THE KINETICS AND MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN SF₄ AND FLUORINE AT 365 nm
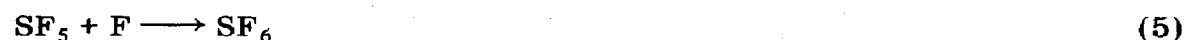
P. F. ARAMENDÍA and H. J. SCHUMACHER

Instituto de Investigaciones Fisicoquímicas, Teóricas y Aplicadas, Sucursal 4, Casilla de Correo 16, 1900 La Plata (Argentina)

(Received July 23, 1984)

Summary

The photochemical reaction between SF_4 and fluorine at 365 nm was investigated in the temperature range 213 - 244 K. It is a chain reaction of medium length. SF_6 and small amounts of S_2F_{10} are the only reaction products. The experimental results can be quantitatively explained by the following mechanism:

$$F_2 + h\nu \longrightarrow 2F \tag{1}$$

$$SF_4 + F_2 \longrightarrow SF_5 + F \tag{1'}$$

$$SF_4 + F \longrightarrow SF_5 \tag{2}$$

$$SF_5 + F_2 \longrightarrow SF_6 + F \tag{3}$$

$$SF_5 + SF_5 \longrightarrow S_2F_{10} \tag{4}$$

$$SF_5 + F \longrightarrow SF_6 \tag{5}$$

$$F + F + M \longrightarrow F_2 + M \tag{6}$$

Under the conditions of this investigation reaction (1') makes only a small contribution to the total initiation rate. In general more than 80% of the chain carriers are consumed by reaction (4):

$$\frac{k_3}{k_4^{1/2}} = 10^{4.18 \pm 0.01} \exp\left(-\frac{4.0 \pm 0.2 \text{ kcal mol}^{-1}}{RT}\right) M^{-1/2} s^{-1/2}$$

At 225.2 K $k_{1'} = 1.0 \times 10^{-4}$ M^{-1} s^{-1}. In combination with the previously measured values this gives

$$k_{1'} = 10^{10.20 \pm 0.07} \exp\left(-\frac{14.6 \pm 0.5 \text{ kcal mol}^{-1}}{RT}\right) M^{-1} s^{-1}$$

For $E_4 \approx 0$, $E_3 = 4.0 \pm 0.2$ kcal mol^{-1} and $E_2 = 2.0 \pm 1.5$ kcal mol^{-1}.

---

1. Introduction

Several reactions in which SF_5 radicals appear as intermediates have been investigated in our laboratories during the last few years [1 - 9]. Among these, the thermal reaction between SF_4 and fluorine has been thoroughly studied in the temperature range 270.6 - 297 K [8]. It is a chain reaction of moderate length. A mechanism describing the experimental data quantitatively has been proposed. Under the conditions of the experiment at least 80% of the chain carriers were consumed by the reaction $SF_5 + F \rightarrow SF_6$. However, no data for the photochemical reaction, which was investigated in the work reported here, exist in the literature.

2. Experimental details

2.1. Apparatus

In order to reduce the influence of the thermal reaction to a minimum, it was necessary to work at low temperatures. Consequently, the experiments were carried out in the temperature range 244 - 213 K.

Since the pressure decreases as the reaction proceeds, it was decided to monitor its progress by pressure measurements at constant temperature and volume. A conventional apparatus for this type of reaction, which has been described in detail in ref. 10, was used.

The reaction cell was a quartz cylinder 10 cm long with plane parallel windows 5 cm in diameter. It was connected to a quartz U-tube where the reacting mixture could be frozen out and later distilled. The temperature was controlled with a Lauda UK 80 cryostat to ±0.1 K. In order to avoid moisture condensation on the cell windows, additional windows were attached at the back and front of the cell. The closed compartments formed in this way were kept dry with silica gel, and the outer windows could be heated.

A high pressure mercury lamp (Osram HBO 200) was used as the light source. The 365 nm line was selected by putting a combination of two glass filters (Schott-Mainz UG2 and WG3) in the light path. The light intensity was measured using an F_2O actinometer [11] and was periodically checked because of lamp aging.

2.2. Purification of gases

SF_4 was a technical product of Dupont de Nemours. It contained about 20% SOF_2 and was purified by low temperature distillation in a Podbielniak apparatus [12]. The final product contained less than 1% SOF_2 as demonstrated by IR measurements. The fluorine (Air Products) contained small amounts of HF and oxygen. It was purified by passing it through a Pyrex spiral cooled at liquid oxygen temperature. F_2O (Allied Chemicals) contained some fluorine, oxygen and other fluorine oxides. It was purified by distillation at liquid oxygen temperature and condensed in liquid air;

since it was the volatile fraction it was continually pumped off. CF_4 (Matheson) was condensed in liquid oxygen and the volatile fraction was removed.

3. Experiments and results

Preliminary experiments showed that the only reaction products were SF_6 and S_2F_{10}. They were separated by distillation at 163 K and identified by their IR spectra. The SF_6 corresponded almost exactly to the pressure decrease, while the amount of S_2F_{10} was a factor of 10 - 20 less.

A short induction period was observed in most experiments. It was proved to be due to the added fluorine, which obviously contained a small amount of an impurity which was rapidly consumed. The pressure decrease during this period was a few per cent of the total pressure of the reactants. This decrease was taken into account in the determination of the correct pressure of the reactants at the beginning of the reaction. The reproducibility of the experiments was very good.

As discussed above, the overall stoichiometry of the reaction can be described by the following equations:

$$SF_4 + F_2 \longrightarrow SF_6 \qquad (90\% - 95\%)$$
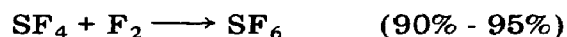
$$2SF_4 + F_2 \longrightarrow S_2F_{10} \qquad (10\% - 5\%)$$

The pressure decrease can be related to either the formation of products or the consumption of the reactants:

$$-\Delta P = \Delta[SF_6] + 2\Delta[S_2F_{10}] = -\Delta[SF_4] = -\Delta[F_2] + \Delta[S_2F_{10}]$$

According to the preceding equation the SF_4 pressure at any time can be directly obtained from the pressure decrease, whereas in order to determine the fluorine pressure the amount of S_2F_{10} produced during the corresponding time must be known. Since this amount is always very small, and is negligible in the initial stages of the reaction, the first time interval after the induction period was taken into account in every experiment and the S_2F_{10} formation was ignored.

Most of the experiments were carried out at 225 K, although some were performed at 244 and 213 K. The fluorine and SF_4 pressures were varied from 20 to 200 Torr. Some experiments were carried out in the presence of up to 500 Torr of CF_4 as an inert gas. In others the light intensity was reduced to one-third of its normal value by inserting a blackened mesh filter into the light path.

The reaction rate, which was determined by measuring the total pressure decrease, was found to be approximately proportional to the square root of the absorbed light intensity and the fluorine pressure:

$$v = -\frac{\Delta[SF_4]}{\Delta t} = -\frac{\Delta P}{\Delta t} \approx k I_{abs}^{1/2}[F_2] \qquad (I)$$

TABLE 1

Results of 35 experiments at various temperatures

Number	Δt (min)	$-\Delta P$ (Torr)	$[\overline{F_2}]$ (Torr)	$[\overline{SF_4}]$ (Torr)	$\overline{I}_{abs}$ (Torr min⁻¹)	v_{exp} (Torr min⁻¹)	f (Torr⁻¹ᐟ² min⁻¹)	$[F_2]/[SF_4]$	v_{calc} (Torr min⁻¹)	v'_{calc} (Torr min⁻¹)
T_{eff} = 243.9 K, T_{meas} = 243.2 K										
84	3.00	2.4	18.3	18.9	0.029	0.80	0.225	0.971	0.81	0.80
93	3.50	6.3	34.7	14.3	0.049	1.80	0.212	2.44	1.86	1.80
90	3.00	6.5	34.4	74.0	0.051	2.17	0.223	0.465	2.21	2.22
91	1.00	3.0	37.5	198.8	0.054	3.00	0.223	0.188	2.95	2.99
77	1.00	3.7	55.3	12.9	0.089	3.70	0.207	4.30	3.76	3.51
78	2.00	8.1	55.0	34.3	0.088	4.05	0.219	1.60	4.14	4.06
79	2.00	9.4	54.9	76.5	0.088	4.70	0.234	0.718	4.56	4.55
89	1.00	3.9	73.6	33.5	0.035	3.90	0.222	2.20	3.77	3.65
87	2.20	9.1	93.1	11.3	0.045	4.14	0.187	8.28	4.21	3.79
T_{eff} = 225.2 K, T_{meas} = 223.2 K										
40	4.00	2.4	19.7	19.0	0.042	0.60	0.128	1.04	0.60	0.60
70	10.00	2.7	17.7	38.8	0.011	0.27	0.131	0.467	0.27	0.27
83	5.00	2.6	18.7	198.2	0.031	0.52	0.130	0.094	0.52	0.53
33	2.00	3.1	37.3	17.5	0.078	1.55	0.133	2.14	1.47	1.44
41	3.00	2.5	39.0	18.0	0.029	0.83	0.114	2.17	0.90	0.89
34	3.00	4.6	37.5	37.3	0.078	1.53	0.130	1.006	1.52	1.52
36	2.00	3.4	39.3	78.3	0.082	1.70	0.134	0.502	1.66	1.68
30	1.00	2.8	56.8	16.0	0.116	2.80	0.132	3.55	2.58	2.49
28	2.00	5.3	55.4	35.2	0.114	2.65	0.129	1.58	2.62	2.60
31	1.50	3.6	57.0	77.4	0.099	2.40	0.120	0.736	2.56	2.58
54	3.00	7.2	52.4	112.3	0.096	2.40	0.132	0.466	2.37	2.40
74	3.00	7.9	57.0	196.2	0.091	2.63	0.134	0.291	2.55	2.59
43	2.50	5.2	79.8	17.0	0.056	2.08	0.103	4.69	2.36	2.25
44	1.00	3.1	96.8	17.9	0.067	3.10	0.117	5.51	3.09	2.92
51	1.00	3.4	97.8	78.0	0.064	3.40	0.125	1.25	3.44	3.43
71	1.00	3.9	114.9	34.8	0.063	3.90	0.127	3.30	3.76	3.64

(continued)

494

TABLE 1 (continued)

Number	Δt (min)	$-\Delta P$ (Torr)	$\overline{[F_2]}$ (Torr)	$\overline{[SF_4]}$ (Torr)	$\overline{I}_{abs}$ (Torr min^{-1})	ν_{exp} (Torr min^{-1})	f (Torr$^{-1/2}$ min$^{-1/2}$)	$\overline{[F_2]}/\overline{[SF_4]}$	ν_{calc} (Torr min^{-1})	ν'_{calc} (Torr min^{-1})
T_{eff} = 213.3 K, T_{meas} = 208.2 K										
111	12.000	3.3	19.2	122.5	0.024	0.28	0.076	0.157	0.27	0.27
104	4.00	2.8	38.2	18.7	0.047	0.70	0.073	2.04	0.73	0.73
96	4.00	3.1	37.9	122.4	0.048	0.77	0.080	0.310	0.75	0.74
100	2.00	2.7	58.0	18.7	0.071	1.35	0.078	3.11	1.33	1.33
57	1.50	2.5	57.8	38.8	0.102	1.66	0.079	1.49	1.63	1.63
60	5.50	8.4	55.8	76.5	0.097	1.53	0.077	0.729	1.54	1.53
56	1.50	8.2	70.4	29.7	0.124	2.13	0.076	2.37	2.14	2.15
55	1.00	3.4	94.8	34.3	0.163	3.40	0.080	2.76	3.26	3.28
102	1.00	3.6	174.6	38.6	0.064	3.60	0.078	4.52	3.51	3.56
103	1.00	3.9	199.1	18.3	0.071	3.90	0.070	10.91	4.05	4.26

TABLE 2

Influence of the total pressure on the reaction rate

Number	Δt (min)	$-\Delta P$ (Torr)	$\overline{[F_2]}$ (Torr)	$\overline{[SF_4]}$ (Torr)	$\overline{I}_{abs}$ (Torr min^{-1})	$\overline{[CF_4]}$ (Torr)	$\overline{P}$ (Torr)	ν_{exp} (Torr min^{-1})
67	3.00	7.4	55.5	35.6	0.092	–	96.0	2.47
81	3.00	6.9	57.1	36.2	0.091	–	97.8	2.30
62	3.00	6.4	54.4	36.9	0.094	220.4	311.7	2.13
63	4.00	7.7	55.5	35.8	0.093	511.4	602.7	1.93
61	3.00	7.0	55.3	75.7	0.096	–	135.9	2.33
64	3.50	7.9	55.9	75.5	0.094	510.7	652.1	2.26
54	3.00	7.2	52.4	112.3	0.108	–	172.2	2.40
73	3.00	7.1	56.1	116.5	0.089	486.4	659.0	2.37

The reaction rate decreased slightly with increasing total pressure, whereas the SF_4 pressure did not affect the rate at 213 K but had a small increasing effect at higher temperatures. The quantum efficiency of SF_4 consumption was generally between 10 and 90 molecules quantum^{-1}. A relatively small dark reaction due to thermal initiation was observed. It was measured periodically in almost all the experiments.

The experimental results for the initial conditions, i.e. with no correction for S_2F_{10} formation, are given in Tables 1 and 2. In these tables $\overline{[F_2]}$, $\overline{[SF_4]}$ and $\bar{P}$ represent the mean pressures of the reactants and the mean total pressure during the reaction time Δt. ΔP is the total pressure difference in this interval, I_{abs} is the mean absorbed light intensity, which is calculated as the light absorbed at the mean fluorine pressure, v_{exp} is the experimental reaction rate $-\Delta P/\Delta t$, v_{calc} and v'_{calc} are rates calculated using the method described in Section 4 and f is a parameter that will be defined later.

Since we had to work at low temperatures and the outer windows of the cell were heated, the effective reaction temperature T_{eff} differed from the measured value T_{meas} which was the temperature of the liquid surrounding the cell. The former was measured using the reactor itself as an ideal gas thermometer at constant volume. The temperature obtained in this way was used.

4. Discussion of the results

It can be deduced from the quantum efficiency measurements that the reaction proceeds via a chain of medium length. The primary process after light absorption is the dissociation of the fluorine molecules:
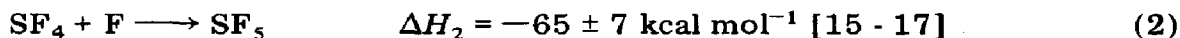
$$F_2 + h\nu \longrightarrow 2F \tag{1}$$

This is accompanied by the thermal initiation step [8]:
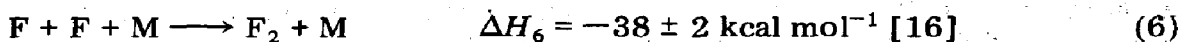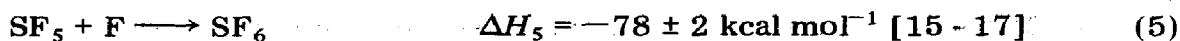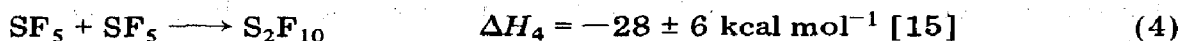
$$SF_4 + F_2 \longrightarrow SF_5 + F \tag{1'}$$

The rates of these two reactions can be readily evaluated because both the incident light intensity and the fluorine extinction coefficient at 365 nm [13] are known and the rate constant for reaction (1') has been measured in previous work [14]. Its extrapolated value was used in the preliminary calculations.

The following two steps are the same as those in the thermal reaction:

$$SF_4 + F \longrightarrow SF_5 \qquad \Delta H_2 = -65 \pm 7 \text{ kcal mol}^{-1} \text{ [15 - 17]} \tag{2}$$

$$SF_5 + F_2 \longrightarrow SF_6 + F \qquad \Delta H_3 = -40 \pm 6 \text{ kcal mol}^{-1} \text{ [15 - 17]} \tag{3}$$

These reactions are highly exothermic, so that the back reactions do not have to be considered and no product effect is to be expected (SF_6 acts as an inert gas in most chemical systems).

Three pathways for the termination reaction are possible:

$$SF_5 + SF_5 \longrightarrow S_2F_{10} \qquad \Delta H_4 = -28 \pm 6 \text{ kcal mol}^{-1} \text{ [15]} \qquad (4)$$

$$SF_5 + F \longrightarrow SF_6 \qquad \Delta H_5 = -78 \pm 2 \text{ kcal mol}^{-1} \text{ [15 - 17]} \qquad (5)$$

$$F + F + M \longrightarrow F_2 + M \qquad \Delta H_6 = -38 \pm 2 \text{ kcal mol}^{-1} \text{ [16]} \qquad (6)$$

The first of these justifies the formation of S_2F_{10} and must therefore be considered in the actual reaction scheme.

When only reactions (1) - (4) are taken into account we obtain, assuming quasi-stationary state conditions,

$$- \frac{d[SF_4]}{dt} = v = \frac{k_3}{k_4^{1/2}} v_i^{1/2}[F_2] + 2v_i$$

$$v_i = I_{abs} + k_1' [SF_4][F_2] \qquad (II)$$

If (4) were the only termination step, the parameter f (see Table 1) defined by

$$f = \frac{v - 2v_i}{v_i^{1/2}[F_2]} \qquad (III)$$

should be a constant equal to $k_3/k_4^{1/2}$. Table 1 shows that, although this is true within about $\pm 10\%$, a systematic decrease of f is seen as the ratio of $[F_2]$ to $[SF_4]$ increases. This tendency increases with temperature. If all the chain carriers are consumed in reaction (5) the reaction rate should be proportional to $I_{abs}^{1/2}[F_2]^{1/2}[SF_4]^{1/2}$, whereas if they are consumed in reaction (6) exclusively the rate should be proportional to $I_{abs}^{1/2}[SF_4]$. Obviously none of these equations agrees with the experimental evidence.

In order to explain the experimental results quantitatively at least one of the pathways (5) or (6) must be taken into account, although it can be deduced from the above discussion that (4) is the principal termination reaction (f is constant to a first approximation). Therefore only a small correction term is expected.

The reaction scheme with all three termination reactions can be solved by assuming a very long chain length, i.e. by assuming that the rates of the initiation and termination reactions are negligible compared with the chain propagation rates. The following rate equation is obtained:

$$v = - \frac{d[SF_4]}{dt} = \frac{k_3}{k_4^{1/2}} v_i^{1/2}[F_2] \left(1 + \frac{k_3 k_5}{k_2 k_4} \frac{[F_2]}{[SF_4]} + \frac{k_3^2 k_6}{k_2^2 k_4} [M] \frac{[F_2]^2}{[SF_4]^2} \right)^{-1/2}$$

$$(IV)$$

This expression explains the negative influence of the total pressure on the reaction rate and the decrease of f with increasing $[F_2]/[SF_4]$.

However, the chain length is not very great, and therefore eqn. (IV) will show systematic deviations if it is employed to determine the constant k of eqn. (I). A direct extrapolation of f to $[F_2]/[SF_4] \rightarrow 0$ is inaccurate

because of the curved lines obtained in the representation. In order to obtain the correct values for the rate constants a more exact method of calculation must be used.

At 280 K reaction (5) is by far the most important termination, with a maximum of 20% of the chain carriers being consumed in reaction (4) and a negligible quantity in reaction (6) [8]. Under our experimental conditions, however, reaction (4) is the most important termination and the other two have only a second-order effect. Reaction (6) remains unimportant at lower temperatures where the pressure effect is very small (see Table 2). The second-order effect was therefore assigned to the influence of reaction (5) only.

The reaction rate for the mechanism involving reactions (1) - (5) was obtained numerically by employing an iterative calculation method under the quasi-stationary state assumption. It can easily be demonstrated that the numerical value of the reaction rate depends only on the values of two independent constants which are defined as

$$k_a = \frac{k_3}{k_4^{1/2}}$$

$$k_b = \frac{k_3 k_5}{k_2 k_4}$$

The value for $k_{1'}$ obtained in previous work [14] was used:

$$k_{1'} = (9.55 \pm 0.42) \times 10^7 \exp\left(-\frac{11.9 \pm 0.6 \text{ kcal mol}^{-1}}{RT}\right) \text{ M}^{-1} \text{ s}^{-1}$$

Values were assigned to k_a and k_b for each temperature, and the reaction rates were obtained numerically for the conditions corresponding to the experiments listed in Table 1. The values of k_a and k_b were varied systematically. The minimum value of the mean-square relative difference between the experimental and calculated rates was taken as the best fit criterion for their adjustment at each temperature. The zone in the rate constant space which provided an adjustment with a mean quadratic error within a difference of 10% of the minimum value was used to define the uncertainty in the determination of the constants. The error surface has a deep minimum in the k_a variation direction, while k_b has a large error because, as noted above, reaction (5) has only a second-order effect on the kinetics.

The calculation scheme described can now be used to calculate the fluorine pressure throughout an experiment, and the data for the dark reaction can be used to obtain $k_{1'}$ at 225 K. The rate expression for the thermal reaction (eqn. (V)) can be derived directly from eqn. (IV) by putting $v_6 = 0$ and $v_i = k_{1'}[\text{SF}_4][\text{F}_2]$. It is not worth performing a least-squares numerical calculation because we are looking for a small correction term only and eqn. (IV) is an adequate approximation:

$$v = \frac{k_3 k_1{'}^{1/2}}{k_4^{1/2}} [SF_4]^{1/2} [F_2]^{3/2} \left(1 + \frac{k_3 k_5}{k_2 k_4} \frac{[F_2]}{[SF_4]}\right)^{1/2}$$

$$= \left(\frac{k_1{'} k_2 k_3}{k_5}\right)^{1/2} [SF_4][F_2] \left(1 + \frac{k_2 k_4}{k_3 k_5} \frac{[SF_4]}{[F_2]}\right)^{-1/2} \tag{V}$$

which can be rearranged to give

$$\left(\frac{[SF_4][F_2]}{v}\right)^2 = \frac{k_5}{k_1{'} k_2 k_3} + \frac{k_4}{k_1{'} k_3^2} \frac{[SF_4]}{[F_2]} \tag{VI}$$

A value of $k_1{'} = 1.0 \times 10^{-4} \, M^{-1} \, s^{-1} = 4.3 \times 10^{-7} \, Torr^{-1} \, min^{-1}$ at 225 K is obtained from the slope of the straight line $([SF_4][F_2]/v)^2$ *versus* $[SF_4]/[F_2]$ shown in Fig. 1 by using the preliminary value of $k_a = 2.0 \, M^{-1/2} \, s^{-1/2}$.

When this value is combined with those measured previously [14] and the Arrhenius parameters are calculated, we obtain a new expression for $k_1{'}$:

$$k_1{'} = 10^{10.20 \pm 0.07} \exp\left(-\frac{14.6 \pm 0.5 \, \text{kcal mol}^{-1}}{RT}\right) \, M^{-1} \, s^{-1}$$

This was used to recalculate k_a and k_b but modified them only slightly.

The values obtained in the way described are listed in Table 3 and give the following value for k_a:

$$k_a = 10^{4.18 \pm 0.01} \exp\left(-\frac{4.0 \pm 0.2 \, \text{kcal mol}^{-1}}{RT}\right) \, M^{-1/2} \, s^{-1/2}$$
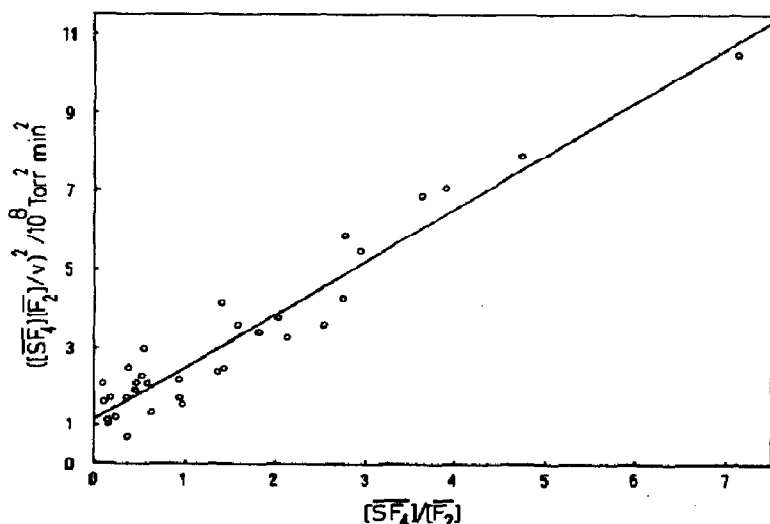

Fig. 1. Thermal reaction at 225.2 K. The rate constant for the thermal primary process obtained from the slope of the straight line with $k_3/k_4^{1/2} = 0.134 \, Torr^{-1/2} \, min^{-1/2}$ is $k_1{'} = (4.3 \pm 0.3) \times 10^{-7} \, Torr^{-1} \, min^{-1} = (1.0 \pm 0.1) \times 10^{-4} \, M^{-1} \, s^{-1}$.

TABLE 3

k_a and k_b best fit values at various temperatures

T_{eff} (K)	k_a (Torr$^{-1/2}$ min$^{-1/2}$)	k_a (M$^{-1/2}$ s$^{-1/2}$)	k_b
213.3	0.079 ± 0.001	1.18 ± 0.01	0.012
225.2	0.134 ± 0.004	2.05 ± 0.06	0.050
243.9	0.242 ± 0.002	3.85 ± 0.03	0.061

The reaction rates calculated using the best fit values of k_a and k_b are listed in Table 1, tenth column. The agreement with the experimental rates is quite satisfactory.

Considering the values in Table 3 we might object to the exclusion of reaction (6) in the calculations. This criterion can, however, be justified. The calculation method outlined above was applied to restricted sets of experiments, namely those with $[F_2]/[SF_4]$ less than 4, 3 and 2. Especially in the last case reaction (6) can be safely excluded. The best fit in the three cases agreed within the error limits given above with the values of k_a given in Table 3 and k_b did not undergo any substantial changes (for $[F_2]/[SF_4] <$ 4, k_b was 0.000 at 213 K, 0.041 at 225 K and 0.073 at 244 K; for $[F_2]/[SF_4] < 2$, k_b was 0.000 at 213 K, 0.090 at 225 K and 0.120 at 244 K). The rates calculated for all experiments with the k_a and k_b values fitted to the experiments with $[F_2]/[SF_4] < 2$ are listed in Table 1, eleventh column.

The uncertainty of the relative importance of reaction (6) at high $[F_2]/[SF_4]$ ratios remains. This problem can be solved by a systematic investigation of the pressure effect. The numerical analysis itself, which is regarded as an extrapolation method, seems to be reliable for k_a computation.

Although reaction (4) is the most important termination path under our conditions, reaction (5) is the most important near 270 K [8] so that a relative rate inversion between these two reactions must take place at an intermediate temperature. If the chain is assumed to be very long, we obtain

$$\frac{v_4}{v_5} = \frac{k_2 k_4}{k_3 k_5} \frac{[SF_4]}{[F_2]} = \frac{1}{k_b} \frac{[SF_4]}{[F_2]}$$

In order to account for the inversion, the activation energy of k_b given by

$$E_b = (E_3 + E_5) - (E_2 + E_4) \tag{7}$$

should be greater than zero. This is in agreement with the tendency of k_b to increase with temperature.

In the study of the thermal reaction between SF_4 and fluorine near 270 K [8], reaction (4) was neglected in the calculations although it was reported to contribute about 15% to the total termination rate. If we now take it into account, the second-order rate constant can be reinterpreted from eqn. (V) as

$$k_{exp} = \frac{v}{[SF_4][F_2]}$$

$$= \left(\frac{k_{1'}k_2k_3}{k_5}\right)^{1/2} \left(\frac{v_5}{v_4 + v_5}\right)^{1/2} \quad \text{(long chain)} \qquad \text{(VII)}$$

The positive contribution of the increase in v_5/v_4 with temperature to the global activation energy is evident from this equation. If we use the expression [8]

$$k_{exp} = (3.85 \pm 0.20) \times 10^8 \exp\left(-\frac{10.8 \pm 0.7 \text{ kcal mol}^{-1}}{RT}\right) \text{M}^{-1} \text{ s}^{-1}$$

and assume that 80% of the chain terminations proceed through reaction (5) at 270 K and 95% proceed through this reaction at 297 K, we obtain

$$E_2 + E_3 - E_5 = 6.0 \pm 1.5 \text{ kcal mol}^{-1}$$

($E_{1'}$ is assumed to be 14.6 $\pm$ 0.5 kcal mol^{-1}).
    From k_a we have

$$E_3 - \tfrac{1}{2} E_4 = 4.0 \pm 0.2 \text{ kcal mol}^{-1}$$

If we assume zero activation energy for reactions (4) and (5) and use the last two equations, we obtain

$$E_3 = 4.0 \pm 0.2 \text{ kcal mol}^{-1}$$

$$E_2 = 2.0 \pm 1.5 \text{ kcal mol}^{-1}$$

Furthermore, with $k_4 < 10^7$ M^{-1} s^{-1} [3, 4], $E_4 \approx 0$, and when the expression for k_a is taken into account the pre-exponential factor for reaction (3) is

$$A_3 < 4.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

    In view of the very different experimental conditions under which the experiments were carried out, the agreement between the data for the thermal [8] and the photochemical reactions between SF_4 and fluorine is quite satisfactory.

References

1 J. Czarnowski and H. J. Schumacher, *Int. J. Chem. Kinet.*, *10* (1978) 111.
2 J. Czarnowski and H. J. Schumacher, *Int. J. Chem. Kinet.*, *11* (1979) 613.
3 J. Czarnowski and H. J. Schumacher, *Int. J. Chem. Kinet.*, *11* (1979) 1089.
4 J. Czarnowski and H. J. Schumacher, *J. Fluorine Chem.*, *12* (1978) 497.
5 M. Feliz and H. J. Schumacher, *J. Photochem.*, *15* (1981) 109.
6 J. Czarnowski and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *123* (1980) 91.
7 M. Feliz and H. J. Schumacher, *An. Asoc. Quim. Argent.*, *68* (1980) 217.

8 A. C. González and H. J. Schumacher, *Z. Naturforsch.*, *36b* (1981) 66.

9 A. C. González and H. J. Schumacher, *J. Photochem.*, *20* (1982) 85.

10 E. Castellano and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *65* (1969) 62.

11 R. Gatti, E. Staricco, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *35* (1962) 343.

12 W. J. Podbielniak, *Ind. Eng. Chem., Anal. Edn.*, *3* (1931) 177; *5* (1933) 119; *5* (1933) 172.

13 E. Staricco, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *31* (1962) 385.

14 A. C. González and H. J. Schumacher, *Z. Phys. Chem. N.F.*, *127* (1981) 167.

15 S. W. Benson and J. Bott, *Int. J. Chem. Kinet.*, *1* (1969) 451.

16 J. J. de Corpo, R. P. Stieger, J. L. Franklin and J. L. Margrave, *J. Chem. Phys.*, *53* (1970) 936.

17 D. R. Stull and H. Prophet (eds.), *JANAF Thermochemical Tables*, 2nd edn., *NBS Natl. Stand. Ref. Data Ser. 37*, June 1971 (National Bureau of Standards, U.S. Department of Commerce).