Kinetics of Reactions of Methyl and Ethyl Radicals with Chlorine in the Gas Phase Studied by Photochlorination of Methane

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Rate constants of the reactions of methyl and ethyl radicals with chlorine were determined in the temperature range 298–423 K from time-resolved methyl radical absorption and from product concentrations analysed by gas chromatography. Values of $\lg(k/dm^3\ mol^{-1}\ s^{-1})$ were obtained and are reported herein.

The photoinduced chlorination of alkanes occurs by a chain mechanism. Chlorine atoms formed in the photolysis of chlorine molecules abstract hydrogen from alkane molecules producing alkyl radicals, which then react rapidly with chlorine molecules to produce chlorine atoms and monochloroalkanes. Only two measurements of the rate of the reaction between methyl radicals and molecular chlorine have been reported[1,2] and one measurement[1] of the reaction between a chlorine atom and a methyl radical; whereas, several measurements of the rate constant of the reaction between a chlorine atom and methane have been published.[3] These reactions are important steps in the chain mechanism of the photochlorination of methane. We have investigated the kinetics of reactions of methyl and ethyl radicals with chlorine molecules by the flash photolysis method in the temperature range 298–423 K.

Experimental

Materials. Methane and ethane (The Matheson Co.), chlorine (E. Merck AG), carbon dioxide (AGA AG) and monochloromethane (Fluka AG) were of highest purity available. Chlorine was dried with P_4O_{10} and degassed at reduced pressure and at the temperature of liquid nitrogen. Methane contained about 0.00030%

ethane. This amount was taken into account in the calculations.

Apparatus. The discharge flash lamp was a 200 cm long 9 mm diameter quartz tube filled with 3–7 kPa xenon. It was placed parallel to the 200 cm long 9 mm diameter reaction quartz tube in order to produce a homogeneous light intensity within the reaction. The lamp and reaction were surrounded by a metal tube covered with a reflecting magnesium oxide layer. It could be heated electrically, and the temperature was kept constant within about 2 °C. The reaction mixture was heated about 1 °C by one flash. A 14.7 μF capacitor, charged at about 11 kV, was connected to the flash lamp producing approximately a 900J flash of about 30 μs half-width. The flash consisted of nearly continuous black body radiation with a maximum at about 400 nm. The quartz tube cut off the radiation at about 200 nm; at 215 nm, the transmittance was about 65%.

Methane and carbon dioxide did not absorb the flash light. The molar absorptivity[4] of chlorine molecules is 6.7 $dm^2\ mol^{-1}$ at the maximum of 330 nm.

The flash source and reactor were cleaned with solutions of hydrogen fluoride, sodium hydroxide, water and ethanol.

The reactor was connected to a Hewlett-Pack-

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ard 5720A gas chromatograph with a 2 cm³ gas inlet system. The reaction products were analysed with a FID detector using ⅛ inch wide and 2 m long columns filled with 80/100 mesh Chromosorb 102, Porapak T, or Carbowax 20 M. Methane was used as a reference standard when calibrating the peak areas and calculating the amounts of reaction products.
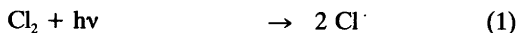
The concentration of methyl radicals was measured using an Oriel 6242 xenon lamp, with a Hilger Watts medium quartz spectrograph. The molar absorptivity[5] of methyl radicals is $\varepsilon = 1010 \pm 80$ m² mol⁻¹ at 216.36 nm.

The decay of absorption of methyl radicals was displayed on a Telequipment DM53A oscilloscope and photographed for calculation of methyl radical concentration. The weak absorbance, $\varepsilon = 1.2 \cdot 10^{-2}$ m² mol⁻¹ at 216.36 nm, of the reaction product, methyl chloride, was subtracted from the measured total absorbance.
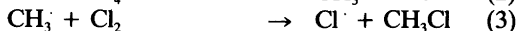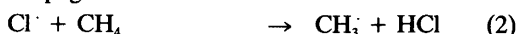
Calculations. Values of rate constants of the reactions between a methyl radical and chlorine molecule, and between a methyl radical and chlorine atom, were calculated by two different methods, either from the experimental values of methyl radical decay curves, or from the amounts of final products.

The radical reactions were initiated by photodissociation[1] of chlorine molecules. About 8 % of chlorine was dissociated by one flash. Rate constants of reactions 2–16 were used in the calculations of the rate constants of reactions 3 and 7 of an ethyl radical with a chlorine molecule and a chlorine atom.
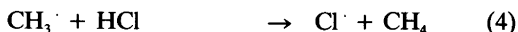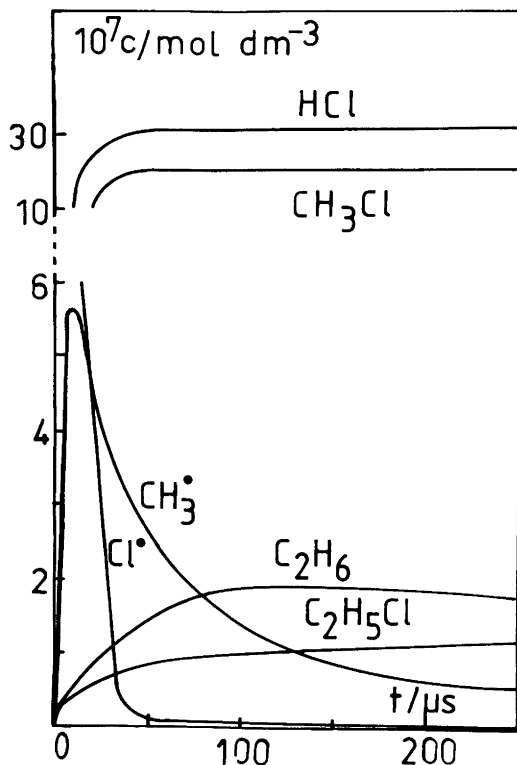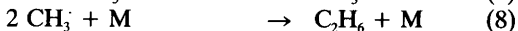
Initiation:

$$Cl_2 + h\nu \qquad \rightarrow \quad 2\ Cl^{\cdot} \qquad (1)$$

Propagation:

$$Cl^{\cdot} + CH_4 \qquad \rightarrow \quad CH_3^{\cdot} + HCl \quad (2)$$
$$CH_3^{\cdot} + Cl_2 \qquad \rightarrow \quad Cl^{\cdot} + CH_3Cl \quad (3)$$

Retardation:

$$CH_3^{\cdot} + HCl \qquad \rightarrow \quad Cl^{\cdot} + CH_4 \quad (4)$$

Termination:

$$2\ Cl^{\cdot} + wall \qquad \rightarrow \quad Cl_2 \qquad\qquad (5)$$
$$2\ Cl^{\cdot} + M \qquad \rightarrow \quad Cl_2 + M \qquad (6)$$
$$Cl^{\cdot} + CH_3^{\cdot} + M \quad \rightarrow \quad CH_3Cl + M \quad (7)$$
$$2\ CH_3^{\cdot} + M \qquad \rightarrow \quad C_2H_6 + M \quad (8)$$

460
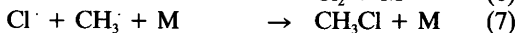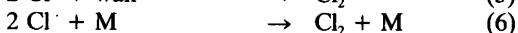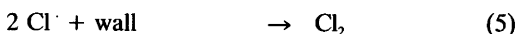
Fig. 1. Calculated concentrations of transients and products formed by one flash in a mixture containing 0.085 kPa chlorine, 2.65 kPa methane and 13.2 kPa carbon dioxide at 25 °C.

Reactions of minor importance:

$$Cl^{\cdot} + C_2H_6 \qquad \rightarrow \quad C_2H_5^{\cdot} + HCl \quad (9)$$
$$C_2H_5^{\cdot} + Cl_2 \qquad \rightarrow \quad C_2H_5Cl + Cl^{\cdot} \quad (10)$$
$$Cl^{\cdot} + C_2H_5^{\cdot} + M \quad \rightarrow \quad C_2H_5Cl + M \quad (11)$$
$$CH_3^{\cdot} + C_2H_5^{\cdot} + M \quad \rightarrow \quad C_3H_8 + M \quad (12)$$
$$Cl^{\cdot} + CH_3Cl \qquad \rightarrow \quad CH_2Cl^{\cdot} + HCl \quad (13)$$
$$CH_2Cl^{\cdot} + Cl_2 \qquad \rightarrow \quad CH_2Cl_2 + Cl^{\cdot} \quad (14)$$
$$CH_2Cl^{\cdot} + Cl^{\cdot} + M \quad \rightarrow \quad CH_2Cl_2 + M \quad (15)$$
$$CH_2Cl^{\cdot} + CH_3^{\cdot} + M \quad \rightarrow \quad C_2H_5Cl + M \quad (16)$$
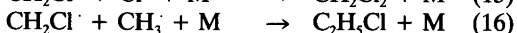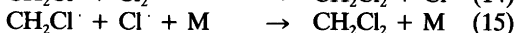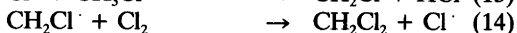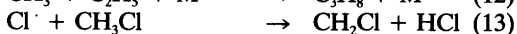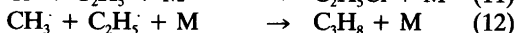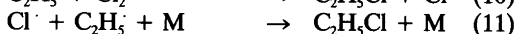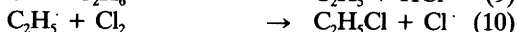
Values of rate constants of reactions 2, 4, 6, 8 and 12–15 were taken from the literature and used as constant input values in the calculations: $k_2 = 6.38 \cdot 10^9 \exp(-1415/TK^{-1})$ cm³ mol⁻¹ s⁻¹, from Ref. 6; $k_4 = 4.72 \cdot 10^8 \exp(-1072/TK^{-1})$ dm³ mol⁻¹ s⁻¹, from Ref. 7; $k_6 = 1.56 \cdot 10^9 \exp(750/TK^{-1})$ dm⁶ mol⁻² s⁻¹, from Ref. 8; $k_8 = 2.70 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹, from Ref. 5; $k_{12} = 2.72 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹, from Ref. 9; $k_{13} = 1.24 \cdot 10^{11}$ exp-

Table 1. Rate constants of reactions 3, 7 and 5 calculated from experimental values of methyl radical absorbance in mixtures containing different initial amounts of Cl_2, CH_4 and CO_2, at different temperatures.

T/K 298	P/kPa Cl_2	CH_4	CO_2	Cl	$10^8 k_3$ $dm^3 mol^{-1} s^{-1}$	$10^{11} k_7$ $dm^3 mol^{-1} s^{-1}$	k_5 s^{-1}
	0.028	0.56	6.52	0.006	2.00	1.07	77
	0.120	2.31	8.75	0.025	1.90	0.98	81
	0.192	2.03	8.64	0.043	2.00	0.70	75
	0.045	0.92	10.6	0.010	2.89	0.92	75
	0.168	3.23	13.2	0.037	2.04	1.09	80
	0.191	3.79	14.3	0.043	1.98	1.01	71
	0.104	3.01	15.2	0.023	2.59	1.25	81
	0.075	1.51	17.7	0.016	3.17	0.92	83
	0.253	7.87	22.1	0.059	2.40	2.48	69
	0.312	6.18	23.3	0.069	2.03	0.95	77
	0.161	4.98	24.9	0.033	3.51	1.62	74
	0.121	2.45	28.3	0.025	3.24	1.97	76
	mean value				2.48 (0.5)	1.29 (0.4)	77 (5)
323	0.035	1.04	5.42	0.005	4.43	1.23	75
	0.064	1.91	9.92	0.012	3.08	2.25	89
	0.101	3.03	15.7	0.020	4.99	2.28	73
	mean value				4.17 (0.8)	1.92 (0.4)	79 (5)
373	0.063	1.79	8.67	0.015	4.16	1.72	75
	0.111	3.19	15.3	0.031	4.59	1.67	71
	0.196	5.64	27.3	0.053	7.19	1.29	74
	mean value				5.31 (1.1)	1.56 (0.4)	73 (5)
423	0.063	1.81	8.28	0.007	8.06	1.21	80
	0.095	2.64	12.5	0.015	7.28	1.48	68
	0.141	3.99	18.8	0.020	6.74	1.42	69
0.212	5.96	28.1	0.039	10.4	2.37	77	
	mean value				8.11 (1.6)	1.62 (0.4)	74 (5)

$(-1787/TK^{-1})$ $dm^3 mol^{-1} s^{-1}$, from Ref. 10; $k_{14} = 3.98 \cdot 10^9 \exp(-15.08/TK^{-1})$ $dm^3 mol^{-1} s^{-1}$, from Ref. 1; and $k_{15} = 2.51 \cdot 10^{11}$ $dm^3 mol^{-1} s^{-1}$, from Ref. 1.

Photolysis of chlorine at 355 nm produces[11] mainly ground state $Cl(^2P_{3/2})$ shlorine atoms, together with about 1 % of $Cl(^2P_{1/2})$. $Cl(^2P_{1/3})$ reacts with methane faster[10] than does $Cl(^1P_{3/2})$. However, the relaxation of $Cl(^2P_{1/2})$ to $Cl(^2P_{3/2})$ is faster than the reactions 2 and 5–7 of chlorine atoms in our experiments.

The rate constant k_5 of the recombination reaction 5 between chlorine atoms on the walls of the reactor was calculated from the chlorine absorbance at 330 nm by separate experiments of flash photolysis of pure chlorine gas. We obtained the value $k_5 = 75\pm5$ s⁻¹, which was independent of temperature between 298 K and 423

K. The rate constant of reaction 5 depends on the material of the wall and its treatment. The rate of combination of chlorine atoms on the walls was less than 10 % of the rate of homogeneous third order combination of chlorine atoms by reaction 6 in our experiments.

The rate constants of the third order reaction 6 of chlorine atom combination depends on the pressures of the third bodies CO_2, Cl_2 and CH_4 of our experiments. The values of these three rate constants are approximately equal.[8] Carbon dioxide was always present in large excess. We therefore calculated the rate constant of reaction 6 by using the total pressures of Cl_2, CH_4 and CO_2, and the rate constant published[8] for CO_2.

Agreement between the calculated and experimental values of amounts of C_2H_5Cl could be obtained only when a value of $k_9 = 6.8 \cdot 10^{10}$ $dm^3 mol^{-1} s^{-1}$ at 298 K for the reaction 9 between

chlorine atom and ethane was used in the calculations. This value is about twice as large as the values reported previously: $10^{-10} \cdot k_9/\text{dm}^3 \text{ mol}^{-1}$ $\text{s}^{-1} = 1.6^2$, 1.7^3, 2.4^4, 3.1^8, 3.3^3, 3.6^5 and 3.8^6. Because C_2H_5Cl was a minor product (Table 2), a possible error in this value of the rate constant k_9 influenced the values of the rate constants k_3 and k_7 less than the experimental error.

No propane was observed among the products by gas chromatography. Reaction 12 could therefore be neglected in the calculations. Amounts of CH_2Cl_2 were alweays much less than the amounts of C_2H_6 or C_2H_5Cl. Reactions 13–16 were therefore neglected when calculating the rate constants of reactions 3, 7, 10 and 11.

Values of rate constants of reactions 3 and 7 were calculated from the values of time-resolved methyl radical absorbance by a computer integration program involving the rate equations of reactions 2–11. The calculated values of methyl radical concentrations were compared with the experimental values obtained from the methyl radical decay curves by a least-squares fit program. By iteration, the best values of rate con-

stants of reactions 3 and 7 were then obtained (Table 1).

After being produced by the flash of light, the chlorine atoms were consumed[6] by the fast reaction, 2, with methane (Fig. 1), followed by reaction 3 between a methyl radical and a chlorine molecule which is about ten times faster than the next important competing reaction, 8, the combination of methyl radicals; whereas, the other competing reactions are slower. Errors in the input values of the rate constants of the reactions 2, 4, 6 and 8 used in the calculations influenced therefore only slightly the calculated value of the rate constant 3. The influence of the half-width, about 30 μs, of the flash was minimised by using values of methyl radical concentrations obtained about 200 μs or more after the flash.

Values of rate constants of reactions 3, 7, 10 and 11 were calculated from the amounts of products which were calculated by a computer integration program of the rate equations of reactions 2–11 by using constant values of rate constants of reactions 2, 4, 6 and 8 from the literature,[1,5–10] and varying the values of rate constants

Table 2. Initial pressures of Cl_2, CH_4, CO_2 and Cl and final concentrations of products formed by one flash at different temperatures.

No.	T/K 298	P/kPa Cl_2	CH_4	CO_2	Cl	c/mol dm^{-3} 10^6 [CH_3Cl]	10^9 [C_2H_6]	10^9 [C_2H_5Cl]
1	298	0.034	1.36	6.7	0.005	1.19	48	49
2		0.045	1.37	6.9	0.009	2.12	44.1	101
3		0.053	0.17	9.7	0.007	1.84	0.7	13.6
4		0.064	2.45	12.0	0.010	2.53	105	88
5		0.085	2.63	13.2	0.013	3.22	106	228
6		0.115	4.48	22.0	0.017	4.38	153	197
7		0.161	4.98	24.9	0.032	7.84	169	429
8		0.210	8.18	40.0	0.031	8.78	217	392
9	323	0.075	1.04	5.3	0.005	1.10	60	63
10		0.064	1.92	9.9	0.008	1.73	101	85
11		0.101	3.03	15.7	0.019	3.93	161	187
12		0.172	5.11	26.5	0.033	7.21	222	290
13	373	0.074	1.01	4.9	0.007	1.71	77	66
14		0.067	1.79	8.7	0.012	2.74	136	122
15		0.111	3.19	15.7	0.023	5.79	223	241
16		0.196	5.69	27.3	0.043	9.87	372	405
17	423	0.063	1.77	8.3	0.011	1.63	118	59
18		0.095	2.64	12.4	0.015	3.34	218	134
19		0.141	4.00	18.8	0.020	4.47	310	203
20		0.212	5.99	28.2	0.039	8.73	452	415

of reactions 3, 7, 10 and 11. The best values were obtained by a least-squares iteration program. These results are shown in Tables 2 and 3.

The values of the rate constants k_3 and k_7, obtained by two experimental methods, were in good agreement. It was difficult to estimate the experimental error due to the length of the flash which had a half-life of about 30 μs. An error of about 20 % in the calculated rate constants may therefore be underestimated. Errors due to competing reactions were minimized by analyzing all reaction products and taking all interfering reactions into account in the calculation of rate constants. The values of rate constants k_3 and k_7 were approximately constant, as calculated from experiments using different initial concentrations. Values of the rate constants obtained by the two different experimental methods were in good agreement.

Discussion

About 8 to 13 % of chlorine dissociated during one flash in our experiments. most of the chlorine atoms had reacted with methane by reaction 2 within about 50 μs after the flash (Fig. 1). Reaction 2 was followed by the somewhat slower reaction 3 between a methyl radical and chlorine. All reactions proceeded to completion within a few microseconds. The most important termination reaction was 8, the combination of two methyl radicals. The main products of flash photolysis of a mixture of chlorine, methane and carbon dioxide were CH_3Cl and HCl, together with small amounts of C_2H_6, C_2H_5Cl, C_2H_4 and CH_2Cl_2 (see Fig. 1 and Table 2).

The value of the rate constant k_3 of reaction 3 calculated from experimental values of time evolution of methyl radical absorbance and from the

Table 3. Rate constants of reactions 3, 7, 10 and 11 calculated from experimental amounts of reaction products formed by one flash at different temperatures.

No.	T/K	$10^{-8} k_3$ dm³ mol⁻¹ s⁻¹	$10^{-11} k_7$ dm³ mol⁻¹ s⁻¹	$10^{-9} k_{10}$ dm³ mol⁻¹ s⁻¹	$10^{-11} k_{11}$ dm³ mol⁻¹ s⁻¹
1	298	3.22	1.32	2.69	2.77
2		3.51	1.48	2.74	2.81
3		3.10	1.15	2.66	2.70
4		3.52	1.49	2.80	2.66
5		2.89	1.06	2.77	2.76
6		3.47	1.41	2.73	2.68
7		3.30	1.23	2.74	2.59
8		3.44	1.46	2.76	2.70
	mean value	3.31 (0.3)	1.33 (0.2)	2.73 (0.3)	2.71 (0.3)
9	323	3.40	1.30	3.67	2.64
10		3.51	1.45	3.54	2.76
11		3.52	1.34	3.38	2.79
12		3.69	1.44	3.63	3.07
	mean value	3.53 (0.4)	1.38 (0.2)	3.56 (0.3)	2.82 (0.3)
13	373	5.77	1.52	4.03	2.62
14		5.74	1.49	4.15	2.76
15		5.32	1.47	4.17	2.61
16		6.47	1.51	3.91	3.52
	mean value	5.83 (0.6)	1.50 (0.2)	4.07 (0.3)	2.63 (0.3)
17	423	9.34	1.70	4.63	2.85
18		9.36	1.70	4.52	2.74
19		9.41	1.70	4.63	2.76
20		8.24	1.58	4.57	2.80
	mean value	9.09 (0.9)	1.68 (0.2)	4.59 (0.3)	2.79 (0.3)

Table 4. Mean values of rate constants k_3, k_7, k_{10} and k_{11} calculated from values of methyl radical absorbance and from concentrations of reaction products.

T/K	$10^8 k_3$ dm³ mol⁻¹ s⁻¹	$10^{11} k_7$ dm³ mol⁻¹ s⁻¹	$10^9 k_{10}$ dm³ mol⁻¹ s⁻¹	$10^{11} k_{11}$ dm³ mol⁻¹ s⁻¹
298	2.90 (0.6)	1.29 (0.4)	2.73 (0.3)	2.71 (0.3)
323	3.85 (0.8)	1.65 (0.4)	3.56 (0.4)	2.83 (0.3)
373	5.57 (1.1)	1.57 (0.4)	4.07 (0.4)	2.63 (0.3)
423	8.60 (1.7)	1.65 (0.4)	4.59 (0.5)	2.79 (0.3)
		mean 1.54 (0.4)		mean 2.74 (0.3)

amounts of final products were approximately equal, the difference being within the estimated experimental error (Tables 1 and 3). The mean value of the rate constant of reaction 3 between a methyl radical and a chlorine molecule is $k_3 =$ $(2.90\pm0.6) \cdot 10^8$ cm³ mol⁻¹ s⁻¹ at 298 K (Table 4).

The values of the rate constant k_3 calculated from the amounts of products were approximately constant, within experimental error, when the total pressure of carbon dioxide varied from 6.7–40 kPa (Table 3). The increase of the rate constant k_3, calculated from methyl radical absorbance when the pressure of carbon dioxide was increased, was expected to be due to experimental errors in measuring the methyl radical absorbance (Table 1). The rate constant k_3 is independent of a change in the ratio of initial amounts of methane and chlorine from 3 to 39. These results together with the product analysis indicate that impurities such as oxygen or water were absent.

Eckling *et al.*[1] reported $k_3 = 1.75 \cdot 10^8$ dm³ mol⁻¹ s⁻¹ at 298 K which was calculated from amounts of reaction products. Our results differ by a factor of about 3 from the value of $k_3 =$ $(9.03\pm0.6) \cdot 10^8$ dm³ mol⁻¹ s⁻¹ at 298 K, obtained by Kovalenko and Leone[2] from time-resolved infrared vibrational fluorescence measurements of the reaction product CH_3Cl formed by laser flash photolysis of methyl iodide, chlorine and argon mixtures. Kovalenko and Leone[2] used low pressures of methyl iodide and chlorine, together with about 0.40–1.60 kPa of argon. We used about 6.7–27 kPa of carbon dioxide in order to obtain a fast thermal equilibration of the methyl radicals in the flash experiments.

Evans and Whittle[7] measured the ratio of the

$$CH_3 + Br_2 \rightarrow CH_3Br + Br \qquad (17)$$

rate constants $k_3/k_{17} = 0.028$. Kovalenko and Le-

Table 5. Rate constants and activation parameters of reactions of halogens with methyl, ethyl and trifluoromethyl radicals.

Reaction	$\dfrac{10^8 \cdot k^{298}}{dm^3\ mol^{-1}\ s^{-1}}$	$\lg\left(\dfrac{A}{dm^3\ mol^{-1}\ s^{-1}}\right)$	$\dfrac{E}{kJ\ mol^{-1}}$	Ref.
$CH_3 + Cl_2$	2.90	10.03	9.00	this work
	9.03			2
	3.35			2, 17
	1.75	9.9	9.6	1
$C_2H_5 + Cl_2$	27.3	10.17	4.04	this work
	23	10.1	4.2	1
$CF_3 + Cl_2$	177	12.89	15.1	18
$CH_3 + Br_2$	103		0.3	12 and this work
	120			2
$CF_3 + Br_2$	7000	12.36	2.9	18
$CF_3 + I_2$	26000	12.41	0	18

one[2] measured the rate constant $k_{17} = 10 \cdot 10^9$ dm^3 mol^{-1} s^{-1}. Using these values $k_3 = 3.3 \cdot 10^8$ dm^3 mol^{-1} s^{-1} can be calculated at 298 K, which is in agreement with the value obtained in this work (Table 4). The following equation was fitted to the values of the rate constants measured at different temperatures from 298 K to 423 K (Table 4):

$$\lg(k_3/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (10.03 \pm 0.2) - (470 \pm 70)/T\text{K}^{-1}.$$

The activation energy $E = (9.0 \pm 1.1)$ kJ mol^{-1} is close to the value $E_3 = 9.63$ kJ mol^{-1} reported by Eckling et al.[2]

The reaction 10 between ethyl radical and chlorine was about 10 times faster than the reaction between a methyl radical and chlorine. At 298 K, $k_{10} = (2.73 \pm 0.3) \cdot 10^9$ dm^3 mol^{-1} s^{-1} and in the temperature range from 298 K to 423 K (Table 4):

$$\lg(k_{10}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (10.17 \pm 0.12) - (211 \pm 40)/T\text{K}^{-1}.$$

The activation energy $E_{10} = (4.0 \pm 0.8)$ kJ mol^{-1} is close to the value $E_{10} = 4.19$ kJ mol^{-1} obtained by Eckling et al.[1]

An ethyl radical is more reactive than a methyl radical in the reaction with molecular chlorine, due to approximately 5 kJ mol^{-1} lower activation energy. The activation energy[18] of the reaction between a trifluoromethyl radical and chlorine, 15.1 kJ mol^{-1}, is about 6 kJ mol^{-1} larger than the activation energy of reaction 3 between a methyl radical and chlorine. The polar substituent effects of reactions of alkyl radicals with chlorine indicate that a methyl radical reacts as a nucleophile with a chlorine molecule.

Evans and Whittle[17] measured the difference of the activation energies, E_3-$E_{17} = (8.7 \pm 1.3)$ kJ mol^{-1}. Using our value of $E_3 = (9.0 \pm 0.6)$ kJ mol^{-1}, we calculated $E_{17} = (0.3 \pm 1.5)$ kJ mol^{-1}.

$$CH_3^\cdot + Br_2 \rightarrow CF_3Br + Br^\cdot \tag{18}$$

Weeks and Whittle[19] obtained for reaction 18, at 298 K, the values $k_{18} = 4.5 \cdot 10^8$ dm^3 mol^{-1} s^{-1} and $E_{18} = 2.9$ kJ mol^{-1}. Reaction 17 of a methyl radical with bromine was about 36 times as fast as reactin 3 of a methyl radical with chlorine. For the corresponding reactions of a trifluoromethyl rad-

ical with these halides, the ratio of rate constants is approximately the same: about 39. The increase in the rate is due to a smaller activation energy of about 9 to 12 kJ mol^{-1} for the reaction of a methyl radical with bromine as compared with the reaction with chlorine (Table 4).

The rate constant $k_7 = (1.54 \pm 0.4) \cdot 10^{11}$ dm^3 mol^{-1} s^{-1} of the combination reaction between a methyl radical and a chlorine atom at 298 K was found to be independent of the variation of CO_2 pressure over a wide range (Tables 1, 3 and 4) and is therefore the high pressure limit value. The activation energy of reaction 7 was zero, within experimental error. Eckling et al.[1] obtained $k_7 = 3.98 \cdot 10^{11}$ dm^3 mol^{-1} s^{-1} at 298 K. The rate of recombination of chlorine atoms with methyl radicals was about 5 times faster than the combination reaction 8 between two methyl radicals, and about 4 times faster than the combination reaction between chlorine atoms and nitrogen oxide molecules[20] in spite of the approximately equal size of the radicals.

The rate constant of combination of radicals may vary by approximately one order of magnitude due to rotational barrier differences between tight and loose transition states.[20] The rate constant of reaction 11 between an ethyl radical and a chlorine atom, $k_{11} = (2.74 \pm 0.3) \cdot 10^{11}$ dm^3 mol^{-1} s^{-1}, is approximately twice as large as that for the corresponding reaction 7 between a methyl radical and a chlorine atom, indicating a tighter transition state for the ethyl radical reaction than for the methyl radical reaction.

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