Recombination Constants Calculation of Reactions between Fluorine Atoms and O_2, CO, NO_2, SO_3, FSO_3, ClO_2, NF_2, and ClF

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Recombination constants for reactions between fluorine atoms and O_2, CO, NO_2, SO_3, FSO_3, ClO_2, NF_2 and ClF were calculated by means of a method developed by J. Troe. N_2 was used as bath gas and a temperature of 300 K was considered. The following values were obtained: 1.7×10^{16}, 9.2×10^{16}, 2.2×10^{17}, 7.0×10^{18}, 1.7×10^{19}, 2.6×10^{17}, 1.0×10^{17}, 2.3×10^{16} $cm^6\ mol^{-2}\ s^{-1}$ respectively.

Introduction

While studying thermal and photochemical gas reactions in which fluorine atoms intervene, recombination steps of fluorine atoms with different species A to form FA ought to be considered. The rate constants of these steps are not known experimentally. It is necessary to estimate their magnitude in order to accept or to discard a specific process in a mechanism.

Troe [1, 2] developed a theory in which the rate constant of a thermal unimolecular reaction in the limiting low pressure range is expressed as

$$k_0 = \beta_c\, k_0^{SC}, \qquad (1)$$

where β_c is the collision efficiency to be calculated as in reference [1] and k_0^{SC} the strong collision rate constant,to be evaluated as in reference [2]:

$$k_0^{SC} = [M] Z_{LJ} \left[\varrho_{vib,h}(E_0)\, k\, T / Q_{vib}\right] \cdot \exp(-E_0/k\,T)\, F_{anh}\, F_E\, F_{rot}\, F_{rot.int}\, F_{corr}\,, \qquad (2)$$

where $[M]$ is bath gas concentration, E_0 the threshold energy of the reaction, Z_{LJ} the Lennard-Jones collision frequency, $\varrho_{vib,h}(E_0)$ the vibrational harmonic density of sates, Q_{vib} the vibrational partition function, F_{anh} the anharmonicity factor, F_E the energy dependence factor for the density of states, F_{rot} the rotational factor and $F_{rot.int}$ the internal rotation factor F_{corr} is a factor which corrects for coupling between the various factors and the approximation made in their calculation, and which estimated to be unity.

$$k_{rec,0} = \frac{k_0 (Q_t\, Q_r\, Q_e)_{FA}\, N}{(Q_t\, Q_e)_F\, (Q_t\, Q_r\, Q_v\, Q_e)_A}\,, \qquad (3)$$

where Q_t, Q_r, Q_v and Q_e are the translational, rotational, vibrational and electronic partition functions of the species F, A and FA, N being the Avogadro number.

Results and Discussion

The recombination constants for the reactions between F atoms and the species O_2, CO, NO_2, SO_3, FSO_3, ClO_2, NF_2 and ClF were calculated.

The recombination constants for all the reactions were calculated using a thermal bath $[M] = N_2$ ($\sigma = 3.738$ Å and $\varepsilon/k = 82$ K [3]). The average energy transferred in every transition $\langle \Delta E \rangle$ used in the β_c calculation was 4.6 kJ mol^{-1} [4]. If the ground state quantum weight was not known, a value of one for stable molecules and two for radicals was assumed in the Q_e calculation.

The molecular properties of A and FA are shown in Table I. Table II shows the different factors for the calculation of the recombination constants, the calculated values and the experimental values found in the literature.

I. $F + O_2$: In the photochemical reaction between F_2 and CO_2[5], an inhibitory effect was found. This effect was explained by the reaction $F + O_2 \rightleftarrows FO_2$, which was later confirmed through other research [6–8]. The Lennard-Jones well depth for FO_2 (ε/k), used in the Z_{LJ} calculation, was assumed to be similar to that of FNO [2]. The activation energy for the recombination process found in the literature was almost zero [9–11]; thus the rotational factor F_{rot} was calculated using a potential of type II of

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Table 1. Molecular properties of A and FA

$F + A \xrightarrow{M} FA$	A			FA				
	w^{c}	I^{d}	g^{e}	$\sigma_{\mathrm{LJ}}{}^{\mathrm{a}}$	$\varepsilon_{\mathrm{LJ}}/k^{\mathrm{b}}$	w^{c}	I^{d}	g^{e}
$F + O_2 \xrightarrow{N_2} FO_2$	1580.2^{f}	$1.937 \times 10^{-39\,\mathrm{f}}$	1^{f}	3.9	380	1495–584.5–370	$7.75 \times 10^{-116\,\mathrm{f}}$	2^{f}
$F + CO \xrightarrow{N_2} FCO$	2169.2^{f}	$1.45 \times 10^{-39\,\mathrm{f}}$	1^{f}	4.0	380	1018–626–1855	$2.19 \times 10^{-115\,\mathrm{f}}$	2^{f}
$F + NO_2 \xrightarrow{N_2} FNO_2$	1357–757–1665	$1.539 \times 10^{-116\,\mathrm{f}}$	2^{f}	3.9	230	1793–570–460 742–1312–822	$6.40 \times 10^{-115\,\mathrm{f}}$	1^{f}
$F + SO_3 \xrightarrow{N_2} FSO_3$	1068–495–1391 (2) 529 (2) $^{\mathrm{f}}$	$1.08 \times 10^{-114\,\mathrm{f}}$	1^{f}	4.8	278	1055–839–534– 1176 (2)–604 (2)– 369 (2)	$4.80 \times 10^{-114\,\mathrm{i}}$	2
$F + FSO_3 \xrightarrow{N_2} F_2SO_3$	1055–839–1176 (2) 534–604 (2)–369 (2) $^{\mathrm{h}}$	$4.80 \times 10^{-114\,\mathrm{i}}$	2	6.0	278	1501–1248–879– 852–789–575– 520–500–395– 390–292–137 $^{\mathrm{j}}$	$1.886 \times 10^{-113\,\mathrm{j}}$	1
$F + ClO_2 \xrightarrow{N_2} FClO_2$	945–447–1109 $^{\mathrm{f}}$	$1.495 \times 10^{-115\,\mathrm{f}}$	2^{f}	5.2	307	1106–630–547– 402–1271–367 $^{\mathrm{k}}$	$1.47 \times 10^{-114\,\mathrm{l}}$	1
$F + NF_2 \xrightarrow{N_2} NF_3$	1069–573–931 $^{\mathrm{g}}$	$3.76 \times 10^{-115\,\mathrm{g}}$	2	3.9	166	1031–642– 907 (2)–497 (2) $^{\mathrm{g}}$	$1.49 \times 10^{-114\,\mathrm{g}}$	1
$F + FCl \xrightarrow{N_2} F_2Cl$	784 $^{\mathrm{f}}$	$5.445 \times 10^{-39\,\mathrm{f}}$	1^{f}	5.0	260	578–570–500 $^{\mathrm{m}}$	$9.576 \times 10^{-115\,\mathrm{m}}$	2

[a] Estimated Lennard-Jones collision diameter in Å.
[b] Lennard-Jones well depth in K.
[c] Vibrational frequencies in cm^{-1}.
[d] Product of the Moments of Inertia in $\mathrm{g}^3\,\mathrm{cm}^6$.
[e] Ground state quantum weight.
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Waage and Rabinovitch [12-2] in the reaction coordinate.

II. $F + CO$: This process was postulated in the thermal reaction between CO, F_2 and O_2 [13] and also in the photochemical reaction between CO and F_2O [14]. A value of $\varepsilon/k(FCO) = \varepsilon/k(FNO)$ was used. Milligan et al. [15] found that F atoms and CO combine with almost zero activation energy; thus F_{rot} was calculated as in I.

III. $F + NO_2$: This process was included in the mechanism of the thermal reaction between F_2 and NO_3F [16]. The $\varepsilon/k(FNO_3)$ was estimated from the boiling point of the compound [17, 18]. The activation energy for the recombination process is 3.35 kJ mol^{-1} [9]; thus F_{rot} was calculated as in I.

IV. $F + SO_3$: This process was included in several mechanisms [19 – 21]. The $\varepsilon/k(FSO_3)$ was assumed to be the same as that of F_2SO_3 (see below). The primary process in the unimolecular decomposition of the F_2FO_3 is the rupture of the OF bond with an activation energy of 138.0 kJ mol^{-1} [24, 25]; thus the SF bond energy must be greater than that of OF. The average energy of the SF bond in SF_4 is 181.9 kJ mol^{-1} [26]. It was assumed that the energy of the SF bond in FSO_3 would be between the values mentioned above; a value of 163.1 ± 20.9 kJ mol^{-1} was used. It was found [19] that the activation energy of the recombination process was nearly zero; thus F_{rot} was calculated as in I.

V. $F + FSO_3$: This step was formulated in several mechanisms [19 – 23]. The $\varepsilon/k(F_2SO_3)$ was estimated from the boiling point of the compound [27]. As it was assumed that E_0 is similar to the activation energy in the high pressure limit $E_{a\infty}$ [28, 29], the value found in [24] was used. As the recombination energy is almost zero [19], F_{rot} was calculated as in I.

VI. $F + ClO_2$: P. Aymonino and H. J. Schumacher [30, 31] had proposed this step in the kinetics of the thermal reaction between F_2 and ClO_2. $\varepsilon/k(FClO_2)$ was estimated from the boiling point of the compound [32]. As the E_0 for this process was

Table 2. Factors for the calculation of the recombination constants, calculated and experimental values.

Reaction	E_0[a]	T[b]	$Z_{LJ}M/10^{14}$[c]	$\varrho_{\mathrm{vib,h}}(E_0)$[d]	Q_{vib}[e]	F[f] $\binom{\mathrm{anh}}{s,m}$[g]	F_E[h]	F_{rot}[i]	β_c[j]	$k^{\mathrm{calc.}}_{\mathrm{rec,o}}/[N_2]$[k]	$k^{\mathrm{exp.}}_{\mathrm{rec,o}}/[M]$[l]
F + O_2	62.7 ± 21.8	373	2.05	5.23	1.46	1.72 (3.2)	1.16	10.40	0.45	(1.7 ± 2.0) × 10^{16} 1.1	(1.7 ± 0.3) × 10^{15}[m] 5.8 × 10^{15}[n]
F + CO	134.7 ± 63.6	303	2.23	5.95	1.06	1.72 (3.2	1.06	27.30	0.50	(9.2 ± 16.5) × 10^{16} 7.3	(2.07 ± 0.72) × 10^{16}[ñ]
F + NO_2	215.9 ± 22.6	383	2.00	7.22 × 10^3	1.55	1.37 (6.3	1.09	19.60	0.45	(2.2 ± 1.5) × 10^{17} 1.0	2.3 × 10^{17}[o]
F + SO_3	163.1 ± 20.9	373	2.42	4.06 × 10^5	2.64	1.21 (9.6)	1.17	10.82	0.43	(7.0 ± 10.3) × 10^{18} 4.4	—
F + FSO_3	138.0 ± 4.1	373	3.09	2.72 × 10^7	11.43	1.15 (12.3)	1.25	7.12	0.42	(1.7 ± 0.9) × 10^{17} 0.4	—
F + ClO_2	217.5 ± 29.3	237	2.52	3.37 × 10^4	1.30	1.37 (6.3)	1.06	4.63	0.56	(2.6 ± 0.9) × 10^{17} 0.6	—
F + NF_2	238.4 ± 8.4	418	1.93	2.75 × 10^4	1.89	1.37 (6.3)	1.09	19.23	0.43	(1.0 ± 0.2) × 10^{17}	(3.3 ± 1.2) × 10^{17}[p] 5.0 × 10^{16}[q]
F + FCl	129.7 ± 20.9	303	2.49	34.58	1.26	2.37 (3.3)	1.07	4.48	0.50	(2.3 ± 0.8) × 10^{16} 0.8	—

[a] Threshold energy in kJ mol^{-1}.

[b] Temperature in K.

[c] Lennard-Jones frequency in cm^3 mol^{-1} s^{-1}; $[M]$ = heat bath gas.

[d] Harmonic density of states at E_0 in (kJ $mol^{-1})^{-1}$.

[e] Vibrational partition function.

[f] Anharmonicity factor.

[g] s = number of harmonic oscillators; m = number of Morse oscillators.

[h] Energy dependence factor for the density of states.

[i] Rotational Factor.

[j] Weak collision efficiency.

[k] Calculated recombination constants in cm^6 mol^{-2} s^{-1}. The deviation is due to E_0 only.

[l] Experimental recombination constants in cm^6 mol^{-2} s^{-1}.

[m] P. P. Chegodaev, V. I. Topikov, E. G. Strikov, and S. Ya Ashezhetskii. Khim. Vys. Energ. **12,** 116 (1978) ($[M]$ = Ar; between 228 and 301 K).

[n] W. Wang and D. D. Davis, Int. J. Chem. Kinetics **6,** 401 (1974) ($[M]$ = Ar; between 220 and 360 K).

[ñ] E. H. Appelman and M. A. A. Clyne, J. Chem. Soc. Faraday Trans. I, **71,** 2072 (1975) ($[M]$ = Ar, at 298 K).

[o] European Symposium of the Combustion Institute (ed. F. S. Weinberg-Ac. Press, London, 35 (1973), C. Zetzsch) ($[M]$ = He, between 248 and 368 K).

[p] M. A. A. Clyne and R. T. Watson, J. Chem. Faraday Trans. I, **70,** 1109 (1974), $[M]$ = He, at 298 K).

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not known, the corresponding $D_{O-ClOF} = 188.2$ kJ mol^{-1} [33] was taken as the lower limit for that value. Now, this value was taken from the unimolecular decomposition of $FClO_2$, where the primary process was $FClO_2 \rightarrow O + FClO$. The higher limit is the value of the bond energy of FCl (246.8 kJ mol^{-1} [26]). F_{rot} is a function of the pseudo rotational partion function I^{+}/I for a centrifugal barrier as derived by Eyring et al. [34]. As the process has an activation energy of 17.2 kJ mol^{-1} [31], it could be assumed that the normal configuration of the $FClO_2$ molecule and the activation complex could not be very different, and I^{+}/I would not be higher than one. According to the theory, if a value of $I^{+}/I = 1$ was used in equations (7 – 27) of reference [2], a lower limit for F_{rot} and $k_{rec,0}$ was obtained.

VII. $F + NF_2$: This process was included in the mechanism of the thermal reaction between N_2F_4 and F_2O [35]. $\varepsilon/k(NF_3)$ was estimated from the boiling point of the compound [18]. E_0 was taken from tables [36]. As the activation energy for this process was not known, the recombination constant that appears on Table II was calculated with the supposition that the recombination energy was almost zero. A lowest recombination constant $k_{rec,0} = 1.9 \times 10^{16}$ cm^6 mol^{-2} s^{-1} was obtained. It was assumed that this process, as in case VI, has an appreciable activation energy.

VIII. $F + FCl$: This step was included in the mechanism of the photochemical reaction between F_2 and ClF [37]. $\varepsilon/k(F_2Cl)$ was assumed as a value between that of FCl and ClF_3 (calculated from the boiling points [18]). San Roman [38] obtained from thermochemical considerations an energy $D_{FCl-F} = 129.7$ kJ mol^{-1}. This value was used as E_0. As the activation energy of this process was unknown, in addition to the recombination constant that appears in Table II, a value of $k_{rec,0} = 2.3 \times 10^{16}$ cm^6 mol^{-2} s^{-1} was obtained as the lowest limit.

Conclusions

A critical study of the errors involved in the calculation of the recombination constants with the input data showed that the eminent factor was E_0 through $\varrho_{vib,h}(E_0)$.

If a variation of σ_{LJ} of 10% was considered, a deviation of 10% resulted in the calculated recombination constants.

It should be stated that the calculated rotational factors are fairly uncertain [4].

It has to be noted that several of the reactions under typical experimental conditions are not in the third order regime but in the transition to second order.

In view of the uncertainties in the measurements, the agreement between calculated and experimental values can be considered satisfactory. The recombination constants for four processes given here are not found in up to date literature.

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