79	4.50	0.63	0.04	2.30	100
17.00	7.08	2.64	4.61	0.68	0.04	2.27	100

(Dotted line indicates negligible yield of product)

TABLE B5

Computer Calculated Yields of Reaction Products at Various $F_{C_2H_4}$

Temperature = 503 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_4}$		$F_{products}$				Stoichiometry	Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$		
0.84	0.84	1.21	0.23	--	--	3.47	100
2.70	2.70	2.61	1.34	0.03	--	3.00	100
3.84	3.84	3.02	2.23	0.07	--	2.77	100
5.10	4.98	3.00	3.27	0.13	--	2.58	100
8.10	6.09	2.53	4.39	0.27	0.01	2.38	100
11.50	6.69	2.19	4.95	0.39	0.02	2.27	100
15.00	7.07	1.94	5.28	0.50	0.03	2.20	100
17.00	7.22	1.83	5.39	0.53	0.03	2.18	100

(Dotted line indicates negligible yield of product)

TABLE B6

Computer Calculated Yields of Reaction Products at Various $F_{C_2H_4}$

Temperature = 603 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_4}$		$F_{products}$				Stoichiometry	Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	$n-C_4H_{10}$		
0.84	0.84	1.15	0.26	--	--	3.38	100
2.70	2.70	2.40	1.45	0.03	--	2.88	100
3.84	3.84	2.76	2.36	0.06	--	2.70	100
5.10	5.05	2.79	3.48	0.12	--	2.53	100
8.10	6.23	2.30	4.67	0.26	0.01	2.33	100
11.50	6.83	1.96	5.22	0.38	0.01	2.23	100
15.00	7.19	1.73	5.53	0.48	0.02	2.17	100
17.00	7.34	1.62	5.63	0.52	0.02	2.15	100

(Dotted line indicates negligible yield of product)

TABLE B7

Reaction Products Formed at Various $F_{C_2H_3F}$

Temperature = 303 ± 2°K

$F_H = 13.70 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_3F}$		$F_{products}$						Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_2H_2	
0.79	0.73	1.07	0.07	--	0.01	--	0.03	88
1.51	1.18	1.55	0.28	--	0.07	--	0.05	100
3.00	1.66	1.71	0.45	0.02	0.20	0.03	0.10	101
4.90	1.98	1.67	0.69	0.03	0.38	0.06	0.15	110
8.40	2.90	1.68	0.79	0.05	0.68	0.08	0.16	92
10.80	2.90	1.70	0.82	0.05	0.91	0.10	0.18	103
13.65	2.85	1.60	0.86	0.06	1.10	0.12	0.21	114
16.70	3.30	1.55	0.85	0.07	1.30	0.14	0.20	104

(Dotted line indicates negligible yield of product)

TABLE B8

Reaction Products Formed at Various $F_{C_2H_3F}$

Temperature = 503 ± 2°K

$F_H = 13.70 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_3F}$		$F_{products}$						Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_2H_2	
0.79	0.62	0.76	0.16	--	0.02	--	0.05	98
1.51	1.11	1.00	0.38	--	0.05	0.02	0.08	94
3.00	1.54	1.20	0.56	0.02	0.19	0.03	0.11	100
4.90	2.00	1.25	0.70	0.03	0.40	0.07	0.15	101
8.40	2.60	1.10	0.89	0.03	0.80	0.10	0.20	101
10.80	2.70	1.05	0.94	0.04	1.00	0.12	0.22	108
13.65	3.65	1.00	0.98	0.05	1.20	0.15	0.23	88
16.70	3.70	0.95	0.98	0.05	1.35	0.15	0.25	91

(Dotted line indicates negligible yield of product)

TABLE B9

Reaction Products Formed at Various $F_{C_2H_3F}$

Temperature = 603 ± 2°K

$F_H = 13.70 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_3F}$		$F_{products}$						Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_2H_2	
0.79	0.62	0.71	0.19	--	0.02	--	0.05	99
1.51	1.01	0.95	0.39	0.01	0.09	0.03	0.07	106
3.00	1.60	1.07	0.62	0.01	0.19	0.05	0.11	97
4.90	2.20	1.17	0.86	0.03	0.38	0.07	0.16	97
8.40	2.50	0.95	0.96	0.04	0.76	0.12	0.20	105
10.80	3.05	0.93	0.98	0.04	0.95	0.16	0.21	95
13.65	3.65	0.85	1.07	0.05	1.20	0.17	0.23	89
16.70	3.30	0.81	1.07	0.05	1.45	0.20	0.25	108

(Dotted line indicates negligible yield of product)

TABLE B10

Computer Calculated Yields of Reaction Products at Various $F_{C_2H_3F}$

Temperature = 303 ± 2°K

$F_H = 13.70 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_3F}$		$F_{products}$							Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_2H_2	HF	
0.79	0.68	1.08	0.08	--	0.01	--	0.04	0.69	100
1.51	1.11	1.51	0.10	0.01	0.06	0.01	0.07	1.11	100
3.00	1.66	1.80	0.40	0.02	0.18	0.03	0.10	1.66	100
4.90	2.12	1.85	0.56	0.03	0.37	0.05	0.13	2.11	100
8.40	2.67	1.74	0.70	0.05	0.71	0.08	0.17	2.66	100
10.80	2.95	1.65	0.76	0.06	0.93	0.10	0.18	2.94	100
13.65	3.22	1.54	0.79	0.07	1.17	0.12	0.20	3.21	100
16.70	3.45	1.44	0.80	0.07	1.40	0.13	0.21	3.57	100

(Dotted line indicates negligible yield of product)

TABLE B11

Computer Calculated Yields of Reaction Products at Various $F_{C_2H_3F}$

Temperature = 503 ± 2°K

$F_H = 13.70 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_3F}$		$F_{products}$							Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_2H_2	HF	
0.79	0.64	0.80	0.16	--	0.02	0.01	0.04	0.64	100
1.51	1.03	1.05	0.32	0.01	0.08	0.02	0.07	1.03	100
3.00	1.59	1.22	0.57	0.02	0.22	0.04	0.10	1.59	100
4.90	2.07	1.24	0.75	0.03	0.42	0.07	0.14	2.07	100
8.40	2.67	1.15	0.89	0.04	0.79	0.10	0.17	2.66	100
10.80	2.97	1.08	0.94	0.05	1.02	0.13	0.19	2.97	100
13.65	3.26	1.00	0.96	0.05	1.27	0.15	0.21	3.26	100
16.70	3.52	0.93	0.96	0.05	1.51	0.17	0.23	3.51	100

(Dotted line indicates negligible yield of product)

TABLE B12

Computer Calculated Yields of Reaction Products at Various $F_{C_2H_3F}$

Temperature = 603 ± 2°K

$F_H = 13.7 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{C_2H_3F}$		$F_{products}$							Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_2H_2	HF	
0.79	0.65	0.77	0.18	--	0.02	0.01	0.05	0.65	100
1.51	1.05	1.01	0.36	0.01	0.07	0.02	0.07	1.05	100
3.00	1.62	1.16	0.63	0.02	0.20	0.04	0.11	1.62	100
4.90	2.10	1.16	0.82	0.03	0.40	0.07	0.15	2.10	100
8.40	2.70	1.07	0.98	0.04	0.76	0.11	0.19	2.69	100
10.80	3.00	1.00	1.02	0.05	0.98	0.13	0.21	3.00	100
13.65	3.35	0.93	1.04	0.05	1.23	0.16	0.23	3.28	100
16.70	3.54	0.86	1.04	0.05	1.46	0.17	0.25	3.53	100

(Dotted line indicates negligible yield of product)

TABLE B13

Reaction Products Formed at Various $F_{1,1\text{-}C_2H_2F_2}$

Temperature = 603 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{1,1\text{-}C_2H_2F_2}$		$F_{products}$						Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_2H_4	C_3H_6	C_2H_2	C_2H_3F	
1.20	0.60	0.38	0.05	--	--	0.14	0.19	95
3.00	1.11	0.58	0.06	0.04	--	0.31	0.51	109
5.10	1.61	0.65	0.09	0.07	--	0.38	0.70	98
7.90	2.25	0.71	0.11	0.12	--	0.50	1.10	97
11.00	2.50	0.71	0.12	0.14	0.01	0.58	1.40	104
13.10	2.90	0.71	0.13	0.17	0.01	0.66	1.61	101
14.50	3.20	0.73	0.15	0.19	0.01	0.70	1.70	97
17.20	3.40	0.65	0.14	0.20	0.02	0.75	1.89	97

(Dotted line indicates negligible yield of product)

TABLE B14

Reaction Products Formed at Various $F_{1,1-C_2H_2F_2}$

Temperature = 503 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{1,1-C_2H_2F_2}$		$F_{products}$						Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_2H_4	C_3H_6	C_2H_2	C_2H_3F	
1.20	0.60	0.33	0.05	--	--	0.21	0.24	96
3.00	1.54	0.44	0.13	0.07	--	0.38	0.53	86
5.10	1.80	0.44	0.15	0.13	0.01	0.56	0.90	109
7.90	2.60	0.47	0.17	0.14	0.01	0.70	1.28	99
11.50	3.15	0.41	0.15	0.22	0.02	0.84	1.78	103
13.10	3.50	0.40	0.16	0.20	0.02	0.92	1.94	99
14.50	3.70	0.39	0.15	0.21	0.02	0.95	2.01	96
16.75	3.75	0.38	0.14	0.23	0.02	1.04	2.21	102

(Dotted line indicates negligible yield of product)

TABLE B15

Reaction Products at Various $F_{1,1\text{-}C_2H_2F_2}$

Temperature = 603 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{1,1\text{-}C_2H_2F_2}$		$F_{products}$						Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_2H_4	C_3H_6	C_2H_2	C_2H_3F	
1.20	0.69	0.32	0.06	--	--	0.24	0.19	94
2.95	1.54	0.39	0.14	0.08	--	0.42	0.58	92
5.10	2.10	0.44	0.16	0.10	0.01	0.65	0.94	100
7.60	2.75	0.46	0.16	0.14	0.01	0.73	1.33	95
11.30	3.40	0.40	0.18	0.22	0.02	0.94	1.80	99
13.10	3.65	0.36	0.16	0.19	0.02	1.03	1.96	97
14.50	3.70	0.39	0.19	0.23	0.02	1.09	2.05	102
16.75	3.85	0.37	0.15	0.23	0.02	1.16	2.21	103

(Dotted line indicates negligible yield of product)

TABLE B16

Computer Calculated Yields of Reaction Products at Various $F_{1,1\text{-}C_2H_2F_2}$

Temperature = 303 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{1,1\text{-}C_2H_2F_2}$		$F_{products}$							Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_2H_4	C_3H_6	C_2H_2	C_2H_3F	HF	
1.10	0.56	0.41	0.03	--	--	0.13	0.16	0.96	100
3.00	1.18	0.61	0.07	0.04	--	0.27	0.45	1.90	100
5.00	1.66	0.69	0.10	0.07	0.01	0.38	0.73	2.59	100
8.00	2.23	0.72	0.12	0.12	0.01	0.50	1.09	3.35	100
11.00	2.67	0.71	0.13	0.14	0.01	0.60	1.41	3.84	100
13.00	2.93	0.70	0.13	0.17	0.01	0.65	1.59	4.27	100
14.50	3.11	0.69	0.13	0.19	0.01	0.69	1.72	4.56	100
17.00	3.38	0.66	0.14	0.20	0.01	0.75	1.93	4.82	100

(Dotted line indicates negligible yield of product)

TABLE B17

Computer Calculated Yields of Reaction Products at Various $F_{1,1-C_2H_2F_2}$

Temperature = 503 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{1,1-C_2H_2F_2}$		$F_{products}$							Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_2H_4	C_3H_6	C_2H_2	C_2H_3F	HF	
1.10	0.64	0.32	0.06	0.03	--	0.18	0.21	1.07	100
3.00	1.37	0.44	0.11	0.07	0.01	0.38	0.57	2.17	100
5.00	1.94	0.47	0.14	0.11	0.01	0.53	0.70	2.97	100
8.00	2.60	0.46	0.15	0.16	0.01	0.70	1.32	3.86	100
11.50	3.20	0.43	0.16	0.20	0.02	0.85	1.74	4.64	100
13.00	3.41	0.41	0.16	0.21	0.02	0.90	1.89	2.92	100
14.50	3.61	0.39	0.16	0.22	0.02	0.95	2.04	5.16	100
16.50	3.85	0.37	0.15	0.23	0.02	1.01	2.22	5.46	100

(Dotted line indicates negligible yield of product)

TABLE B18

Computer Calculated Yields of Reaction Products at Various $F_{1,1-C_2H_2F_2}$

Temperature = 603 ± 2°K

$F_H = 16.75 \times 10^{-6}$ mole·sec^{-1}

F = Flow Rate (mole·sec^{-1}) x 10^6

$F_{1,1-C_2H_2F_2}$		$F_{products}$							Carbon Balance %
Input	Reacted	CH_4	C_2H_6	C_2H_4	C_3H_6	C_2H_2	C_2H_3F	HF	
1.10	0.68	0.32	0.07	0.03	--	0.20	0.21	1.14	100
3.00	1.44	0.43	0.13	0.07	0.01	0.43	0.58	2.30	100
5.00	2.04	0.45	0.16	0.11	0.01	0.60	0.92	3.16	100
7.50	2.63	0.44	0.17	0.15	0.01	0.76	1.29	3.96	100
11.50	3.35	0.40	0.18	0.19	0.02	0.96	1.78	4.91	100
13.00	3.57	0.38	0.17	0.21	0.02	1.02	1.94	5.19	100
14.50	3.77	0.36	0.17	0.22	0.02	1.07	2.08	5.45	100
16.50	4.01	0.34	0.17	0.23	0.02	1.14	2.26	5.75	100

(Dotted line indicates negligible yield of product)

APPENDIX C

Summary of the Mechanisms for the Reactions of H Atoms with 1,1-$C_2H_2F_2$, C_2H_3F and C_2H_4

$$H\cdot + C_2H_2F_2 \rightleftharpoons C_2H_3F_2\cdot^{*} \xrightarrow[M]{} C_2H_3F_2\cdot \qquad (1)$$

$$H\cdot + C_2H_3F_2\cdot \rightleftharpoons C_2H_4F_2^{**} \longrightarrow C_2H_3F + HF \qquad (2)$$

$$H\cdot + C_2H_2F_2 \longrightarrow C_2H_2F\cdot + HF \qquad (3)$$

$H + 1,1\text{-}C_2H_2F_2$

$$H\cdot + C_2H_3F \rightleftharpoons C_2H_4F\cdot^{*} \xrightarrow[M]{} C_2H_4F\cdot \qquad (4)$$

$$H\cdot + C_2H_4F\cdot \rightleftharpoons C_2H_5F^{**} \longrightarrow C_2H_4 + HF \qquad (5)$$

$H + C_2H_3F$

$$H\cdot + C_2H_4 \rightleftharpoons C_2H_5\cdot^{*} \xrightarrow[M]{} C_2H_5\cdot \qquad (6)$$

$$H\cdot + C_2H_5\cdot \rightleftharpoons C_2H_6^{**} \longrightarrow CH_3\cdot + CH_3\cdot \qquad (7)$$

$$H\cdot + CH_3\cdot \rightleftharpoons CH_4^{*} \xrightarrow[M]{} CH_4 \qquad (8)$$

$H + C_2H_4$

$$CH_3\cdot + CH_3\cdot \rightleftharpoons C_2H_6^{*} \xrightarrow[M]{} C_2H_6 \qquad (9)$$

$$CH_3\cdot + C_2H_5\cdot \longrightarrow C_3H_8 \qquad (10)$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_4H_{10} \qquad (11)$$

$$H\cdot \xrightarrow{\text{wall}} 1/2\ H_2 \qquad (12)$$

$$H\cdot + C_2H_3F \longrightarrow C_2H_2F\cdot + H_2 \qquad (13)$$

$$H\cdot + C_2H_2F\cdot \rightleftharpoons C_2H_3F^{**} \longrightarrow C_2H_2 + HF \qquad (14)$$

$$CH_3\cdot + C_2H_4F\cdot \rightleftharpoons 1\text{-}C_3H_7F^{**} \longrightarrow C_3H_6 + HF \qquad (15)$$

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