Tab. C

Optimierter Parametersatz zur Darstellung der individuellen partiellen Paarkorrelationsfunktionen der reinen Komponenten SiCl₄, GeCl₄, SnCl₄. Z steht für das zentrale Atom Si, Ge, Sn, L für das Cl-Atom. Die Parameter a_{kl} , b_{kl} , r_{kl} , d, D sind durch Gln. (11)–(13) definiert. R ist der R-Faktor

Typ k	ı	$a_{\mathbf{k}l}$	SiCl ₄ b _{kl} /Å	r _{ki} /Å	$a_{\mathbf{k}i}$	GeCl ₄ b _{ki} /Å	r _{ki} ∕Å	a _{ki}	SnCl₄ b _{ki} /Å	$r_{\mathbf{k}l}/\mathbf{\mathring{A}}$
ZZ	1	0,5186	0,7604	5,8324	0,5252	0,6788	5,8408	0,5201	0,7357	5,8488
	2	0,7163	0,4693	5,7567	0,7698	0,4496	5,6907	0,7496	0,4430	5,7488
	3	0,7943	0,6113	6,6727	0,7843	0,6564	6,6925	0,7893	0,6419	6,7702
	4	0,1039	1,9842	12,4437	-0,2005	0,7664	14,1941	0,1158	2,0535	13,3578
	5	-0,1832	0,6459	14,0326	0,1175	1,9951	12,9403	-0,1553	1,0769	14,4956
ZL	1	0,7098	1,0957	4,9039	0,7333	0,9438	4,6029	0,8283	0,8962	4,5702
	2	0,6166	0,2118	5,3896	0,5961	0,3106	5,5675	0,6469	0,2733	5,6239
	3	0,2552	0,5226	7,4782	0,1022	0,2472	7,4921	0,2483	0,3082	7,5172
	4	0,3819	0,6185	7,3172	0,4682	0.8481	7,3538	0,4280	0,8125	7,5708
	5	0,0890	1,9157	8,3042	0,1018	1,6530	8,2143	0,0765	1,7808	8,2330
LL	1	0,8020	0,2144	3,7430	0,9732	0,3142	3,8164	1,2248	0,3703	3,8413
	2	0,8943	0,5503	4,4465	0,8878	0,4735	4,8134	0,8408	0,3904	5,0090
	3	0,8516	0,7098	6,3037	0,8416	0,6254	6,4091	0,9891	0,5492	6,4337
	4	0,2424	0,9348	8,6610	0,1933	1,4608	8,7529	0,2234	1,0648	9,1201
	5	0,0140	1,8049	9,2291	-0,0080	1,9874	11,9854	-0,0054	2,1753	12,4995
						· · · · ·				

R = 0,0513

d = 3,5 Å, D = 12,0 Å

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R = 0,0650

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Kinetic Study of Chemically Activated Fluorocyclopropane

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Chemical Activation / Chemical Kinetics / Gases

The photolysis of ketene at 313 nm was studied in the presence of fluoroethene and oxygen. The product formation was observed as a function of total pressure between 12 and 1080 mbar. Chemically activated fluorocyclopropane was formed by addition of singlet methylene to the double bond, and subsequent isomerization to the fluoropropenes as well as decomposition of these primary products to allene, propyne and HF was observed. The product yield was described by RRKM calculations; a stepladder deactivation model was used.

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Introduction

The isomerization of monofluorocyclopropane (FCP) to the four isomeric fluoropropenes (FP) has been studied some time ago by chemical activation [1]. The thermal system was also investigated [2]. Two publications discuss the behaviour of the four product channels in the fall-off region [3, 4].

As shown for the parent compound, cyclopropane, elimination of CH_2 can be observed as a second channel in addition to isomerization when the molecule is highly energized [5]:

$$CH_{3}CH = CH_{2}$$

 $E_{a} = 272 \text{ kJ/mol}$
 $\log A(s^{-1}) = 15.2$
 $CH_{2} = CH_{2} + CH_{2}$
 $E_{a} = 418 \text{ kJ/mol}$
 $\log A(s^{-1}) = 15$

For the elimination pathway the given Arrhenius parameters have only been estimated. An elimination process is the dominant reaction, however, in the decomposition of the highly fluorinated cyclopropanes [6-8]; this is apparently due to the increased ring strain in these compounds [9]. The elimination process is considered to be negligible in the case of the monofluorocompound [1, 2]. We are interested in these dual channel systems and have therefore repeated the experiments of Casas et al. [1] under improved experimental conditions: monochromatic light was used in the photolysis of ketene and molecular oxygen was added to suppress reactions of triplet methylene [10]. We also wanted to compare the reactions of chemically activated FCP with those of the monochlorocompound studied previously in our laboratory [11].

The reaction scheme adopted to interpret our results and the symbols used for the rate constants are given in Fig. 1.



Fig. 1

Reaction mechanism of the photolysis of ketene in the presence of fluoroethene; asterisks indicate high vibrational energy by chemical activation

This scheme takes account of $CH_2({}^{1}A_1)$ inserting into the CH bonds as well as adding to the double bond as verified before [1]. It also includes the secondary chemical activation steps which have already been suggested by Casas et al. [1] but which were not used in their evaluations. Similar secondary processes were described by Eichler and Heydtmann for the chlorocyclopropane system [11]. Reactions of CH_2 with ketene and the recombination processes for CH_2 [12] which lead to C_2H_4 and C_2H_2 have been omitted in Fig. 1.

Experimental

Materials

Ketene was prepared by pyrolytic decomposition of acetic anhydride in a quartz tube at 500°C according to a procedure described by Jenkins [13] and purified by several trap-to-trap distillations between 77 and 196 K. The substance obtained by this method contains only slight impurities of ethene and diketene (both less than 0.3%). Oxygen (99.98% pure) and fluoroethene (99.9% pure) were obtained from Matheson Gas Products and used without further purification. The 1-fluoropropenes and 3-fluoropropene were synthesized by standard methods [14, 15]. 2-fluoropropene, allene and propyne which were also required for calibrations were purchased from PCR Research Chemicals (2-FP) and from Matheson Gas Products.

Apparatus

All experiments were performed in a static vacuum system equipped with greaseless stopcocks. A quartz cylinder of 250 mm length and 40 mm i.d. with Suprasil I quartz windows served as the reaction vessel. The reactants were transferred into a small cold trap connected to the reaction vessel from a calibrated vessel joined to precision manometers (Heise CM 12 and Heise 710 A) and then evaporated into the reaction vessel. For ketene photolysis a 200 W high-pressure mercury arc and a high-intensity monochromator (Bausch and Lomb) were used.

Experiments and Analysis

Experiments were carried out with mixtures containing fluoroethene, ketene, and oxygen in the ratio 10:1:1. They were irradiated with 313 nm light at total pressures between 12 and 1080 mbar. Photolysis time was usually 3 hours. After this time the conversion was estimated to be about 10%. Longer irradiation times did not lead to change in product composition thus proving the stability of the products under our experimental conditions. Pulsed laser photolysis at 308 nm of the same system leading to much lower conversion (about 1%) gave very similar results [36]. These experiments also proved that heterogeneous effects cannot be important.

Product analysis was performed with a Perkin-Elmer 900 HF gas chromatograph equipped with a flame ionization detector and a gas-sampling valve directly coupled to the reaction vessel. Considerable effort was necessary to accomplish the quantitative analysis of all compounds. Three columns were used to this end:

- 1. 12 m column filled with di-n-decylphthalate on chromosorb R NAW 60-80 mesh at 300 K.
- 1.8 m column with AgNO₃ and diethyleneglycole on chromosorb R coupled to the 12 m column as described under 1. at 273 K.
- 12 m column filled with 10% carbowax 20 M on chromosorb R, NAW 60-80 mesh at 333 K.

With all columns a 30 cm³/min He flow was applied. All components were identified by comparison with known samples except for the cis- and trans-isomers of 1-FP. The first peak of a 1-FP mixture was considered to be the trans-compound, as proposed by Casas et al. [1] for a column similar to column 1.

This assumption is not critical, however, since the calculations described later do not distinguish the cis and trans components. Column 1 could not separate 2-FP from allene and t-1-FP from propyne. With column 2 propyne was absorbed by reaction with

AgNO₃, but now 2-FP and ethene, a side product, were detected together. With column 3 propyne could be determined but 3-FP had the same retention time as CFP, and t-1-FP was not separated from allene. Thus columns 2 and 3 were required to analyze allene and propyne, respectively.

Results

1. Primary and Secondary Reaction Products

The results of four typical product analyses are given in Table 1. It is evident that the yield of the secondary reaction products propyne and allene drops from high values at low pressure to almost zero at the highest pressure used. Among other products ethene was detected and certainly ethyne was also present although it could not be separated from fluoroethene on any of the columns used. The occurence of these species is well known from the photolysis of pure ketene [11, 12]. Acetone which was found in the chlorocyclopropane system [11] was also detected. One additional product was present in appreciable amounts but could not be identified. We could exclude the formation of CH_3F , CH_2F_2 , 1,1-difluoroethene, 1,2-difluoroethane, 1,1-difluoropropane, butadiene and CH_2O . Trace amounts of other products were always present and consisted probably of C₄ hydrocarbons. Polymerization which occurred in the chlorocyclopropane [11] system was not observed.

Table 1

Compositions of four reaction mixtures characterized by the initial pressures p_0 after 3 h-irradiation at 313 nm given in %. Only products of primary and secondary reactions are shown

P0 total	(mbar)	32	240	640	1080
p_0 fluoroethene	(mbar)	26.6	200	533.3	900
p_0 ketene	(mbar)	2.7	20	53.3	90
p_0 oxygene	(mbar)	2.7	20	53.3	90
c, t-1-fluoropropene		5.4	23.3	23.0	18.7
2-fluoropropene		0.2	4.5	6.4	4.7
3-fluoropropene		10.9	19.4	16.7	13.2
fluorocyclopropane		0.2	5.8	21.2	31.4
propyne		34.8	9.5	3.4	1.6
allene		15.3	4.1	1.6	0.9
other products*)		33.2	33.4	27.7	29.5

*) Ethene, acetone and one unidentified product.

Although some other reactions apparently occurred we propose that the scheme of reactions shown in Fig. 1 can be treated independently. In this scheme the main primary process is the addition of ${}^{1}CH_{2}$ to the double bond forming chemically activated FCP, which isomerizes or is stabilized by collisions. Four isomerization channels are observed, but since two of the products are found in almost the same ratio under all conditions (cis-1-FP: trans-1-FP = 0.7 ± 0.1) only three channels are considered.

2. Evaluation of Raw Data

The apparent rate constant for a unimolecular reaction of a chemically activated substance is defined by

$$\langle k_{\mathbf{a}} \rangle_i = \omega(I_i / S) \tag{1}$$

where I_i denotes the yield of isomerization (or decomposition) products in the *i*-th channel, S the yield of the stabilized molecules, and ω the first order collision rate constant [16]. The evaluation of $\langle k_a \rangle$ which was straightforward in the case of chlorocyclopropane [11] is more complicated in the present system because of two reasons: ¹CH₂ also reacts to some extent by insertion and furthermore the secondary decomposition of 2-FP leads to both allene and propyne, whereas 2-chloropropene was formed only in negligible amounts in our previous study of the ketene/chloroethene system [11].

We deal first with the question how the secondary products allene and propyne can be divided into contributions from the primary channels concerned. For the final concentrations of propyne we can write

$$[propyne] = [propyne_{2-FP}] + [propyne_{1-FP}]$$

where the subscript indicates the channel of formation. With the basic relation (1) assuming strong collisions for the secondary processes, i.e. $\omega = Z \cdot p$, we arrive at

$$[\text{propyne}] = (Z \cdot p)^{-1} \{ [2 - \text{FP}] \cdot \langle k_a \rangle_5 + [1 - \text{FP}] \cdot \langle k_a \rangle_4 \}.$$
(2)

Z denotes the second order collision rate constant and p the total pressure. Hence a plot of [propyne] · p/[1-FP] versus [2-FP]/[1-FP] should give a straight line. From the slope and the ordinate value of this line the two rate constants can be obtained. In a similar manner $\langle k_a \rangle_6$ and $\langle k_a \rangle_7$ can be evaluated. The two plots are shown in Fig. 2. The apparent rate constants for the secondary reactions with error limits (standard deviation) are given in Table 2. The collision rate constant Z is given in Table 3. The fraction of propyne (allene) contributing to the *i*-th channel was determined by doubleweighting its concentration with the relative rate constant for this channel and with the relative importance of this channel which was approximated by $[FP_i]_{\infty}/\Sigma$ $[FP_i]_{\infty}$; the sum extends only over two channels, namely those which can form propyne (allene) in a secondary process. The amount of propyne or allene formed can now be calculated for each channel and must be added to the amount of the primary isomerization product I_i of the channel considered. So far this procedure neglects the contribution of the insertion processes to the yield of primary and secondary products. To correct for insertion the percentage of insertion product as determined in the high pressure limit by Casas et al. [1], i.e. 7.4% for the 1fluoropropenes and 2.1% for 2-fluoropropene, was used [18]. According to Eq. (1), S/I_i in a plot against pressure should give straight lines in the strong collision limit. Such plots for the three primary channels after correction for the secondary channels and the insertion pathway are shown in Fig. 3. The curvature at low pressures is due to multistep collisional deactivation. The curves drawn in





this figure are best fits from RRKM calculations (see below). The parameters Z and σ were chosen as shown in Table 3. These Table also gives the high-pressure values $\langle k_a \rangle_{1\infty}$, $\langle k_a \rangle_{2\infty}$ and $\langle k_a \rangle_{3\infty}$ as determined by the calculations mentioned.

Pressure dependance of product ratios $FCP/(C_3H_5F + C_3H_4)$; 313 nm, oxygen added; $\blacktriangle C_3H_5F = 1$ -FP; $\blacksquare C_3H_5F = 2$ -FP; $\blacksquare C_3H_5F = 3$ -FP

Table 2 Apparent Rate Constants for the secondary elimination processes of the fluoropropenes (in s⁻¹); in the calculations a collision diameter $\sigma = 5.33 \cdot 10^{-8}$ cm was used

$\langle k_a \rangle_4$	$\langle k_a \rangle_5$	$\langle k_{a} \rangle_{6}$	$\langle k_a \rangle_7$
$(9.3 \pm 0.5) \cdot 10^8$	$(3.4 \pm 2.3) \cdot 10^8$	$(1.20 \pm 0.14) \cdot 10^9$	$(2.63 \pm 0.5) \cdot 10^8$

3. RRKM Calculations

For the four isomerization reactions of chemically activated FCP **RRKM** calculations were carried out using a three-channel model since the formation of cis- and trans-1-fluoropropene was not treated separately. The standard **RRKM** expression [16] of the microscopic unimolecular rate constant $k_{a,i}$ is

$$k_{\mathrm{a},i}(E^*) = \frac{\alpha_i W(E_i^*)}{h \cdot N(E_v^*)},\tag{3}$$

where E^* is the internal molecular energy, α_i is the reaction path degeneracy of the *i*-th channel, $W(E_i^*)$ is the sum of states of the activated complex for the *i*-th channel, $N(E_i^*)$ is the density of vibrational states of the activated molecules, and E_i^* denotes the energy in excess of the threshold energy, E_{0i} ; hence $E_{0i} + E_i^* = E^*$.

As in Ref. [19], which should be consulted for further details, two refinements were made in the calculations: a stepladder model for collisional deactivation was used and an energy distribution function for the activated molecules was employed. This required the construction of four activated complex models, three for the isomerization channels and one for the decomposition reaction of FCP into ¹CH₂ plus fluoroethene. All complexes for the isomerization of the ring compound assumed migration of a hydrogen atom to an adjacent carbon atom and no breaking of C-F bonds was considered [1, 2]; C-H deformation frequencies were used as reaction coordinates. The necessary agreement between the Arrhenius parameters of the thermal isomerization processes and the chosen frequencies for the complex models was observed. The final parameters and the transition state frequencies giving the best agreement with our experimental results are listed in the Appendix. Other parameters used in the calculations are given in Table 3. The results for the primary channels are represented by the curves shown in Fig. 3.

The four secondary reaction channels were likewise modelled by RRKM theory, also using a stepladder deactivation model. The initial distribution function for the activated fluoropropenes was assumed in rough approximation to be the same as in the case of the activated fluorocyclopropane. For these eliminations no thermal data exist, however, and the Arrhenius parameters had to be estimated. This matter is dealt with in the discussion section. The transition states were modelled by choosing vibrational frequencies intermediate between those of the fluoropropenes [20, 21], and those for propyne and allene [22], respectively. For reactions leading to propyne CH stretch frequencies were used as reaction coordinates, for the formation of allene C-C-F deformation frequencies were chosen. The sets of frequencies finally chosen are again listed in the Appendix and results of our calculations are shown together with the experimental data points in Fig. 4.

The choice of the parameters is a very critical procedure and was performed in a systematic manner. Results of earlier work from this laboratory were used [11, 19]. A few comments have to be added.

1. E_{\min} is the minimum of energy that is contained in a chemically activated molecule. Its value is derived from thermochemical data (see Appendix) and the critical energy of the formation reaction of FCP, which was estimated to be $E_0 = 5 \text{ kJ} \cdot \text{mol}^{-1}$. For the secondary processes E_{\min} equals E_{\min} of the primary step plus the difference in the heats of formation between the fluorocyclopropane and the fluoropropene considered. The adopted value ΔH_1^{ℓ} (CH₂, ¹A₁) = 414 ± 8 kJ/mol is now generally accepted [23-27]. The energy content of CH₂ was no longer a

Table 3
Some parameters used in the RRKM calculations and calculated apparent rate constants of the isomerization and decomposition reactions of Fig. 1

E _{min} *) kJ∕mol	$\langle E^+ \rangle$ kJ/mol	E ₀ kJ/mol	α	Z**) s ⁻¹ mbar ⁻¹	$\langle k_{a} \rangle$ s ⁻¹	
395.5	448.5	243.0	4	0.964 · 10 ⁷	4.9 · 10 ⁹	
395.5	448.5	251.5	2	$0.964 \cdot 10^{7}$	1.3 · 10 ⁹	
395.5	448.5	257.0	4	0.964 · 10 ⁷	3.3 · 10 ⁹	
423.5	<476	301	1	$1.07 \cdot 10^{7}$	8.8 · 10 ⁸	
423.5	<476	308	1	1.07 · 10 ⁷	3.7 · 10 ⁸	
423.5	<476	242	6	$1.07 \cdot 10^{7}$	1.1 · 10 ⁹	
416.0	<469	236	2	1.07 · 10 ⁷	$2.7 \cdot 10^{8}$	
	E _{min} *) kJ/mol 395.5 395.5 423.5 423.5 423.5 423.5 423.5 416.0	$\begin{array}{c c} E_{\min}^{*} & \langle E^{+} \rangle \\ \text{kJ/mol} & \text{kJ/mol} \\ \hline \\ 395.5 & 448.5 \\ 395.5 & 448.5 \\ 395.5 & 448.5 \\ 423.5 & <476 \\ 423.5 & <476 \\ 423.5 & <476 \\ 423.5 & <476 \\ 416.0 & <469 \\ \hline \end{array}$	$\begin{array}{c cccc} E_{min}^{*} & \langle E^{+} \rangle & E_{0} \\ \hline kJ/mol & kJ/mol & kJ/mol \\ \hline \end{array} \\ \hline \end{array} \\ \begin{array}{c} 395.5 & 448.5 & 243.0 \\ 395.5 & 448.5 & 251.5 \\ 395.5 & 448.5 & 257.0 \\ 423.5 & <476 & 301 \\ 423.5 & <476 & 308 \\ 423.5 & <476 & 242 \\ 416.0 & <469 & 236 \\ \hline \end{array} \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



) $E_{\min} = \langle E^ \rangle - E_{CH_2} - \langle E_{therm} \rangle$. $E_{CH_2} = 49 \text{ kJ} \cdot \text{mol}^{-1}$ and $\langle E_{therm} \rangle = 4 \text{ kJ} \cdot \text{mol}^{-1}$ were assumed in agreement with our earlier work [11]. **) T = 298 K; collision diameters for FCP-fluoroethene: $\sigma = 5.07 \cdot 10^{-8} \text{ cm}$, for FP-fluoroethene: $\sigma = 5.33 \cdot 10^{-8} \text{ cm}$ [11, 17].

fitting variable as in Ref. [11] but was transferred from this work (see footnote of Table 3).

2. The critical energies E_{01} , E_{02} and E_{03} can be calculated from the experimental Arrhenius activation energies [4] using the equation

$$E_0 = E_{A_{\infty}} - RT - RT^2 \frac{d\ln(Q^*/Q)}{dT}$$
(4)

with Q and Q^{+} sums of states. The fit to the experimental results was mainly achieved by choosing the frequencies of the transition state. Starting with the molecular frequencies one vibration was selected as the reaction coordinate and three other frequencies were lowered by the same (variable) percentage. Some variation of $E_{A_{\infty}}$ and A, which were estimated by Flowers [4], was permitted. But reproduction of the thermal rate constants in the high pressure limit at T = 748 K was required and achieved for all primary channels.

3. ΔE , the stepsize for the stepladder deactivation process was adapted from the work of Eichler et al. [11] and no longer served as an adjustable parameter.



Pressure dependance of product ratios, C₃H₅F/C₃H₄, for the secondary reactions; 313 nm, oxygen added;
a) △ 3-FP → allene + HF, ● 1-FP → propyne + HF
b) ■ 2-FP → propyne + HF, ○ 2-FP → allene + HF

Discussion

The RRKM calculations resulted in a good fit to the experimental data for the primary isomerization processes (Fig. 3). Since on principle the influence of rotational energy has to be included [16], we calculated the ratio of the sums

of states for the rotations: $Q_R^*/Q_R = 1.03$. This was done by using a transition state model for the cyclopropane isomerization published by Jug [28]. Our calculations indicate a very small influence of rotation and justify its neglection.

The energy distribution function for fluorocyclopropane starts at some energy $E_{\min} + E_{CH_2}$, where E_{\min} is the lowest energy possible due to the shape of the potential energy surface and $E_{CH_2} = 49 \text{ kJ mol}^{-1}$ is the mean energy content of the photolysis product $CH_2({}^{1}A_1)$. It should be noted that E_{CH_2} , which was chosen in agreement with our earlier work [11], is given relative to the triplet ground state, which means 14 kJ mol⁻¹ of internal energy in the singlet state. This value appears at least 5 kJ mol⁻¹ too high when compared with recent discussions on the vibrational energy distributions of singlet methylene produced by photolysis of ketene [29]. It must, however, be remembered that addition of $CH_2({}^{1}A_1)$ to double bonds is a much faster reaction than insertion, which was the relevant process in the work of Simons et al. [29].

At 366 nm without oxygen addition no products were detected. At this wavelength only $CH_2({}^{3}B_1)$ can be formed which apparently reacts rather slowly with C_2H_3F as expected [12]. At 313 nm about 15% of the methylene is formed in the triplet state [30] which reacts with the added O_2 [10].

The average energy transferred by collisions of the chemically activated species, $\Delta E = 25$ kJ mol⁻¹ [11], compares very well with the values recently reported in similar work: $\Delta E = 29-46$ kJ/mol was suggested for the CH₂ + C₂F₄ systems [8] and $\Delta E = 25$ kJ mol⁻¹ was used for CH₂ + cyclo-C₄H₈ studies [29]. The reader should be aware that more direct measurements for energy transfer from highly excited azulene [31] and toluene or cycloheptatrienes [32] are available, which yield ΔE values that are significantly lower. This apparent discrepancy was recently discussed by Arbilla et al. [33].

The secondary elimination reactions could be modelled without major problems. The apparent rate constants at high pressure from the experiments (Table 2) are in close agreement with the calculated ones (last column of Table 3). The linear dependence of S/D on pressure shown in Fig. 4 indicates that the isomerization allene \rightarrow propyne [34] is negligible under the conditions of our experiments. Allene and propyne may also be formed by reaction of ¹CH₂ with ethyne; $k = 2.5 \cdot 10^{-10}$ cm³ s⁻¹ [35]. This reaction path need not be considered in presence of a large excess of C₂H₃F. ¹CH₂ reacts with fluoroethene in a fast elementary step; $k = 1.4 \cdot 10^{-10}$ cm³ s⁻¹ [36].

For the secondary HF elimination processes there are many adjustable parameters available. For propyne formation the thermal decomposition of fluoroethene (log $A(s^{-1}) = 14-14.4$; $E_A = 296-340$ kJ/mol) [37] was used to arrive at estimates for the Arrhenius parameters. For allene formation the HF elimination from fluoroethane (log $A(s^{-1}) = 12.2-14.4$; $E_A = 244-262$ kJ/mol) [38] was used as a guidance. The adopted parameters can be found in the Appendix. It seems logical that $\Delta E = 25$ kJ mol⁻¹ was also assumed for the collisional deactivation of the fluoropropenes. The most serious simplification is probably the assumption of a specific initial energy distribution for the intermediate fluoropropenes, which does not take into account the formation of these compounds from partially deactivated FCP*. It would be worthwhile to make corrections for this provided that thermal rate constants for the secondary elimination processes become available.

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Appendix

Normal Vibrations (in cm^{-1})

- Fluorocyclopropane [3]: 3100, 3095, 3065, 3020, 2980, 1450, 1415, 1305, 1275, 1200, 1165, 1090, 1045, 1025, 935, 885, 865, 810, 770, 355, 325.
- (2) Activated complex of the formation reaction of FCP: 3052(5), 1359(4), 1080(4), 895(3), 790(2), 340(2).
- (3) Activated complex of the isomerization reaction to 1-FP: 2918(5), 1432(2), 1190(5), 818(6), 475(2); this complex corresponds to $\log A(s^{-1}) = 13.92$, $E_A = 247.4$ kJ mol⁻¹.
- (4) Activated complex of the isomerization reaction to 2-FP: 2918(5), 1432(2), 1153(5), 818(6), 530(2); this complex corresponds to $\log A(s^{-1}) = 13.58$, $E_A = 255.9$ kJ mol⁻¹.
- (5) Activated complex of the isomerization reaction to 3-FP: 2918(5), 1432(2), 1190(5), 818(6), 360(2); this complex corresponds to $\log A(s^{-1}) = 14.15$, $E_A = 262.4$ kJ mol⁻¹.
- (6) trans-1-FP (estimated from the spectra of propene [22] and trans-1-chloropropene [39]) 3074, 3042, 2975, 2959, 2934, 1648, 1456, 1447, 1387, 1295, 1247, 1076, 1045, 962, 930, 864, 760, 422, 264, 236, 208.
- (7) Activated complex of the reaction 1-FP \rightarrow propyne + HF: 2985(4), 1895, 1382(4), 984(4), 760, 377(2), 232(4); this complex corresponds to log $A(s^{-1}) = 14.65$, $E_A = 312.6$ kJ mol⁻¹.
- (8) 2-FP [20]: 3141, 3059, 3012, 2975, 2942, 1687, 1448(2), 1429, 1401, 1270, 1048, 1008, 944, 862, 846, 629, 472, 404, 352, 191.
- (9) Activated complex of the reaction 2-FP \rightarrow propyne + HF: 3017(4), 1540(4), 1028(2), 894(3), 629, 452(2), 316(4); this complex corresponds to log $A(s^{-1}) = 14.44$, $E_A = 319.6$ kJ mol⁻¹.
- (10) Activated complex of the reaction 2-FP \rightarrow allene + HF: 3025(5), 1822(1), 1431(4), 1241(2), 1028(2), 918(3), 554(3); this complex corresponds to $\log A(s^{-1}) = 12.88$, $E_A = 239.2$ kJ mol⁻¹.
- (11) 3-FP [21]: 3092, 3026, 2990(2), 2939, 1630, 1459, 1426, 1362, 1289, 1240, 1163, 1027, 1006, 989, 935, 916, 642, 432, 345, 163.
- (12) Activated complex of the reaction 3-FP \rightarrow allene + HF: 3008(5), 1939(2), 1415(3), 1189(3), 969(5), 713(2); this complex corresponds to log $A(s^{-1}) = 12.19$, $E_A = 231.8$ kJ mol⁻¹.

Thermochemical Data

 $\Delta H_{1,298}^{0}$ values from the literature in kJ/mol: CH₂(³B₁), 395.5 [23]; CH₂(¹A₁), 414.2 [23, 26]; fluoroethene, -144.6 [41]; fluorocyclopropane, -143.0 [41]; 3-FP, -163.4 [42]; allene, 192.0 [43]; propyne, 185.4 [44].

 $\Delta H_{0.298}^{0}$ values adopted in this work because literature data are lacking:

2-FP, -170.9 estimated from $\Delta H_1^0(3$ -FP) + D(allyl-F) + D(vinyl-H) - D(vinyl-F) - D(allyl-H); 1-FP, -170.9.

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Integral Carbon Mass Balance in Premixed Sooting Flames

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In sooting C_2H_4 -air, C_6H_6 -air and C_2H_2 -air flames the burned gases have been analyzed for different fuel-air ratios and the fractions of carbon which end up as CO and CO₂, as soot and as hydrocarbons have been determined. The amount of soot formed increases strongly with increasing fuel content beyond the threshold of soot formation, following approximately the same formal relation for the different fuels. At a given fuel concentration above the soot threshold the soot mass per cm³ rises from C_2H_2 to C_2H_4 and to C_6H_6 -air flames. The concentrations of hydrocarbons in the burned gases increase also with increasing fuel concentrations but in different ways for the different fuels. For benzene-air flames the carbon present as soot exceeds that present as hydrocarbon already at fuel concentrations slightly above the soot threshold. The same happens in C_2H_4 -air flames only at C/O ratios close to one and not at all for the C_2H_2 -air flames. — There is no uniquely simple correlation between the soot mass per cm³ formed in these flames of various fuels and the concentrations of hydrocarbon in their burned gases.

Introduction

The burned gases of sooting premixed laminar hydrocarbon-air flames contain the water gas components (CO, CO₂, H₂, H₂O), soot and hydrocarbons, mostly alkynes but also aromatic species [1, 2]. Hydrocarbons together with the other components can also be detected in the burned gases of flames which do not yet form soot and are slightly leaner than the corresponding threshold of soot formation. In both cases the further oxidation of the hydrocarbons in the burned gases proceeds rather slowly [3].

It is not yet clear how the final concentrations of the main three carbon containing species in the burned gases, namely CO and CO₂, soot, and thermodynamically relatively stable hydrocarbons (mostly C_2H_2) are related to different fuels and burning conditions.

The purpose of the measurements described here was to find out which fraction of the carbon present in the fuel ends up in each of these three products. Three different fuels have been chosen in mixture with air, namely C_2H_4 , C_2H_2 and C_6H_6 . The burning conditions for the C_2H_2 -air and the C_6H_6 -air flames have been selected such that the maximum flame temperatures were similar and that the benzene flames did not form polyhedral flames [4]. The temperatures of the C_2H_4 flames were on the average about 150 to 200 K lower than those of corresponding C_2H_2 and C_6H_6 -air flames.

Small variations of the maximum temperature resulted from differing C/O-ratios. The temperature drop along the flame axis in the burned gases depended on the C/O-ratio and could hardly be influenced. Most of the gasanalytical experiments have been performed on flames burning near the threshold of soot formation. Towards rich mixtures, the experimental range was limited by flame stability.

Experimental

Measurements on C_2H_4 and C_6H_6 -air-flames have been performed at atmospheric pressure and different fuel-air ratios using a flat capillary burner with a diameter of 56 mm [5].

This burner was surrounded by a 20 mm wide annular burner. The annular burner served to reduce edge effects and especially heat losses from the central flame to ambient environment and was operated with a fuel rich, just non sooting C_2H_4 -air flame at the same flow speed as the actual flame.

The acetylene-air flame was investigated using a 60 mm i.d. cooled porous sinter plate burner [7]. This burner was surrounded by a glass-tube to isolate the flame from the surrounding air. The volume flow rates of the reactant gases were controlled by capillary flow meters. Liquid benzene was vaporized by passing air through a two stage saturator.

A quartz sampling probe was inserted along the flame axis. The lower and hottest part of the probe could be filled with quartz wool which acted as a soot filter. The amount of soot in the gas mixture could be determined by elementary analysis, by gravimetric or by optical methods.

The flame gases were analyzed either by mass spectroscopy or by gaschromatography.

For the gas analysis two Packard-Becker gaschromatographs modell 419 with heat conduction and flame ionisation detectors and a CH4-mass spectrometer were used. The CH4 mass spectrometer was equipped with a continuous sampling inlet system [8]. The pressure variations in the suction line, which arose from the soot particles depositing in the probe orifice had to be taken into account for the quantitative analysis in sooting flames. In order to compensate this effect and to obtain a known mass flow the sample pressure for mass spectrometric analysis was reduced in three steps; in the first step the gas sample was expanded behind the probe orifice to 4-2 mbar in the second step, it was expanded to 10^{-2} mbar and the third step was the expansion of the gas flow through a teflon and a gold nozzle. The pressure was regulated in the second stage.

For the gas chromatographic analysis, the flame gases were introduced into the gaschromatograph by a sample loop for which the volume flow was continuously registered. The flow was determined by a calibrated capillary with two pressure-difference transducers and continuous calibration.

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