J. Phys. Chem. 1990, 94, 3005-3008 3005

Kinetics of the Reactions of Alkyl Radicals (CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9) with Molecular Bromine

R. S. Timonen, J. A. Seetula, and D. Gutman*

Department of Chemistry, Catholic University of America, Washington, D.C. 20064

(Received: August 28, 1989; In Final Form: November 7, 1989)

The gas-phase kinetics of the reactions of four alkyl radicals (CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9) with molecular bromine have been studied over the temperature range 296–532 K. The reactions were isolated for quantitative study in a heatable tubular reactor coupled to a photoionization mass spectrometer. Radicals were homogeneously generated in the reactor by pulsed photolysis of suitable precursor molecules at 193 or 248 nm. The subsequent decays of the radical concentration in the presence of different Br_2 concentrations were monitored in time-resolved experiments. Rate constants were obtained at five temperatures. The Arrhenius expressions ($k = A \exp(-E/RT)$) that describe the temperature dependencies of the measured rate constants of the $R + Br_2 \rightarrow RBr + Br$ reactions are as follows [numbers in brackets are log $A/(\mathrm{cm^3\ molecule^{-1}\ s^{-1}})$, $E/(\mathrm{kcal\ mol^{-1}})$]: $R = CH_3$ [−10.70 (±0.08), −0.39 (±0.25)]; $R = C_2H_5$ [−10.58 (±0.11), −0.82 (±0.41)]; R = *i*-C_3H_7 [−10.62 (±0.11), −1.07 (±0.45)]; R = *t*-C_4H_9 [−10.70 (±0.11), −0.97 (±0.45)]. The trend in the measured rate constants and the results of prior studies of the dynamics of the $CH_3 + Br_2$ reaction indicate that the reactivity of $R + Br_2$ reactions is determined largely by long-range attractive forces and not by reaction thermochemistry.

Introduction

The current awareness that bromine-containing compounds of anthropogenic origin are increasing in concentration in the troposphere and stratosphere[1,2] is creating concern about the potential of these compounds to transport bromine to the stratosphere where the bromine can be released and participate in ozone-depleting chemical cycles.[3,4] Since some of these compounds are common fire retardants that have particularly long atmospheric lifetimes (e.g., CF_3Br and CF_2BrCl),[5] there is also now a renewed interest in understanding the chemistry of fire suppression by halogen-containing compounds in order to identify effective replacements that have short tropospheric lifetimes (and hence a reduced likelihood of diffusing to the stratosphere).

Bromine-containing compounds (RBr) are particularly effective fire suppressants.[6,7] This is due, at least in part, to free-radical mechanisms involving reactions of bromine released by these compounds which catalytically remove hydrogen atoms from the flame and thus prevent the H atoms from participating in the chain branching (and reaction accelerating) step $H + O_2 \rightarrow OH + O$. A representation of such a mechanism is as follows:[8,9]

$$H + HBr \rightarrow H_2 + Br \tag{A}$$

$$RBr + H \rightarrow R + HBr \tag{B}$$

$$R + Br_2 \rightarrow RBr + Br \tag{C}$$

$$Br + Br + M \rightarrow Br_2 + M \tag{D}$$

$$\text{net: } H + H + M \rightarrow H_2 + M$$

The development of detailed chemical kinetic models that can accurately predict fire suppression properties will require, among other things, knowledge of the rate constants of reactions A–D, particularly for the more abundant free radicals present in combustion processes. While information is currently available on the kinetics of reactions A and D,[10] essentially none is available on reactions B and C, particularly at elevated temperatures.

We have now begun an investigation of the kinetics of $R + Br_2$ reactions both because of the need for this information for modeling fire suppression processes and because of our continuing interest in the chemical behavior and thermochemistry of reactions between polyatomic free radicals and diatomic molecules containing halogen atoms.[11-15]

We have now investigated the kinetics of four reactions of alkyl radicals (R) with molecular bromine (reaction enthalpies in kcal mol^{-1} [16-18]):

$$CH_3 + Br_2 \rightarrow CH_3Br + Br \qquad \Delta H^\circ_{298} = -25 \tag{1}$$

$$C_2H_5 + Br_2 \rightarrow C_2H_5Br + Br \qquad \Delta H^\circ_{298} = -24 \tag{2}$$

$$i\text{-}C_3H_7 + Br_2 \rightarrow i\text{-}C_3H_7Br + Br \qquad \Delta H^\circ_{298} = -25 \tag{3}$$

$$t\text{-}C_4H_9 + Br_2 \rightarrow t\text{-}C_4H_9Br + Br \qquad \Delta H^\circ_{298} = -19 \tag{4}$$

The reactions were studied in a heatable tubular reactor coupled to a photoionization mass spectrometer. Rate constants were measured as a function of temperature. In the study of reaction 1, it was also possible to provide verification of the reaction mechanism. The results of this investigation are reported here.

While there have been several studies of bromination processes that have resulted in the determination of functions of[19-23] or ratios

---

(1) Lal, S.; Borchers, R.; Fabian, P.; Krüger, B. C. *Nature* **1985**, *316*, 135.

(2) Rasmussen, R. A.; Lhalil, M. A. K. *Geophys. Res. Lett.* **1984**, *11*, 433.

(3) McElroy, M. B.; Salawitch, R. J.; Wofsy, S. F.; Logan, J. A. *Nature* **1986**, *321*, 759.

(4) Yung, Y. L.; Pinto, J. P.; Watson, R. J.; Sander, S. P. *J. Atmos. Sci.* **1980**, *37*, 339.

(5) Atmospheric Ozone 1985. WMO Report No. 16; World Meteorological Organization: Geneva, 1985; Vol. 1; p 70.

(6) *Halogenated Fire Suppressants*; Gann, R. G., Ed.; ACS Symp. Ser. 16; American Chemical Society: Washington, DC, 1975.

(7) Fire Extinguishing Agents. Purdue Research Foundation and Department of Chemistry, Purdue University; Final Report for the period Sept 1, 1947–June 30, 1950; Contract W44-009 eng-507.

(8) Day, M. J.; Stamp, D. V.; Thompson, K.; Dixon-Lewis, G. *Symp. (Int.) Combust. [Proc.]* **1971**, *13*, 705.

(9) Westbrook, C. K. *Combust. Sci. Technol.* **1983**, *34*, 201.

(10) Baulch, D. L.; Duxbury, J.; Grant, S. J.; Montague, D. C. *J. Phys. Chem. Ref. Data* **1981**, *10* (Suppl. 1).

(11) Timonen, R. S.; Gutman, D. *J. Phys. Chem.* **1986**, *90*, 2987.

(12) Timonen, R. S.; Russell, J. J.; Sarzynski, D.; Gutman, D. *J. Phys. Chem.* **1987**, *91*, 1873.

(13) Russell, J. J.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nava, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3084.

(14) Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.

(15) Russell, J. J.; Seetula, J. A.; Senkan, S. M.; Gutman, D. *Int. J. Chem. Kinet.* **1988**, *20*, 759.

(16) Heats of formation for the alkyl radicals were taken from the assessment in ref 17. The remaining heats of formation were from ref 18.

(17) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.*, in press.

(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

(19) Kistiakowsky, G. B.; Van Artsdalen, E. R. *J. Chem. Phys.* **1944**, *12*, 469.

0022-3654/90/2094-3005$02.50/0

of[24] rate constants that have included an alkyl radical + Br_2 rate constant, there has been only one prior investigation that has resulted in an absolute determination. Kovalenko and Leone have monitored the infrared emission from vibrationally excited $CH_3Br^\ddagger$ produced by reaction 1 in time-resolved experiments.[25] From these measurements, they obtained k_1 at ambient temperature ((2.0 ± 0.4) × 10^{-11}). (All bimolecular rate constants reported here have the units cm^3 $molecule^{-1}$ s^{-1}.)

A significant amount of information has been obtained on the dynamics of reaction 1. Both the chemiluminescence study of Kovalenko and Leone[25] and the molecular beam studies of McFadden et al.,[26] Somssich et al.,[27] and Hoffman et al.[28] report evidence of a direct reaction with substantial translational energy release indicating "rebound dynamics", i.e., repulsion between reaction products in the exit valley of the reaction potential energy surface.

Experimental Section

Rate constants for reactions 1–4 were measured as a function of temperature. The experimental facility[29] as well as its use for kinetic studies of this type[11-15] has been described. Only a summary will be presented here. Pulsed unfocused 193- or 248-nm radiation from a Lambda Physik EMG 201MSC exciplex laser was collimated and then directed along the axis of a heatable 1.05-cm-i.d. coated Pyrex tubular reactor. Gas flowing through the tube at 5 m s^{-1} 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 (>99%). The free-radical precursor used for CH_3 was acetone (>99.5%), for CD_3 (used in one determination of the CD_3 + Br_2 rate constant) was iodomethane-d_3 (>99.5%), for C_2H_5 was bromoethane (>99%), for i-C_3H_7 was 2-bromopropane (>99%), and for t-C_4H_9 was 2,2,4,4-tetramethyl-3-pentanone (99%). These precursors, as well as the Br_2 (>99%), were obtained from Aldrich. Each was degassed by repeated freeze–pump–thaw cycles and used without further purification. He (Matheson, 99.995%) 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 gas 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 30000 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 R:

$$R + Br_2 \rightarrow RBr + Br \qquad (5)$$

$$R \rightarrow \text{heterogeneous loss} \qquad (6)$$

In all sets of experiments conducted to determine a reaction rate constant, tests were also conducted to ensure that radical–radical or radical–atom reactions had negligible rates compared to either reaction 5 or 6. Initial concentrations of R 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.

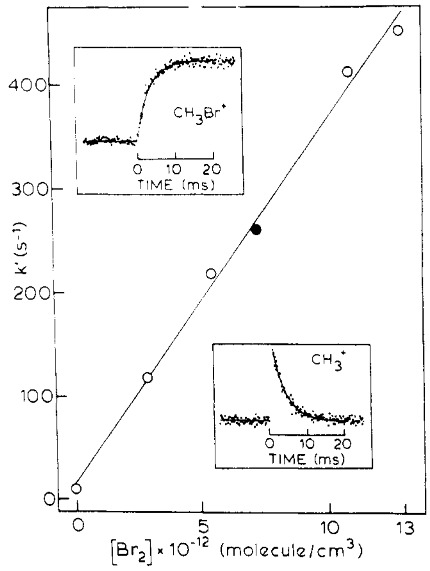

Figure 1. Plot of exponential decay constants of the CH_3^+ ion signals measured at 358 K vs [Br_2] (for additional conditions of experiments see Table I). Inserts are actual ion signal profiles of CH_3^+ and CH_3Br^+ recorded during one of the experiments whose results are plotted here ($[CH_3]_0 \approx 1 \times 10^{10}$ molecules cm^{-3}, [Br_2] = 7.6 × 10^{12} molecules cm^{-3}). The lines through the data are exponential functions fitted by nonlinear least-squares procedures. The first-order decay constant (k') for CH_3^+ is 262 (±8) s^{-1}, and the first-order growth constant for CH_3Br^+ is 275 (±8) s^{-1}.

The laser fluence was attenuated by using screens or quartz plates to reduce the photolysis of Br_2 to a negligible amount (<1%). The fact that radical decay constants in the presence of Br_2 did not depend on laser fluence also indicates that the limited amount of Br_2 photolysis that occurred did not interfere with the determination of R + Br_2 rate constants. Laser fluences used were typically below 10 mJ cm^{-2}.

The stable reactant, Br_2, was always in great excess over the initial concentration of R. Rate constants for reactions 1–4 were obtained from slopes of plots of the exponential radical decay constant, k' (from $[R] = [R]_0 \exp(-k't)$), vs [Br_2]. A representative ion signal decay profile and decay constant plot from one set of experiments to measure k_1 are shown in Figure 1. Also shown is the growth profile of the reaction product CH_3Br. Under the conditions of these experiments, the fact that the exponential growth constant of CH_3Br is the same as the decay constant of CH_3 is verification that CH_3Br is a primary reaction product.

The bromides produced by reactions 2–4 could not be monitored, preventing confirmation of the expected Br atom transfer mechanism. In the case of reactions 2 and 3, product detection was prevented by the use of these same bromides as the alkyl radical precursors. In the case of reaction 4, detection sensitivity for the expected product, t-C_4H_9Br, was extremely poor due to the predominance of fragmentation of the parent ion in the mass spectrometer even at the photoionization energies that could be used to observe this product, 10.2 and 11.6 eV.

The results obtained from all experiments are given in Table I. The rate constants obtained for reactions 1–4 are also shown on an Arrhenius plot in Figure 2.

UV photolysis produces the radicals of interest with an excess of internal energy. From what is known about vibrational deactivation of alkyl radicals,[30] it is likely that, under all our experimental conditions, this relaxation occurs rapidly (<0.5 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

---

(20) Anderson, H. C.; Van Artsdalen, E. R. *J. Chem. Phys.* **1944**, *12*, 479.

(21) Eckstein, B. H.; Scheraga, H. A.; Van Artsdalen, E. R. *J. Chem. Phys.* **1954**, *22*, 28.

(22) Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *28*, 301.

(23) Teranishi, H.; Benson, S. W. *J. Am. Chem. Soc.* **1963**, *85*, 2887.

(24) Evans, B. S.; Whittle, E. *Int. J. Chem. Kinet.* **1978**, *10*, 745.

(25) Kovalenko, L. J.; Leone, S. R. *J. Chem. Phys.* **1984**, *80*, 3656.

(26) McFadden, D. L.; McCullough, E. A.; Kalos, F.; Ross, J. *J. Chem. Phys.* **1973**, *59*, 121.

(27) Somssich, P.; Strein, K.; Schmiedel, H. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 407.

(28) Hoffman, S. M. A.; Smith, D. J.; Bradshaw, N.; Grice, R. *Mol. Phys.* **1986**, *57*, 1219.

(29) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5342.

(30) Donaldson, J. J.; Leone, S. R. *J. Phys. Chem.* **1987**, *91*, 3128.

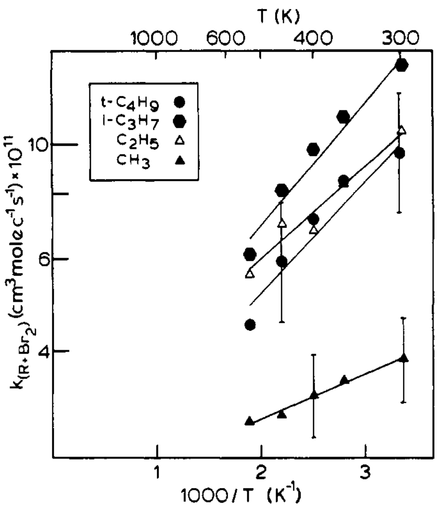

Figure 2. Semilog plot of measured R + Br_2 bimolecular rate constants vs 1000/*T*. The lines fitted through the plotted points by linear least squares were used to obtain the Arrhenius parameters for k_1–k_4 presented in Table I. Vertical bars are representative rate constant uncertainty limits: ±20% for the CH_3 + Br_2 rate constant and ±30% for the remaining R + Br_2 rate constants, k_2–k_4.

pressure was altered without changing the pressure of the reactants). These changes had no systematic effect on the value of the R + 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 possible for heterogeneous *bimolecular* reactions to occur in experiments of this sort. (The heterogeneous *first-order* reaction is taken into account in the data analysis.) In our experiments, such second-order processes, if important and unrecognized, would appear as an addition to the homogeneous bimolecular R + Br_2 rate constant. To test for the presence of such heterogeneous reactions, different wall coatings were used. They included Halocarbon Wax (in the case of reaction 1)[31] and poly(tetrafluoroethylene).[32] In an extensive preliminary study,[33] k_1–k_4 were also determined with boric acid as the wall coating. While coatings did reduce the first-order heterogeneous loss of R (i.e., reduced the value of k_6), they did not affect the value of the R + Br_2 rate constant. Therefore, we conclude that bimolecular heterogeneous R + Br_2 reactions are not significant processes under our experimental conditions.

The most probable error in each measured value of k_1 is ±20% while those of k_2–k_4 are ±30%. (Representative error bars indicating these uncertainties are shown in Figure 2.) 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 the data analysis procedures used to calculate k_1–k_4. The higher uncertainties in k_2–k_4 are a result of their high rate constants. It was necessary to use very low Br_2 concentrations in these experiments (2–8) × 10^{12} molecules cm^{-3}) as well as extremely low initial radical concentrations (10^9–10^{10} molecules cm^{-3}) to assure that [Br_2] was always in great excess. The greater difficulty of measuring low Br_2 flow rates and of monitoring very low radical ion signals increased the possible error of the experimental measurements. The Arrhenius expressions for k_1–k_4 were determined from the measured rate constants. They are given in Table I.

An additional assessment was made of the accuracy of the temperature dependencies of each rate constant (expressed by an Arrhenius activation energy). This latter assessment takes into account the temperature range of the study, the random error in each rate constant determination, and the realization that most possible systematic errors would have little effect on the determination of Arrhenius activation energies.

TABLE I: Conditions and Results of Experiments To Measure Rate Constants of the Reactions of Alkyl Radicals with Molecular Bromine

T,[a] K	10^{-16}[He], molecules cm^{-3}	10^{-12}[Br_2], molecules cm^{-3}	k_w, s^{-1}	wall coating material[b]	$10^{11}k$, cm^3 molecule^{-1} s^{-1}
CH_3 + Br_2 Reaction					
296	4.82	5.75–11.3	7.3	HW	4.03
297	4.81	3.75–10.7	9.9	PTFE	3.98
298	14.8	3.26–11.4	9.6	PTFE	3.62
358	4.68	2.91–12.9	9.8	HW	3.51
358	4.68	4.30–12.4	9.6	PTFE	3.50
399	4.70	4.02–11.9	8.1	PTFE	3.29
456	4.74	2.62–11.4	14	PTFE	3.02
532	4.78	4.17–13.7	18	PTFE	2.93
k_1 = 2.0 (±0.4) × 10^{-11} exp[0.39 (±0.25) kcal mol^{-1}/*RT*]					
CD_3 + Br_2 Reaction					
298	4.79	2.79–8.17	8.8	PTFE	4.49[c]
C_2H_5 + Br_2 Reaction					
298	4.80	2.32–4.80	21	PTFE	9.90
298	14.8	1.98–4.56	24	PTFE	11.3
358	4.69	3.17–6.73	19	PTFE	8.33
399	4.70	3.05–7.97	20	PTFE	6.80
456	4.71	3.04–7.38	15	PTFE	7.00
532	4.78	4.17–8.26	22	PTFE	5.61
k_2 = 2.6 (±0.8) × 10^{-11} exp[0.82 (±0.41) kcal mol^{-1}/*RT*]					
i-C_3H_7 + Br_2 Reaction					
298	4.81	2.11–3.25	77	PTFE	14.1
299	14.9	2.01–3.10	123	PTFE	14.1
358	4.67	2.02–3.85	57	PTFE	11.2
399	4.70	2.38–4.89	42	PTFE	9.71
456	4.71	2.43–6.54	33	PTFE	8.09
532	4.79	3.05–8.15	36	PTFE	6.11
k_3 = 2.4 (±0.7) × 10^{-11} exp[1.07 (±0.45) kcal mol^{-1}/*RT*]					
t-C_4H_9 + Br_2 Reaction					
300	4.80	1.83–5.10	116	PTFE	9.21
300	14.8	1.68–4.60	159	PTFE	9.96
358	4.70	1.87–5.96	95	PTFE	8.45
399	4.68	2.13–6.28	75	PTFE	7.15
456	4.72	3.15–8.41	56	PTFE	5.92
532	4.78	2.11–8.09	45	PTFE	4.48
k_4 = 2.0 (±0.6) × 10^{-11} exp[0.97 (±0.45) kcal mol^{-1}/*RT*]					

[a] Temperature uncertainty: ±2 K (296–358 K), ±4 K (399–456 K), and ±5 K (532 K). [b] Wall coating materials used: HW (Halocarbon Wax) and PTFE (poly(tetrafluoroethylene)). [c] Radical produced by 248-nm photolysis (photolysis at 193 nm used in all other experiments).

The photoionization energies used in the mass spectrometer to detect reactants and products were as follows: 11.6–11.8 eV to detect CH_3Br and Br_2; 10.2 eV to detect CH_3, CD_3, and C_2H_5; and 8.9–9.1 eV to detect C_2H_5, *i*-C_3H_7, and *t*-C_4H_9.

Discussion

Comparisons with Other Rate Constant Determinations. Only k_1 has been determined in a prior investigation. Kovalenko and Leone obtained the value 2.0 (±0.4) × 10^{-11} at room temperature.[25] This value is in reasonable agreement with our determination at this temperature (298 K) obtained from the Arrhenius expression for k_1 in Table I, 3.8 (±0.8) × 10^{-11}. The uncertainty limits of the two determinations can virtually account for the difference in the two values.

Using a competitive method, Evans and Whittle have determined the ratio $R = k(CH_3{+}Br_2)/k(CH_3{+}Cl_2)$ between 321 and 472 K.[24] Near the middle of their temperature range (400 K) their value for this ratio is 15 (±1.5). Using our prior determination of the CH_3 + Cl_2 rate constant at 400 K (obtained from the Arrhenius expression for this reaction in ref 11) and the CH_3 + Br_2 rate constant at this temperature (from the Arrhenius expression for k_1 in Table I), one obtains the result R = 12 (±4), which is in very good agreement with the Evans and Whittle value. Agreement is also very good throughout the temperature range of the Evans and Whittle investigation, but it varies due to differences in the Arrhenius parameters for this ratio between those reported by Evans and Whittle [log R = 0.042 (±0.060) + 2.1

---

(31) Halocarbon Wax Corp., Hackensack, NJ.

(32) Teflon 852-200.

(33) Timonen, R. Ph.D. Thesis, University of Helsinki, 1988 (*Ann. Acad. Sci. Fenn., Ser. A2* **1988**, 218).

(±0.3) kcal mol^{-1}/RT] and those derived from our measured rate constants [log R = 0.6 (±0.2) + 0.9 (±0.7) kcal mol^{-1}/RT]. The values of R obtained from the two expressions agree exactly at 472 K and differ by 60% at 321 K.

Kinetics of the Reactions of Alkyl Radicals with Br_2. Each of the R + Br_2 reactions studied has a small negative activation energy (between −0.4 and −1.1 kcal mol^{-1}), indicating that there is no noticeable potential energy barrier along the reaction coordinate. The large values of the rate constants, k_1 to k_4, are consistent with a direct metathesis process of the repulsive type, the mechanism identified in the molecular beam investigations of reaction 1.[26-28] The insignificant secondary isotope effect observed for the CH_3 + Br_2 reaction at 298 K, $k(CD_3+Br_2)/k(CH_3+Br_2)$ = 1.16, is also in accord with this mechanistic picture.

Apparent negative activation energies could also have arisen in these experiments had undetected *bimolecular* R + Br_2 heterogeneous reactions been important because the relative importance of any heterogeneous processes of this sort would have been less at higher temperatures (where the degree of surface coverage by one or both reactants would be less). From our observations that the R + Br_2 rate constants are independent of the reactor wall coating used in the rate constant determinations (even when the coatings are chemically quite different), we have concluded that heterogeneous processes of this sort are not significant under our experimental conditions.

Kovalenko and Leone report an apparent enhancement in k_1 with increased translational energy of CH_3 which they state is due to a potential energy barrier along the reaction coordinate.[25] Our results do not support this explanation.

Hoffman et al.[28] indicate a small potential barrier in the entrance channel of the CH_3 + Br_2 reaction based solely on the fact that the value of k_1 reported by Kovalenko and Leone[25] corresponds to a thermally averaged cross section that is ≈1/10 that of the "hard-sphere cross section". Minor steric constraints in the dynamics of reaction 1 could also account for this difference.

All of the R + Br_2 reactions studied are very rapid processes, and differences in their rate constants are small. The four rate constants, k_1–k_4, have essentially the same Arrhenius A factor ($(2.0–2.6) \times 10^{-11}$). That difference which is most apparent, the lower rate constant of reaction 1 compared with those of reactions 2–4, is due to the slightly higher (less negative) value of its activation energy.

A general picture is emerging of the kinetics of *exothermic* atom-transfer reactions between alkyl free radicals and halogen-containing diatomic molecules. There is generally no potential energy barrier along the reaction coordinate (activation energies are negative), and reactivity frequently runs counter to expectation based on reaction thermochemistry, i.e., opposite to the direction predicted by the Evans–Polanyi relationship.[34] This behavior has now been observed in the following series of alkyl radical reactions: R + Cl_2,[11] R + HI,[17] R + HBr,[13,14] and now R + Br_2.

For these and other atom-transfer reactions involving halogen-containing diatomic reactants,[35,36] reactivity correlates best with properties that reflect the magnitudes of long-range attractive forces, particularly those associated with the stabilization of intermediate states having some form of charge separation. These properties include the polarizability of the radical,[35] the ionization potential of the free radical,[11,36] and the difference between the ionization potential of one reactant and the electron affinity of the other.[37] The fact that these forces can determine reactivity trends while other reaction properties (such as overall reaction thermochemistry) could have produced the opposite trend in reactivity attests to the importance of these long-range forces. For reactions 1–4, the small differences in reactivity that do exist are consistent with this same mechanistic picture. The larger, more polarizable alkyl radicals react more rapidly than does the smallest (CH_3). The ordering in reactivity ($k_1 < (k_2$ to k_4)) is not that expected when considering only the influence of reaction thermochemistry.

Additional studies of the R + Br_2 reactions are in progress to learn more about the kinetics of these reactions.

Acknowledgment. This research was supported by funds from the National Science Foundation, Chemistry Division, under Grant CHE-8996126. We thank Dr. Irene R. Slagle for her advice, help, and support. J.A.S. thanks the Natural Science Council of the Academy of Finland and the Finnish Cultural Foundation for fellowships. R.S.T. thanks the Maj and Tor Nessling Foundation for financial support.

Registry No. CH_3, 2229-07-4; C_2H_5, 2025-56-1; i-C_3H_7, 2025-55-0; t-C_4H_9, 1605-73-8.

---

(34) (a) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1333.
(35) Krech, R. H.; McFadden, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 8402.
(36) Loewenstein, L. M.; Anderson, J. G. *J. Phys. Chem.* **1985**, *89*, 5371.
(37) Loewenstein, L. M.; Anderson, J. G. *J. Phys. Chem.* **1987**, *91*, 2993.

Ammonia Activation by Sc^+ and Ti^+: Electronic and Translational Energy Dependence

D. E. Clemmer, L. S. Sunderlin, and P. B. Armentrout*,†

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 *(Received: August 30, 1989)*

The reactions of Sc^+ and Ti^+ with ammonia are studied as a function of translational energy in a guided ion beam tandem mass spectrometer. The effect of electronic energy for the Ti^+ reactions is also probed by varying the conditions for forming Ti^+. Excited doublet states of Ti^+ are found to be much more reactive than the a^4F ground and b^4F first excited states. Both metals form the MH^+, MNH^+, and MNH_2^+ products, while only Ti^+ forms MN^+. The results are consistent with reaction that occurs primarily through a covalently bound insertion intermediate, $H-M^+-NH_2$, having a singlet and doublet spin state for M = Sc and Ti, respectively. The reactivities of the different electronic states of the reactant ions can be explained by using spin conservation concepts. The thresholds for the cross sections of the endothermic reactions are interpreted to give the 298 K bond energies of $D^\circ(Sc^+-NH_2) = 3.69 \pm 0.07$ eV, $D^\circ(Sc^+-NH) = 5.16 \pm 0.10$ eV, $D^\circ(Ti^+-NH_2) = 3.69 \pm 0.13$ eV, $D^\circ(Ti^+-NH) = 4.83 \pm 0.12$ eV, and $D^\circ(Ti^+-N) = 5.19 \pm 0.13$ eV. The large bond strengths of the M^+-NH_2 and M^+-NH species indicate that the lone pair electrons on the nitrogen atom are involved in the metal–ligand bond.

Introduction

Recent results from our laboratory have compared the reactions of V^+ with ammonia[1] to those with methane.[2] We find that while the reaction mechanisms are similar, the energetics of these systems are significantly different. The similarities observed in

---

[†] NSF Presidential Young Investigator, 1984–1989; Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher–Scholar, 1988–1993.

(1) Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 208.
(2) Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 6178–6188.

0022-3654/90/2094-3008$02.50/0