

Kinetics of the Reactions of Halogenated Methyl Radicals with Molecular Bromine

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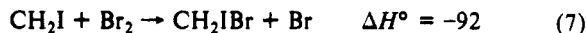
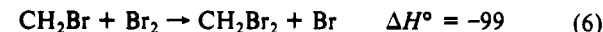
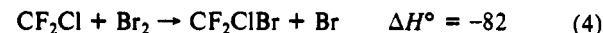
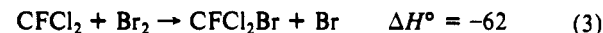
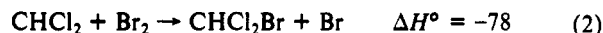
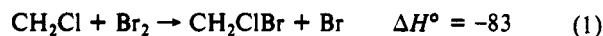
The kinetics of seven reactions of halogenated methyl radicals (CH_2Cl , CHCl_2 , CFCl_2 , CF_2Cl , CF_3 , CH_2Br , and CH_2I) with molecular bromine were studied by using a heatable tubular reactor coupled to a photoionization mass spectrometer. Rate constants were measured as a function of temperature, typically between 296 and 532 K. Arrhenius activation energies were found to be small negative values (typically -2 kJ mol^{-1}) for all reactions studied with the exception of that of the $\text{CF}_3 + \text{Br}_2$ reaction (whose activation energy is positive, but which could not be determined accurately). The pattern in reactivity among 11 reactions of substituted methyl radicals with Br_2 (which includes the 7 reactions studied here and 4 $\text{C}(\text{H})_x(\text{CH}_3)_{3-x} + \text{Br}_2$ reactions ($x = 0-3$) studied earlier) has been accounted for by the inductive effect of the substituent atoms or groups. The sum of the Pauling electronegativities of these substituents provides a useful measure of their total inductive effect on the reaction rate constant.

Introduction

The reactions of carbon-centered free radicals with molecular bromine are exothermic (typically ΔH° is in the range -75 to -100 kJ mol^{-1}) and generally have very high rate constants.¹⁻⁶ For example, Timonen et al.,¹ who recently studied the kinetics of the reactions of four alkyl radicals with Br_2 , report reaction rate constants that are close to the respective collision numbers and have small negative activation energies, indicating that the reactions proceed along attractive reaction coordinates.

Other than the alkyl radical + Br_2 reactions mentioned above, few reactions of carbon-centered radicals with molecular bromine have been studied in detail. Rate constants for the reactions of C_3H_5 ,² and of two perhalogenated radicals (CF_3 and C_2F_5)^{3,4} with Br_2 have been determined at ambient temperature, and that of HCO with Br_2 has been measured as a function of temperature.⁵ Ratios or functions of rate constants involving those of reactions of perhalogenated radicals with Br_2 have also been reported,⁶⁻¹⁰ some as a function of temperature. Finally, the kinetics of two reactions between dihalocarbene radicals (CFCl and CFBr) and Br_2 have also been investigated.^{11,12}

As part of our continuing investigation of the kinetics and thermochemistry of reactions of polyatomic free radicals with diatomic molecules containing halogen atoms, we have now studied the kinetics of the reactions of seven halogenated methyl radicals with Br_2 (reaction enthalpies are in kJ):¹¹



This study was conducted in part to attempt to isolate and characterize the influence of the inductive effect of halogen substituents of the radical site on the rate constants of a selected set of metathesis reactions. The reactions selected for study are ones that are sufficiently exothermic that thermochemistry was not expected to be an important factor in determining differences in reactivity. Hence, other influences on reactivity, such as the inductive effect, were anticipated to be more readily observable and susceptible to quantitative characterization from the observed differences in kinetic behavior.

Only reaction 5 has been isolated for direct investigation before. Rossi et al.³ obtained the rate constant at 298 K (1.3×10^{-12})

using the very-low-pressure-photolysis technique (all bimolecular rate constants are reported in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Whittle and co-workers have determined ratios of rate constants involving either k_4 or k_5 with suitable reference reactions.^{7,8}

Rate constants for reactions 1-7 were measured as a function of temperature. Details of the experiments, the results obtained, and a discussion of the observed substituent effects are reported here.

Experimental Section

The experimental facility¹⁹ as well as its use for kinetic studies of reactions of polyatomic free radicals with Br_2 has been described.¹ Only a summary will be presented here. Pulsed, unfocused, 193- or 248-nm radiation from a Lambda Physik EMG 201 MSC excimer laser was collimated and then directed along the axis of a heatable 1.05- (or 2.20-) cm-i.d. coated Pyrex tubular reactor. (The 1.05-cm-i.d. reactor was used in the studies of reactions 1-5 and the 2.20-cm-i.d. reactor was used in the studies of reactions 6 and 7). Gas flowing through the smaller tube at 5 m s^{-1} (or 2.5 m s^{-1} in the larger one) was completely replaced between laser pulses. The flowing gas contained the free-radical precursor in very low concentration (typically 0.0001%), Br_2 in varying amounts, and the carrier gas, He, in large excess ($>98\%$).

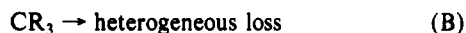
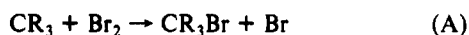
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- (13) Heats of formation used to determine reaction enthalpies were taken from the following sources: CH_2Cl ,¹⁴ CHCl_2 ,¹⁴ CFCl_2 ,¹³ CF_2Cl ,¹⁶ CF_3 ,¹⁴ CH_2Br ,¹⁴ CH_2I ,¹⁷ CH_2ClBr ,¹⁴ CHCl_2Br ,¹⁸ CFCl_2Br ,¹⁸ CF_2ClBr ,¹⁶ CF_3Br ,¹⁸ CH_2Br_2 ,¹⁴ CH_2IBr ,¹⁶ Br ,¹⁶ and Br_2 .¹⁶
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The free radical precursor used for CH_2Cl was CH_2ClBr (Aldrich, 99%), for CHCl_2 was CHCl_2Br (Aldrich, >98%), for CCl_2F was CCl_2F (Aldrich, >99%), for CClF_2 was CCl_2F_2 (Matheson, 99%), for CF_3 was CF_3Br (SCM Chemicals 99%), for CH_2Br was CH_2Br_2 (Aldrich, >99%), and for CH_2I was CH_2I_2 (Aldrich, 99%). He was obtained from Matheson (99.995%), and Br_2 from Aldrich (>99%). The free-radical precursors and Br_2 were degassed by using freeze-pump-thaw cycles. Helium was used as provided.

Gas was sampled through a 0.4-mm-diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the beam traversed the ion source, a portion was photoionized and then mass selected. Temporal ion signal profiles were recorded from a short time before each laser pulse to as long as 26 ms following the pulse by using a multichannel scaler. Data from 2000 to 30 000 repetitions of the experiment were accumulated before the data were analyzed.

Experiments were conducted under conditions where only two significant reactions consumed the labile reactant CR_3 :



In all sets of experiments conducted to determine a reaction rate constant, tests were also conducted to ensure that radical-radical and radical-atom reactions had negligible rates compared to either reaction A or B. Initial concentrations of CR_3 were reduced until the measured atom or radical decay constants in the presence or absence of the stable reactant no longer depended on the initial radical precursor concentration or on the laser fluence.

The laser fluence was attenuated by using quartz plates to reduce the photolysis of Br_2 to a negligible amount (<1%). The fact that the radical decay constants in the presence of Br_2 did not depend on laser fluence indicated that the limited amount of Br_2 photolysis that occurred did not interfere with the determination of the $\text{CR}_3 + \text{Br}_2$ rate constants. Laser fluences used were typically below 10 mJ cm^{-2} . With the highly attenuated laser beam, the photolysis of the radical precursor was too low to be measured. On the basis of previously measured radical sensitivities, the initial concentrations of the halogenated methyl radicals in these experiments are estimated to be in the range $(1\text{--}8) \times 10^{10}$ radicals cm^{-3} .

In the experiments conducted to measure $\text{CR}_3 + \text{Br}_2$ rate constants, Br_2 was always in great excess over the initial concentration of CR_3 . Rate constants for reactions 1–7 were obtained from slopes of plots of the radical's exponential decay constant, k' [from $[\text{CR}_3]_t = [\text{CR}_3]_0 \exp(-k't)$] vs $[\text{Br}_2]$. A representative ion signal decay profile and a decay constant plot from one set of experiments to measure k_2 are shown in Figure 1.

The bromides produced by reactions 1–7 could not be monitored, preventing confirmation of the products of the bromine reactions. Often these same bromides were used as free-radical precursors, and their presence obscured detection of additional amounts produced by the reaction under study.

The results obtained from all experiments are given in Table I. The rate constants obtained for reactions 1–7 are also plotted vs $1000/T$ in Figure 2.

UV photolysis produces the radicals of interest with an excess of internal energy. From what is known about vibrational deactivation rates of the CH_3^{20} and CF_3^{21} radicals, it is likely that under all our experimental conditions this relaxation occurs rapidly (<0.1 ms) compared to the observed reaction time (11–26 ms). To vary the vibrational relaxation time, experiments were conducted at different total gas densities (experiments in which the bath-gas pressure was altered without changing the pressure of the reactants). These changes had no systematic effect on the

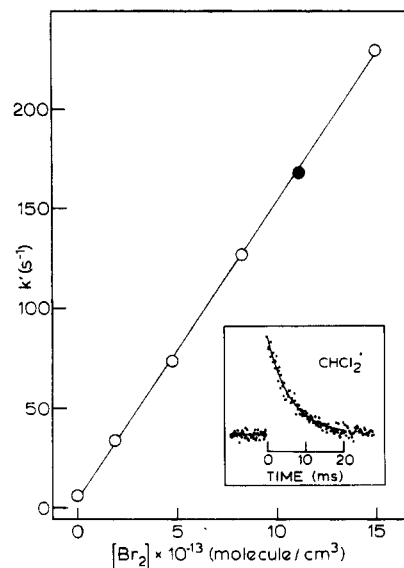


Figure 1. Plot of first-order decay constants k' vs $[\text{Br}_2]$ for one set of experiments conducted to measure k_2 at 399 K. (For additional information see Table I.) Insert is actual ion signal profile of CHCl_2^+ recorded during one of the plotted experiments (solid circle). For this experiment, $[\text{Br}_2] = 1.11 \times 10^{14} \text{ molecules cm}^{-3}$. The line through the data is the exponential function fitted to these points by using a nonlinear fitting procedure. The first-order decay constant of CHCl_2 is $168 \pm 4 \text{ s}^{-1}$.

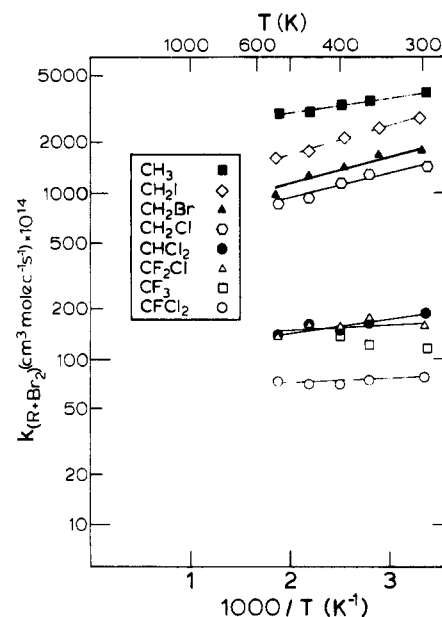


Figure 2. Arrhenius plot of measured $\text{CR}_3 + \text{Br}_2$ rate constants, $k_1\text{--}k_7$. The $\text{CH}_3 + \text{Br}_2$ rate constants shown were obtained earlier¹ and are included for reference.

value of the $\text{CR}_3 + \text{Br}_2$ rate constants obtained from these experiments. From these results we conclude that the alkyl radicals were thermally equilibrated prior to detectable reaction occurring.

It is theoretically possible for heterogeneous bimolecular reactions to have significant rates in experiments of this sort. (The kinetically first-order heterogeneous reaction (reaction B) is taken into account in the data analysis.) In our experiments, a second-order heterogeneous process, if important and unrecognized, would appear as an addition to the homogeneous bimolecular $\text{CR}_3 + \text{Br}_2$ rate constant. To test for the presence of such heterogeneous reactions, different wall coatings were used. They include halocarbon wax²² and PTFE {poly(tetrafluoroethylene)}.²³ While the coatings did reduce the first-order heterogeneous loss of CR_3 (i.e.,

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TABLE I: Conditions and Results of Experiments To Measure Rate Constants of CR₃ + Br₂ Reactions

<i>T</i> , °K	10 ⁻¹⁶ [He], molecules cm ⁻³	10 ⁻¹² [Br ₂], molecules cm ⁻³	<i>k_B</i> , s ⁻¹	wall coating mater ^b	10 ¹² <i>k_A</i> , cm ³ molecule ⁻¹ s ⁻¹
CH ₂ Cl + Br ₂ Reaction (<i>k</i> ₁)					
296	4.79	4.04–17.9	5.4	HW	14.1 ^c
296	4.80	5.78–17.1	4.8	PTFE	13.8 ^c
298	2.30	6.14–44.4	16	HW	15.1 ^c
358	4.68	5.69–26.9	5.9	HW	12.1 ^c
358	14.5	5.18–28.3	4.6	HW	14.2 ^c
358	4.69	6.21–20.2	5.1	PTFE	12.3 ^c
399	4.70	5.11–14.2	8.2	PTFE	11.4 ^c
456	4.74	6.00–21.9	11	PTFE	9.44 ^c
532	4.79	10.7–26.7	26	PTFE	8.63 ^c
<i>k</i> ₁ = (4.8 ± 1.0) × 10 ⁻¹² exp((2.80 ± 0.83) kJ mol ⁻¹ /RT)					
CHCl ₂ + Br ₂ Reaction (<i>k</i> ₂)					
296	4.80	55.0–155	8.3	PTFE	1.87 ^c
298	4.82	68.4–165	1.1	HW	1.76 ^c
298	2.30	36.1–131	5.1	HW	2.04 ^c
358	11.5	38.7–137	4.6	HW	1.61 ^c
358	4.72	32.3–151	1.0	HW	1.47 ^c
358	4.70	51.3–155	7.5	PTFE	1.83 ^c
399	4.73	18.8–149	6.4	PTFE	1.49 ^c
456	4.72	46.9–159	9.2	PTFE	1.61 ^c
532	4.78	58.9–187	25	PTFE	1.39 ^c
<i>k</i> ₂ = (9.8 ± 2.0) × 10 ⁻¹³ exp((1.59 ± 0.58) kJ mol ⁻¹ /RT)					
CFCl ₂ + Br ₂ Reaction (<i>k</i> ₃)					
298	14.8	124–525	8.4	PTFE	0.732
299	4.81	123–486	7.2	PTFE	0.812
358	4.67	95.2–523	3.1	PTFE	0.744
399	4.70	135–475	6.1	PTFE	0.703
456	4.72	106–546	3.5	PTFE	0.706
532	4.78	109–558	7.1	PTFE	0.734
<i>k</i> ₃ = (6.4 ± 1.3) × 10 ⁻¹³ exp((0.42 ± 0.84) kJ mol ⁻¹ /RT)					
CF ₂ Cl + Br ₂ Reaction (<i>k</i> ₄)					
298	4.81	85.9–300	6.6	PTFE	1.53
299	14.8	53.5–275	11	PTFE	1.60
358	4.69	54.5–263	3.3	PTFE	1.75
399	4.70	46.1–244	2.2	PTFE	1.54
456	4.72	55.0–257	1.6	PTFE	1.59
532	4.78	48.4–298	8.0	PTFE	1.36
<i>k</i> ₄ = (1.3 ± 0.3) × 10 ⁻¹² exp((0.54 ± 1.25) kJ mol ⁻¹ /RT)					
CF ₃ + Br ₂ Reaction (<i>k</i> ₅)					
296	4.82	33.2–118	9.2	HW	1.14
358	4.83	41.4–118	6.1	HW	1.20
399	6.63	27.6–128	7.2	PTFE	1.35
no Arrhenius expression recommended					
CH ₂ Br + Br ₂ Reaction (<i>k</i> ₆)					
299	8.05	4.84–14.3	8.2	PTFE	18.8 ^c
304	9.41	5.45–15.9	4.5	HW	16.8
346	7.64	5.35–21.4	4.2	HW	15.7
346	7.66	4.65–15.8	2.2	PTFE	18.0 ^c
393	7.66	4.65–19.1	1.5	PTFE	14.2 ^c
457	7.09	4.54–19.6	6.5	PTFE	12.7 ^c
539	7.10	4.28–22.7	6.7	PTFE	9.75 ^c
<i>k</i> ₆ = (5.5 ± 1.1) × 10 ⁻¹² exp((3.01 ± 0.88) kJ mol ⁻¹ /RT)					
CH ₂ I + Br ₂ Reaction (<i>k</i> ₇)					
304	7.68	2.77–10.8	10	PTFE	26.6 ^c
304	8.56	2.64–10.4	6.7	HW	28.7 ^c
346	7.72	2.45–9.88	3.3	HW	25.1 ^c
346	15.2	3.78–13.2	9.2	HW	22.6 ^c
346	6.92	2.34–10.6	9.3	PTFE	25.3 ^c
393	6.28	2.40–11.9	8.4	PTFE	21.1 ^c
457	6.87	4.29–13.3	5.3	PTFE	17.8 ^c
539	6.95	5.15–15.2	2.4	PTFE	16.1 ^c
<i>k</i> ₇ = (7.8 ± 1.6) × 10 ⁻¹² exp((3.30 ± 0.84) kJ mol ⁻¹ /RT)					

^aTemperature uncertainty: ±2 K (296–358 K), ±4 K (399–456 K), and ±5 (532 K). ^bWall coating materials used: HW (halocarbon wax) and PTFE (poly(tetrafluoroethylene)). ^cRadical produced by 248-nm photolysis (photolysis at 193 nm used in all other experiments).

reduced the value of *k_B*), they did not affect the value of the CR₃ + Br₂ rate constant. Therefore we conclude that bimolecular heterogeneous CR₃ + Br₂ reactions, if they occur at all, have negligible rates under our experimental conditions.

The reactions were typically studied from room temperature to 532 K, the upper limit being determined by the thermal stability

of the PTFE wall coating. Reaction 5 was studied only up to 399 K. This reaction was particularly difficult to study due to very low detection sensitivity for the CF₃ radical. This sensitivity actually decreased with increasing temperature, preventing accurate monitoring of CF₃ above the highest temperature used to monitor its kinetics.

The most probable error in each measured value of k_1 – k_7 is $\pm 20\%$. This assessment of overall accuracy takes into account the accuracies of the measured gas flow rates and total pressure, those of each determination of the radical decay constant, and those arising from the data analysis procedures used to calculate k_1 – k_7 .

The photoionization energies used in the mass spectrometer to detect reactants and products were as follows: 11.6–11.8 eV to detect Br_2 ; 10.2 eV to detect CF_2Cl , CF_2Cl , CF_3 ; 8.9–9.1 eV to detect CH_2Cl , CHCl_2 , CH_2Br , and CH_2I .

Discussion

(A) *Comparisons with Prior Investigations.* There has been only one prior determination of an absolute rate constant for any of the reactions studied. Rossi et al.³ determined a value of $k_5 = 1.3 \times 10^{-12}$ at 298 K using the very low pressure photolysis technique. Our value at 296 K (1.14×10^{-12}) is in very good agreement with theirs.

Older studies by Whittle and co-workers have provided ratios of rate constants that have included k_4 and k_5 .^{7,8} Tuckerman and Whittle⁷ determined the following ratios at 293 K:

$$k(\text{CF}_2\text{Cl} + \text{O}_2)/k(\text{CF}_2\text{Cl} + \text{Br}_2) = 1.4 \pm 0.1$$

$$k(\text{CF}_2\text{Cl} + \text{O}_2)/k(\text{CF}_2\text{Cl} + \text{Cl}_2) = 39 \pm 3$$

The ratios were independent of total gas pressure over the limited range of pressures used (23–51 Torr).

The absolute value of the $\text{CF}_2\text{Cl} + \text{O}_2$ rate constant is unknown, so these ratios cannot be used to obtain a value of k_4 . However, these two ratios can be combined to obtain the ratio of rate constants of the CF_2Cl reactions with Br_2 and Cl_2 , which can be compared with the results of our investigations:

$$k(\text{CF}_2\text{Cl} + \text{Br}_2)/k(\text{CF}_2\text{Cl} + \text{Cl}_2) = 28 \pm 3$$

Using the Arrhenius expression for k_4 in Table I and the Arrhenius expression for the $\text{CF}_2\text{Cl} + \text{Cl}_2$ rate constants reported earlier in our investigation of the kinetics of $\text{R} + \text{Cl}_2$ reactions,²⁴ $k(\text{CF}_2\text{Cl} + \text{Cl}_2) = 1.29 \times 10^{-12} \exp(-8 \text{ kJ mol}^{-1}/RT)$, one obtains 34 ± 10 for the ratio $k(\text{CF}_2\text{Cl} + \text{Br}_2)/k(\text{CF}_2\text{Cl} + \text{Cl}_2)$ at 293 K, which is in excellent agreement with the value derived above from the results of Tuckerman and Whittle.

In a series of experiments on the kinetics of the CF_3 radical, Amphlett and Whittle⁸ measured the relative rates of several pairs of reactions as a function of temperature and obtained Arrhenius expressions for ratios of functions of reaction rate constants including the following: (1) $k(\text{CF}_3 + \text{HCl})/[k(\text{CF}_3 + \text{CF}_3)]^{1/2}$, (2) $k(\text{CF}_3 + \text{Br}_2)/k(\text{CF}_3 + \text{HCl})$, and (3) $k(\text{CF}_3 + \text{Cl}_2)/k(\text{CF}_3 + \text{HCl})$. These expressions were converted to absolute rate constants with the use of a literature value of $k(\text{CF}_3 + \text{CF}_3)$. We have recalculated the Arrhenius expression for k_5 from the ratios (1) and (2) using a more recent determination of the $\text{CF}_3 + \text{CF}_3$ rate constant, reported by Selamoglu et al.²⁵ While these authors measured this rate constant only at 300 K, they also include a literature review and RRKM calculations that indicate that the $\text{CF}_3 + \text{CF}_3$ rate constant has a negligible temperature dependence at least up to 451 K, the temperature at which a numerical value is required for these calculations. (The new rate constant is a factor of 10 lower than that originally used by Amphlett and Whittle.) The result is $k_5 = 1.1 \times 10^{-12} \exp(-2.80 \text{ kJ mol}^{-1}/RT)$. This Arrhenius expression was used for a comparison with our results. Using this expression and extrapolating downward in temperature from 451 K, the lowest temperature of the Amphlett and Whittle study, to 399 K, the highest temperature of our investigation of reaction 5, yield $k_5(399 \text{ K}) = 4.7 \times 10^{-13}$. This value is a factor of 3 below our absolute determination of k_5 at this temperature (1.35×10^{-12}). The disagreement may in part be due to the need to use several different sources of information

to obtain the absolute value of k_5 from the results of Amphlett and Whittle. However, it is worth noting that the redetermined Arrhenius expression for the $\text{CF}_3 + \text{Cl}_2$ reaction obtained by using ratios (1) and (3) from this same investigation by Amphlett and Whittle is in complete agreement with the Arrhenius expression for this reaction obtained from our absolute determinations of the rate constants of this reaction.²⁴

Amphlett and Whittle's experiments to determine k_5 involved two complicating features not present in their study of the $\text{CF}_3 + \text{Cl}_2$ reaction, which could have reduced the accuracy of the determination of k_5 . First, the study of the $\text{CF}_3 + \text{Br}_2$ reaction involved comparing rates of reactions with very different rate constants, more than a factor of 2000 apart. This situation required the determination of very different absolute product yields from the two reactions. Second, the reference reaction ($\text{CF}_3 + \text{HCl}$) produces Cl atoms, which would rapidly react with the Br_2 present and produce ClBr . Reaction of CF_3 with ClBr would yield additional CF_3Br , a product of one of the reactions whose relative rates were under study.

(B) *Patterns of Reactivity.* (1) *Common Trends in Kinetic Behavior.* We have now investigated several groups of exothermic metathesis reactions involving substituted methyl radicals, in particular, the reactions of these intermediates with HI ,^{26,27} HCl ,²⁸ and HBr ^{29,30} (H-atom transfer), with Cl_2 ,^{24,31,32} (Cl-atom transfer), and with Br_2 ¹ (Br-atom transfer). Common trends in reactivity exist among these reactions. They include the following:

(a) Substitution of H in the CH_3 radical with electron-donating groups (e.g., $-\text{CH}_3$) increases reactivity.

(b) Substitution of H in CH_3 with electron-withdrawing substituents (e.g., halogen atoms) reduces reactivity.

(c) Activation energies are low. If the reaction is sufficiently exothermic (typically if $\Delta H < -75 \text{ kJ mol}^{-1}$), the Arrhenius activation energy is near zero and is often a slightly negative number. This situation is particularly noticeable in the case of the $12 \text{ R} + \text{Br}_2$ reactions we have studied to date where the activation energies are essentially all negative (typically -2 to -3 kJ mol^{-1}). The exceptions are the reactions of the perhalogenated radicals with Br_2 (CF_3 and CCl_3) where activation energies are positive but small (6 kJ mol^{-1} in the case of the $\text{CCl}_3 + \text{Br}_2$ reaction³³).

(d) For the reactions that have no activation energies, reaction thermochemistry is not an important factor in determining reactivity differences. For example, the $t\text{-C}_4\text{H}_9 + \text{Br}_2$ (as well as the $t\text{-C}_4\text{H}_9 + \text{HI}(\text{HBr})$) rate constants are greater than those of the $\text{CH}_3 + \text{Br}_2$ (and $\text{CH}_3 + \text{HI}(\text{HBr})$) rate constants in spite of the fact that, in each case, the former reaction is less exothermic, typically by 35 kJ mol^{-1} . (This is also the case for the $\text{R} + \text{Br}_2$ rate constants,¹ which are all greater than the corresponding $\text{R} + \text{Cl}_2$ rate constants.^{24,31,32}) In each case, the latter reaction is more exothermic than the former by 5 – 30 kJ mol^{-1} .

(2) *Kinetic Model for $\text{R} + \text{Br}_2$ Reactions.* *Dipole-induced dipole interaction:* In the absence of potential energy barriers along the reaction coordinate, the role of long-range attractive forces in determining reactivity becomes prominent.^{1,34} In the case of $\text{R} + \text{X}_2$ reactions, $\text{X}_2 = \text{Cl}_2$ or Br_2 , the dominant attractive force must arise from dipole-induced dipole interactions. Two long-range charge distributions can be imagined in the vicinity of the transition state:

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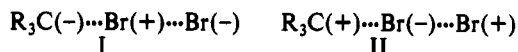
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(On the substituted methyl radical only the charge on the radical site is indicated.)

Only charge distribution I is consistent with the reactivity trends in reactions 1–7. Electron-donating methyl groups (R) increase charge density on the radical site above that which exists in CH₃ and lead to enhanced reactivity. When R is an electron-withdrawing halogen atom, the radical center is more positively charged than in CH₃ and reactivity is reduced. These trends lead to the conclusion that charge distribution I is responsible for the long-range attractive forces in these reactions. (A similar model was proposed and conclusion reached in our investigation of the kinetics of CR₃ + Cl₂ reactions.²⁴) Charge distribution II would be consistent only with reactivity trends opposite to those that are observed.

Support for the contention that charge distribution I stabilizes the reaction transition state in atom-transfer reactions comes from the study of Alfassi and Benson,³⁵ who showed that a simple parameter, the sum of the electron affinities of the end groups A and C in the atom-transfer reaction A + BC → A···B···C → AB + C (which, in a sense, provides a measure of the stability of configuration I above), can be used to correlate the activation energies of 50 reactions involving 15 different end groups. The simplest (and most successful) of the correlation functions used by Alfassi and Benson that associates the lowering of activation energies with high electron affinities of end groups in the A···B···C transition state is

$$E_a = a - bI$$

where E_a is the Arrhenius activation energy, a and b are constants, and I is the sum of the electron affinities of A and C. High electron affinities of the end groups lower activation energies. This is most apparent if one or both of the end groups is an halogen atom, which is the case in the R + X₂ (and R + HX) reactions under discussion here.

Useful Measure of the Dipole Moment of CR₃. The strength of the dipole-induced dipole interaction discussed above is determined by the magnitude of both the dipole moment of CR₃ and the polarizability of Br₂. In our previous investigation of the kinetics of CR₃ + HI reactions, we used a simple but very useful indicator of the influence of the dipole of CR₃ on the reaction rate constant, an indicator linearly related to the free energy of activation of the CR₃ + HI reactions.²⁷ The indicator is the simple scalar sum of the Pauling atomic electronegativities of the three substituents (R) in CR₃. That this simple sum provides a useful measure of the total withdrawal of valence electrons from the central carbon atom to the substituents was discovered by Thomas.³⁶ In his investigation he measured the binding energy of the carbon 1s electrons in halogen-substituted methanes and found that the shift in this energy (from that in CH₄) caused by the withdrawal of valence electrons from the central carbon atom was a linear function of the sum of the Pauling atomic electronegativities of the substituents.

This same indicator also provides a linear free energy relationship with the CR₃ + Br₂ rate constants (provided the rate constants for the reactions of fluorine-containing radicals are excluded (see below)). This is shown in Figure 3, where the CR₃ + Br₂ reaction rate constants, at a fixed temperature (298 K), are plotted on a semilog plot vs this indicator. The abscissa, Δelectronegativity, provides a scale with a value of 0 for CH₃. It is the sum of the electronegativities of the three groups R minus the electronegativities of three H atoms in the parent radical CH₃. In $k(298 \text{ K})$ is used as the measure of the free energy of activation at 298 K.

An electronegativity for the CH₃ group (R) on the Pauling scale was assigned in our investigation of the CR₃ + HI reactions.²⁷ In this earlier study, a single electronegativity was assigned to the methyl group (1.82) to yield compliance of the three alkyl

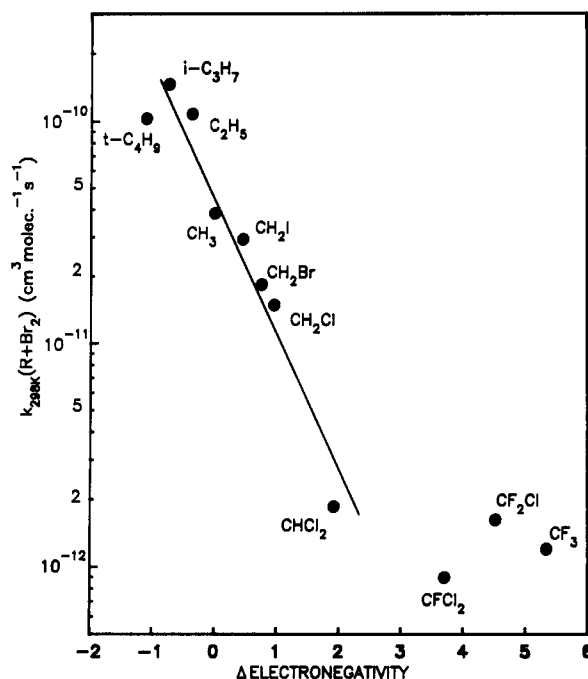


Figure 3. Plot of 298 K CR₃ + Br₂ rate constants vs Δelectronegativity. ΔElectronegativity is the difference between the sum of electronegativities of the three atoms or groups R in the substituted methyl radical and the sum of electronegativities of the three hydrogen atoms in the parent methyl radical. Electronegativities (eV) of F (3.98), Cl (3.16), Br (2.96), I (2.66), and H (2.20) are taken from Pauling,^{37,39} and that for CH₃ (1.82) is taken from Seetula and Gutman²⁷ (see text.)

radical + HI rate constants (where one to three of the groups R is -CH₃) with the linear free energy relationship established by the other R₃C + HI reaction rate constants (where R is H, Cl, and Br).

Electronegativity scales abound,^{37,38} first because the concept is not an easy one to define and second because the influence of electronegativity on physical-chemical properties depends strongly on molecular structure and overall chemical composition. That the earliest of these scales, the Pauling atomic electronegativities^{37,39} ("retrofitted" with an empirical group value for CH₃),²⁷ provides such a useful correlation for the reactions under discussion here is a welcome surprise. Sanderson's comment on electronegativities certainly applies here, "electronegativity is a relatively crude, makeshift, and oversimplifying concept that operates best in the realm of the practical".⁴⁰

Fluorine substitution has long defied compliance with correlations of properties based on electronegativity scales.^{41–43} Our results provide no exception to this observation. The rate constants for the reactions involving fluorine-containing radicals do not conform with the approximately linear free energy relationship in Figure 3. Explanations for such "anomalous" behavior have been offered.^{37,43} For example, Huheey^{37,44} has pointed out that intrinsic atomic electronegativities (such as those indicated by Pauling's definition) do not provide a quantitative indication of charge separation in molecules. He states that electronegativity is not a static property but depends on the magnitude of charge that has transferred to or from the atom or functional group of interest. Huheey has introduced the concept of "charge capacity"

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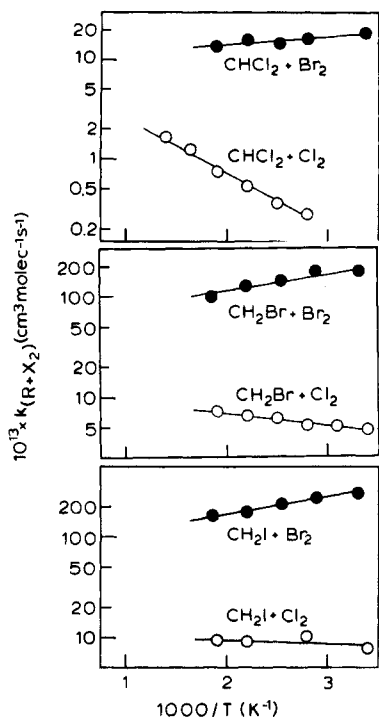


Figure 4. Comparison of $\text{CR}_3 + \text{Br}_2$ and $\text{CR}_3 + \text{Cl}_2$ rate constants for selected reactions. The $\text{CR}_3 + \text{Br}_2$ rate constants are from the current study, and those of the $\text{CR}_3 + \text{Cl}_2$ reactions are from a prior investigation.⁴⁸

to take into account the change in electronegativity with partial charge to provide a more quantitative measure of the actual charge transferred (ionic character) in bonding situations. The exceptionally small size of the fluorine atom has been cited as being at least partially responsible for its anomalously low charge capacity, low compared to what would be expected on the basis of a consideration of only the high intrinsic electronegativity of this element.^{43,44}

Influence of the polarizability of X_2 on the $R + X_2$ rate constants: The strength of dipole-induced dipole interaction depends on the polarizability of X_2 . The high reactivity of highly polarizable molecular reactants is very apparent in a comparison of rate constants of the $\text{CR}_3 + \text{Br}_2$ reactions with those of the corresponding $\text{CR}_3 + \text{Cl}_2$ reactions. Br_2 has a considerably higher molecular polarizability ($69.9 \times 10^{-25} \text{ cm}^3$) than does Cl_2 ($46.1 \times 10^{-25} \text{ cm}^3$).⁴⁵

Thermochemical arguments and arguments based on electron affinity of end groups would both predict that the rate constant of an $R + \text{Br}_2$ reaction should be lower than that of the corresponding $R + \text{Cl}_2$ reactions. The former is not only less exothermic than the latter (typically by 5–30 kJ mol^{-1}) but also has a leaving halogen atom with a lower electron affinity (the electron affinity of Br is 3.36 eV, and that of Cl is 3.61 eV).⁴⁶ Yet exactly the opposite behavior is always the case. The $\text{CR}_3 + \text{Br}_2$ rate constant is typically 5–20 times larger than that of the corresponding $\text{CR}_3 + \text{Cl}_2$ reaction at ambient temperature. Comparisons of some of these rate constants are shown in Figure 4.

The importance of the molecular polarizability of BC in stabilizing the $A \cdots B \cdots C$ transition state was characterized semi-quantitatively by Krech and McFadden.⁴⁷ They discovered a simple correlation between reaction activation energy and molecular polarizability for 12 homologous series of reactions:

$$E_a = C/\alpha_{BC}$$

This relationship was applicable even to some groups of reactions for which reaction thermochemistry would have predicted the opposite trend in reactivity. Significantly, these "exceptions" are series of reactions involving halogen molecules (X_2), $\text{O} + X_2$ and $\text{H} + X_2$.

This relationship of Krech and McFadden cannot be tested on the reactions studied here since where comparisons can be made, the sign of the activation energy often changes, that for the $\text{CR}_3 + \text{Cl}_2$ reaction being a small positive number and that for the $\text{CR}_3 + \text{Br}_2$ reaction being a small negative value (see Figure 4). Nevertheless, it is apparent that the higher polarizability of Br_2 (compared to Cl_2) accounts for its higher reactivity.

Studies of the reactions of polyatomic free radicals with halogen-containing diatomic molecules are continuing to develop a more quantitative understanding of the factors determining their reactivity.

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