at 1900 cm⁻¹, while the observed origin of the $\tilde{A}^1 A''$ state is at 12 274 cm⁻¹,⁵⁴ well below the C(¹D) + HCl entrance energy. Nevertheless, the participation of an abstraction mechanism cannot be ruled out and calculations are clearly needed to sort out the contributions of the different mechanisms.

V. Summary

The reactions of $C({}^{1}D)$ with H_{2} and HCl were studied using two-photon photolysis of $C_{3}O_{2}$ at 248 nm as the source of $C({}^{1}D)$. Both reactions give rise to products (CH, CCl) with high internal excitation. CCl is the major diatomic product in the $C({}^{1}D)$ + HCl reaction, even though the reaction channel yielding CH has comparable exothermicity.

The internal state distributions in the products can be rationalized by an insertion mechanism with short-lived carbene intermediates (i.e., CH_2 , CHCl). The initial, spin-allowed approach is along the \tilde{a}^1A_1 or \tilde{X}^1A' singlet surfaces of HCH(Cl), but the participation of higher singlet surfaces is also possible. The existence of low-lying triplet states, Renner-Teller pairs, Coriolis couplings, and large spin-orbit matrix elements provides many opportunities for subsequent surface crossings, aided by strong bending motions in the intermediate, and both singlet and triplet surfaces may participate in the reactions. The participation of surfaces of B₁ or A" symmetry in the reactions with H₂ and HCl, respectively, may account for the absence of significant Λ -doublet preferences in the CH(X²\Pi) product. In general, the insertion mechanism is analogous to the mechanism of the corresponding O(¹D) reactions, and calculations indicate that abstraction has a substantial barrier. In further analogy with O(¹D) reactions, the reactive intermediate is likely to be short-lived, and the large degree of product internal excitation derives from H–H or H–Cl repulsions. Better potential energy surfaces and dynamical calculations are clearly needed to aid in determining the importance of the different possible mechanisms.

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Registry No. C₃O₂, 504-64-3; C, 7440-44-0; H₂, 1333-74-0; HCl, 7647-01-0; CH, 3315-37-5; CCl, 3889-76-7; CH₃I, 74-88-4; Xe, 7440-63-3.

Temperature-Dependent Kinetics Studies of the Reactions $Br({}^{2}P_{3/2}) + H_{2}S \leftrightarrow SH + HBr$ and $Br({}^{2}P_{3/2}) + CH_{3}SH \leftrightarrow CH_{3}S + HBr$. Heats of Formation of SH and $CH_{3}S$ Radicals

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Time-resolved resonance fluorescence detection of $Br(^{2}P_{3/2})$ atom disappearance or appearance following 266-nm laser flash photolysis of $CF_2Br_2/H_2S/H_2/N_2$, $CF_2Br_2/CH_3SH/H_2/N_2$, $Cl_2CO/H_2S/HBr/N_2$, and $CH_3SSCH_3/HBr/H_2/N_2$ mixtures has been employed to study the kinetics of the reactions $Br(^2P_{3/2}) + H_2S \rightleftharpoons SH + HBr(1, -1)$ and $Br(^2P_{3/2}) + CH_3SH$ \Rightarrow CH₃S + HBr (2, -2) as a function of temperature over the range 273-431K. Arrhenius expressions in units of 10⁻¹² cm³ molecule⁻¹ s⁻¹ which describe the results are $k_1 = (14.2 \pm 3.4) \exp[(-2752 \pm 90)/T]$, $k_{-1} = (4.40 \pm 0.92) \exp[(-971 \pm 90)/T]$ $\pm 73)/T$], $k_2 = (9.24 \pm 1.15) \exp[(-386 \pm 41)/T]$, and $k_{-2} = (1.46 \pm 0.21) \exp[(-399 \pm 41)/T]$; errors are 2σ and represent precision only. By examining Br(${}^{2}P_{3/2}$) equilibration kinetics following 355-nm laser flash photolysis of Br₂/CH₃SH/H₂/N₂ mixtures, a 298 K rate coefficient of $(1.7 \pm 0.5) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ has been obtained for the reaction CH₃S + Br₂ \rightarrow CH₃SBr + Br. To our knowledge, these are the first kinetic data reported for each of the reactions studied. Measured rate coefficients, along with known rate coefficients for similar radical + H₂S, CH₃SH, HBr, Br₂ reactions are considered in terms of possible correlations of reactivity with reaction thermochemistry and with IP - EA, the difference between the ionization potential of the electron donor and the electron affinity of the electron acceptor. Both thermochemical and charge-transfer effects appear to be important in controlling observed reactivities. Second and third law analyses of the equilibrium data for reactions 1 and 2 have been employed to obtain the following enthalpies of feaction in units of kcal mol⁻¹: for reaction 1, $\Delta H_{298} = 3.64 \pm 0.43$ and $\Delta H_0 = 3.26 \pm 0.45$; for reaction 2, $\Delta H_{298} = -0.14 \pm 0.28$ and $\Delta H_0 = -0.65$ \pm 0.36. Combining the above enthalpies of reaction with the well-known heats of formation of Br, HBr, H₂S, and CH₃SH gives the following heats of formation for the RS radicals in units of kcal mol⁻¹: $\Delta H_{f_0}^{\circ}(SH) = 34.07 \pm 0.72, \Delta H_{f_{298}}^{\circ}(SH)$ = 34.18 ± 0.68 , $\Delta H_{1^{\circ}0}(CH_{3}S) = 31.44 \pm 0.54$, $\Delta H_{1^{\circ}298}(CH_{3}S) = 29.78 \pm 0.44$; errors are 2σ and represent estimates of absolute accuracy. The SH heat of formation determined from our data agrees well with literature values but has reduced error limits compared to other available values. The CH₃S heat of formation determined from our data is near the low end of the range of previous estimates and is 3-4 kcal mol⁻¹ lower than values derived from recent molecular beam photofragmentation studies.

Introduction

Accurate thermochemical information for free-radical intermediates is essential to analysis of reaction mechanisms in complex chemical systems. One experimental approach which can be employed to obtain thermochemical parameters for a radical R involves measurement of temperature-dependent rate coefficients for the pair of reactions $RH + R' \leftrightarrow R'H + R$; the ideal reaction pair for such a study is one where the heats of formation and absolute entropies of R', R'H, and RH are well characterized and where kinetic data for the two reactions can be obtained over the same temperature range.

In this paper we report the results of temperature-dependent kinetics studies of the following four reactions:

1.

$$Br(^{2}P_{3/2}) + H_{2}S \rightarrow SH + HBr$$
(1)

$$SH + HBr \rightarrow Br(^{2}P_{3/2}) + H_{2}S \qquad (-1)$$

$$Br(^{2}P_{3/2}) + CH_{3}SH \rightarrow CH_{3}S + HBr$$
(2)

$$CH_{3}S + HBr \rightarrow Br(^{2}P_{3/2}) + CH_{3}SH \qquad (-2)$$

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The kinetic results have been employed to derive the most precise (and hopefully the most accurate) values currently available for the heats of formation of SH and CH₃S, two radicals which are important intermediates in the oxidation of a number of atmospheric reduced sulfur compounds including H₂S, CH₃SH, CH₃SCH₃, and CH₃SSCH₃.^{1,2} To our knowledge there are no kinetics studies of any of the reactions 1, -1, 2, and -2 reported in the literature.

Experimental Technique

The experimental approach involved coupling reactant radical (i.e., Br, SH, CH₃S) production by laser flash photolysis of suitable precursors with time-resolved detection of ground state bromine atom disappearance or appearance by resonance fluorescence spectroscopy. A schematic diagram of the apparatus, as configured for bromine atom detection, can be found elsewhere.³ A description of the experimental methodology is given below.

A Pyrex-jacketed reaction cell with an internal volume of 150 cm³ was used in all experiments; a diagram showing the geometry of the reaction cell is published elsewhere.⁴ The cell was maintained at a constant temperature by circulating ethylene glycol (T > 298 K) or methanol (T < 298 K) from a thermostatically controlled bath through the outer jacket. A copper-constantan thermocouple with a stainless steel jacket was inserted into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment.

The reactant radicals Br, SH, and CH₃S were generated by 266-nm laser flash photolysis of CF_2Br_2 , Cl_2CO/H_2S , and CH_3SSCH_3 , respectively. In a few experiments Br atoms were generated by 355-nm laser flash photolysis of Br_2 . Third (355 nm) or fourth (266 nm) harmonic radiation from a Quanta Ray Model DCR-2 Nd:YAG laser provided the photolytic radiation. The laser could deliver up to 3×10^{16} photons per pulse at 266 nm and up to 1×10^{17} photons per pulse at 355 nm; the maximum repetition rate was 10 Hz and the pulse width was approximately 6 ns.

A bromine resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the bromine atoms produced photolytically or as a reaction product. The resonance lamp consisted of an electrodeless microwave discharge through about 1 Torr of a flowing mixture containing a trace of Br_2 in helium. The flows of a 0.2% Br_2 in helium mixture and pure helium into the lamp were controlled by separate needle valves, thus allowing the total pressure and Br₂ concentration to be adjusted for optimum signal-to-noise ratio. Radiation was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell, the lamp output passed through a flowing gas filter containing 50 Torr cm of methane in nitrogen. The methane filter prevented radiation at wavelengths shorter than 140 nm (including impurity emissions from excited oxygen, hydrogen, nitrogen, and chlorine atoms) from entering the reaction cell, but transmitted the strong bromine lines in the 140-160-nm region.

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and resonance lamp beam and was imaged onto the photocathode of a solar blind photomultiplier with a CsI photocathode. The region between the reaction cell and the photomultiplier was purged with N_2 to prevent absorption of fluorescence photons by O_2 , H_2O , and other trace gases in the laboratory air. Signals were processed using photon counting techniques in conjunction with multichannel scaling. A large number of laser shots were typically averaged to obtain a bromine atom temporal profile with signal-to-noise sufficient for quantitative kinetic analysis. It is worth noting that

TABLE I: Parameters Relevant to in Situ Monitoring of H₂S, CH₃SH, and HBr

| species | λ, nm | light source ^a | λ isolation ^b | $10^{19}\sigma$, cm ² |
|--------------------|-------|---------------------------|----------------------------------|-----------------------------------|
| H ₂ S | 202.6 | A | M | 57.5° |
| - | 228.8 | В | BPF | 4.58 ^c |
| CH ₃ SH | 202.6 | Α | М | 87.1 (ref 67) |
| 5 | 213.9 | Α | М | 14.8° |
| HBr | 202.6 | Α | Μ | 10.2 (ref 24) |

^aA, zinc hollow cathode lamp; B, cadmium penray lamp. ^bM, $^{1}/_{4}$ -m monochromator; BPF, band-pass filter. ^cMeasured during the course of this investigation.

the resonance fluorescence detection scheme is sensitive to both ground-state $({}^{2}P_{3/2})$ and spin-orbit excited-state $({}^{2}P_{1/2})$ bromine atoms.

Tests were carried out to evaluate the sensitivity of the detection system toward O, H, Cl, CO, and Br using 266-nm laser flash photolysis of O_3/N_2 , CH_3SH/N_2 , Cl_2CO/N_2 , and $CF_2Br_2/H_2/N_2$ mixtures as the respective sources for O, H, Cl + CO, and Br (the reason for adding H₂ to the CF_2Br_2/N_2 mixture is discussed below). Production of ~1 × 10¹² O or H cm⁻³ resulted in no observable signal. Similarly, production of 1 × 10¹² Cl cm⁻³ + 5 × 10¹¹ CO cm⁻³ resulted in no observable signal. The detection sensitivity for Br atoms was sufficient to allow temporal profiles to be followed down to [Br] < 1 × 10⁹ atoms cm⁻³ with a reasonable level of signal averaging.

The emission spectrum of the bromine lamp (transmitted through the methane filter) was measured using a scanning vacuum UV monochromator (resolution ~ 0.05 nm) and the same solar blind photomultiplier as was employed in the kinetics experiments. In addition to the ${}^{4}P \rightarrow {}^{2}P$ and ${}^{2}P \rightarrow {}^{2}P$ bromine transitions, major impurity emissions were the ${}^{2}P \rightarrow {}^{2}P$, ${}^{2}P \rightarrow {}^{2}D$, and ${}^{2}D \rightarrow {}^{2}P$ transitions of atomic nitrogen at 174 nm (strong), 149 nm (strong), and 141 nm (weak), respectively, and the ${}^{3}P \rightarrow$ ³P transitions of atomic carbon at 166 nm (weak). The abovementioned sensitivity tests confirmed that $N(^{2}P)$, $N(^{2}D)$, and/or C(³P) were not produced in sufficient quantity in the reaction cell (by multiphoton photodissociation of N₂ or Cl₂CO) to be detected via fluorescence excited by impurity lamp emissions; if this were not the case, then fluorescence signal would have been observed following 266-nm laser flash photolysis of O_3/N_2 , CH_3SH/N_2 , and/or Cl_2CO/N_2 mixtures. The tests described above demonstrate quite conclusively that the detection system was specific to bromine atoms.

To avoid accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was in the range 1.5-4.5 cm s^{-1} and the laser repetition rate was varied over the range 1-10 Hz (5 Hz typical). Hence, no volume element of the reaction mixture was subjected to more than a few laser shots. Reactants and radical photolytic precursors were flowed into the reaction cell from bulbs (12 L volume) containing dilute mixtures in nitrogen while hydrogen and additional nitrogen were flowed directly from their storage cylinders. Except where specified in later discussions, all gases were premixed before entering the reactor. The concentrations of each component in the reaction mixtures were determined from measurements of the appropriate mass flow rates and the total pressure. The excess reactant (i.e., H_2S , CH₃SH, or HBr) concentration was also determined in situ in the slow flow system by UV photometry. Monitoring wavelengths, light sources, and absorption cross sections relevant to the photometric measurements are summarized in Table I. Since it was normally the case that more than one species in the reaction mixtures absorbed at the monitoring wavelength, the excess reactant concentration was usually measured upstream from the photolyte addition point; dilution factors required to correct the measured concentration to the actual reactor concentration never exceeded 1.1. Some experiments were carried out with the absorption cell positioned downstream from the reactor. Although the determinations of the excess reactant concentration were less precise in this experimental configuration (due to the presence in the absorption cell of more than one absorbing species), ex-

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perimental results were found to be independent of whether the absorption cell was positioned upstream or downstream relative to the reactor.

The gases used in this study had the following stated minimum purities: N_2 , 99.999%; H_2 , 99.999%; Cl_2 , 99.99%;⁵ HBr, 99.8%;⁵ H₂S, 99.5%;⁵ CH₃SH, 99.5%.⁵ Nitrogen and hydrogen were used as supplied while Cl₂, HBr, H₂S, and CH₃SH were degassed repeatedly at 77 K before being used to prepare mixtures with N_2 . It is worth noting that HBr gas samples taken directly from the storage cylinder contained significant (25-50%) levels of a noncondensible (at 77 K) impurity which was determined by weighing to be H_2 . The stated minimum purity of the CF_2Br_2 liquid sample was 99%. It was transferred under nitrogen into a vial fitted with a high vacuum stopcock and subjected to repeated freeze (77 K)-pump-thaw cycles before being used to prepare gaseous mixtures with N₂.

Results and Discussion

In studies of reactions 1 and 2 bromine atoms were generated by 266-nm laser flash photolysis of CF₂Br₂ ([CF₂Br₂] ranged from 0.2×10^{14} to 11×10^{14} molecules cm⁻³):

$$CF_2Br_2 + h\nu(266 \text{ nm}) \rightarrow Br + CF_2Br$$
 (3)

The CF₂Br₂ absorption cross section at 266 nm is approximately 8×10^{-20} cm^{2 6-8} while the quantum yield for Br production from CF_2Br_2 photolysis increases from unity at $\lambda \ge 248$ nm to around 2 at $\lambda = 193 \text{ nm.}^9$ Presumably, at $\lambda \ge 248 \text{ nm } \text{CF}_2\text{Br}_2$ photodissociates as indicated in reaction 3 with unit yield. To ensure rapid relaxation of any photolytically generated $Br({}^{2}P_{1/2})$, about 1 Torr of H_2 was added to the reaction mixture. The reaction

$$Br(^{2}P_{1/2}) + H_{2}(v=0) \rightarrow Br(^{2}P_{3/2}) + H_{2}(v=1)$$
 (4)

is known to be fast with $k_4 \approx 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁰ In studies of reaction -1, SH radicals were generated as follows:

$$Cl_2CO + h\nu(266 \text{ nm}) \rightarrow 2Cl + CO$$
 (5)

$$Cl + H_2S \rightarrow SH + HCl$$
 (6)

The Cl₂CO concentration was typically 1×10^{15} molecules cm⁻³ while the H₂S concentration was typically 1×10^{16} molecules cm⁻³. We have recently shown that $k_6 = 3.6 \times 10^{-11} \exp(210/T) \text{ cm}^3$ molecule⁻¹ s⁻¹¹¹ and $k_7 = 2.25 \times 10^{-11} \exp(-400/T)$ cm³ molecule⁻¹ s⁻¹.¹²

$$Cl + HBr \rightarrow Br(^{2}P_{J}) + HCl$$
 (7)

Based on the above rate coefficients, experimental conditions were maintained where >90% of the photolytically generated Cl reacted with H_2S and <10% reacted with HBr. The Cl₂CO absorption cross section at 266 nm is approximately 1×10^{-19} cm²,^{13,14} while the quantum yield for Cl₂CO photodissociation at 253.7 nm has been shown to be unity.¹⁵ Reaction 5 actually occurs in a two-step process involving a ClCO intermediate. However, even in the unlikely event that ClCO is produced without internal excitation, the CICO lifetime toward decomposition to Cl + CO is short compared to the experimental time scale (hundreds of microseconds) for SH removal.¹⁶ Reaction -1 was studied employing reaction mixtures containing no H₂ in order to avoid potential complications from the reaction $Cl + H_2 \rightarrow HCl + H$.

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Figure 1. Typical $Br({}^{2}P_{3/2})$ atom temporal profile observed in the studies of the $Br({}^{2}P_{3/2}) + RSH$ reactions (R = H, CH₃). Reaction: $Br({}^{2}P_{3/2})$ + CH₃SH. Experimental conditions: T = 332 K, P = 50 Torr, $[CF_2Br_2] = 8.1 \times 10^{14}$ molecules cm⁻³, $[CH_3SH] = 5.04 \times 10^{14}$ molecules cm⁻³, $[Br({}^{3}P_{3/2})]_{0} \sim 8 \times 10^{10}$ atoms cm⁻³, number of laser shots averaged = 2000. The inset shows the same data plotted as $\ln S$, versus time. The solid line in the inset is obtained from a least-squares analysis and gives the pseudo-first-order $Br(^{2}P_{3/2})$ decay rate shown in the figure.

In studies of reaction -2, CH₃S radicals were generated by 266-nm laser flash photolysis of dimethyl disulfide:

$$CH_3SSCH_3 + h\nu(266 \text{ nm}) \rightarrow 2CH_3S \tag{8}$$

Concentrations of CH₃SSCH₃ ranged from 2×10^{13} to 32×10^{13} molecules cm⁻³. The CH₃SSCH₃ absorption cross section at 266 nm is approximately 1×10^{-18} cm²,¹⁷ and the quantum yield for producing CH₃S is thought to be 2.¹⁸ Reaction mixtures employed to study reaction -2 did contain 1 Torr of added H₂.

All experiments were carried out under pseudo-first-order conditions with the stable reactant in large excess (factors of $10^{3}-10^{5}$) over the free-radical reactant. Concentrations of photolytically generated radicals were typically in the range (5-15) \times 10¹⁰ cm⁻³, although this experimental parameter was varied over a wide range (factor of 50). For all four reactions studied, observed kinetics were found to be independent of the photolytic precursor concentration(s) and the concentration of photolytically generated radicals. Observed kinetics were also found to be independent of the linear flow rate of the reaction mixture through the reactor and the photolysis laser repetition rate.

In the absence of side reactions which regenerate or deplete the $Br({}^{2}P_{3/2})$ atom concentration, the observed $Br({}^{2}P_{3/2})$ temporal profile following the laser flash in studies of reactions 1 and 2 would be described by the relationship

$$\ln (S_0/S_i) = \ln \{ [Br(^2P_{3/2})]_0 / [Br(^2P_{3/2})]_i \} = (k_i[R_iSH] + k_9)t = k't \quad (i = 1 \text{ or } 2, R_1 = H, R_2 = CH_3)$$
(I)

In the above relationship, S_0 and S_t are the signal levels immediately after the laser fires and at some later time t, $[Br({}^{2}P_{3/2})]_{0}$ and $[Br({}^{2}P_{3/2})]_{t}$ are the bromine atom concentrations corresponding to S_0 and S_i , and k_9 is the first-order rate coefficient for the process

$$Br({}^{2}P_{3/2}) \rightarrow loss$$
 by diffusion from the detector field of view
and reaction with background impurities (9)

The bimolecular rate coefficients of interest, $k_i(P,T)$, are determined from the slopes of k' versus [R_iSH] plots. Observation of $Br({}^{2}P_{3/2})$ temporal profiles which are exponential (i.e., obey eq I), linear dependencies of k' on [R_iSH], and invariance of observed

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TABLE II: Summary of Kinetic Data for the Reaction $Br(^2P_{3/2})$ + $H_2S \rightarrow SH$ + HBr^{α}

| T | Р | no. of expts ^b | [H ₂ S] _{max} | range of k' | $k_1 \pm 2\sigma^c$ |
|-----|-----|---------------------------|-----------------------------------|---------------|---------------------|
| 319 | 100 | 6 | 456 | 10-138 | 2.65 ± 0.10 |
| 334 | 50 | 7 | 198 | 22-99 | 3.77 ± 0.29 |
| 341 | 100 | 6 | 550 | 12-229 | 4.44 ± 0.15 |
| 348 | 250 | 5 | 199 | 15-120 | 5.33 ± 0.42 |
| 351 | 50 | 7 | 197 | 23-135 | 5.23 ± 0.62 |
| 361 | 100 | 7 | 511 | 13-378 | 7.09 ± 0.18 |
| 362 | 50 | 10 | 137 | 28-121 | 6.95 ± 0.73 |
| 376 | 50 | 7 | 152 | 28-168 | 9.08 ± 0.48 |
| 388 | 50 | 11 | 149 | 30-212 | 12.0 ± 0.7 |
| 403 | 50 | 5 | 142 | 31-263 | 16.0 ± 1.0 |
| 417 | 50 | 5 | 157 | 34-333 | 19.0 ± 0.9 |
| 420 | 250 | 7 | 151 | 19-297 | 18.7 ± 0.8 |
| 423 | 100 | 8 | 492 | 13-1065 | 22.3 ± 0.7 |
| 431 | 50 | 5 | 122 | 40-350 | 25.1 ± 0.8 |

^aUnits are T(K); P(Torr); $[H_2S]$ (10¹⁴ molecules cm⁻³); $k'(s^{-1})$; k_1 (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). ^bExpt \equiv measurement of a single pseudofirst order Br(²P_{3/2}) decay rate. ^cErrors represent precision only.

TABLE III: Summary of Kinetic Data for the Reaction $Br(^{2}P_{3/2}) + CH_{3}SH \rightarrow CH_{3}S + HBr^{a}$

| - | | - | | | |
|-----|-----|---------------------------|-------------------------------------|-------------|---------------------|
| T | Р | no. of expts ^b | [CH ₃ SH] _{max} | range of k' | $k_2 \pm 2\sigma^c$ |
| 273 | 50 | 10 | 23.8 | 31-5310 | 2230 ± 50 |
| 297 | 200 | 5 | 14.9 | 42-4000 | 2640 ± 70 |
| 298 | 50 | 10 | 21.8 | 27-5390 | 2480 ± 90 |
| 332 | 50 | 7 | 9.78 | 27-2810 | 2830 ± 90 |
| 383 | 50 | 6 | 12.0 | 34-4120 | 3350 ± 80 |
| 409 | 50 | 10 | 9.86 | 40-3570 | 3590 ± 60 |
| 431 | 50 | 6 | 12.8 | 37-5060 | 3820 ± 50 |
| | | | | | |

^aUnits are T (K); P (Torr); [CH₃SH] (10¹⁴ molecules cm⁻³); k' (s⁻¹); k_2 (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). ^bExpt = measurement of a single psuedo-first-order Br(²P_{3/2}) decay rate. ^cErrors represent precision only.

kinetics to variations in laser photon fluence and photolyte concentration strongly suggest that reactions i and 9 are the only processes which affect the $Br(^{2}P_{3/2})$ time history, although reactions of $Br(^{2}P_{3/2})$ with impurities in the $R_{i}SH$ samples are not ruled out by the above set of observations. A typical $Br(^{2}P_{3/2})$ temporal profile and a typical k'versus [$R_{i}SH$] plot observed in our studies of reactions 1 and 2 are shown in Figures 1 and 2. Kinetic data for reactions 1 and 2 are summarized in Tables II and III.

In the absence of side reactions that remove or produce Br- $({}^{2}P_{3/2})$, the observed Br $({}^{2}P_{3/2})$ temporal profile following the laser flash in studies of reactions -1 and -2 would be described by the relationship

$$S_{t} = k_{a}C_{1}(k_{9} - k_{a})^{-1} \left[\exp(-k_{a}t) - \exp(-k_{9}t)\right] + C_{2} \exp(-k_{9}t)$$
(II)

In eq II, S_t and k_9 are as defined above, k_a is the pseudo-first-order rate coefficient for Br(${}^{2}P_{3/2}$) appearance, and the parameters C_1 and C_2 are defined as follows:

$$C_1 = \alpha [\mathbf{R}_i \mathbf{S}]_0 f \tag{III}$$

$$C_2 = \alpha \left[\operatorname{Br}({}^2\mathrm{P}_{3/2}) \right]_0 \tag{IV}$$

In the above equations $[\mathbf{R}_i \mathbf{S}]_0$ and $[\mathbf{Br}({}^2\mathbf{P}_{3/2})]_0$ are the radical concentrations after photolysis and (in the case of the SH + HBr study) reaction 6 have gone to completion, but before significant removal of $\mathbf{R}_i \mathbf{S}$ radical has occurred, f is the fraction of $\mathbf{R}_i \mathbf{S}$ radicals which are removed via a reaction which produces Br, and α is the proportionality constant which relates S_i to $[\mathbf{Br}({}^2\mathbf{P}_{3/2})]_i$. For the reaction systems of interest, we expect that

$$k_{\rm a} = k_{-i}[\rm HBr] + k_{10} \qquad (V)$$

$$f = k_{-i} [\text{HBr}] / k_a \qquad (\text{VI})$$

where i = 1 or 2, R = H for i = 1 and CH₃ for i = 2, and k_{10} is the rate coefficient for the following reaction(s)

 $R_i S \rightarrow$ first-order loss by processes which do not produce Br (10)



Figure 2. Typical plot of k'versus [RSH] observed in the studies of the $Br(^{2}P_{3/2}) + RSH$ reactions (R = H,CH₃). Reaction: $Br(^{2}P_{3/2}) + CH_{3}SH$. T = 332 K, P = 50 Torr. The solid line is obtained from a linear least-squares analysis and gives the bimolecular rate coefficient shown in the figure. The open circle is the data point obtained from the temporal profile shown in Figure 1.

A nonlinear least-squares analysis of each experimental temporal profile was employed to determine k_a , k_9 , C_1 , and C_2 . The bimolecular rate coefficients of interest, $k_{-i}(P,T)$ (i = 1, 2), were determined from the slopes of k_a versus [HBr] plots. It is worth pointing out that the accuracy with which k_a could be determined via the nonlinear least-squares fitting technique was quite good because it was always the case that $k_a \gg k_9$ and $C_1 \gg C_2$. It was also always the case that the intercepts of the k_a versus [HBr] plots were small compared to the k_a values measured; i.e., k_{10} was always slow enough to exert little or no influence on the precision of the measured bimolecular rate coefficients. Application of eq II for analysis of SH + HBr kinetic data requires that Cl conversion to SH and Br via reactions 6 and 7 is instantaneous on the time scale for SH removal; under our experimental conditions, reactions 6 and 7 were complete within a few microseconds while reaction -1 occurred on a time scale of several hundred microseconds.

Similar to the situation discussed above for the studies of reactions 1 and 2, observation of $Br({}^{2}P_{3/2})$ temporal profiles that obey eq II, linear dependencies of k_a on [HBr], and invariance of k_a to variation in laser photon fluence and photolyte concentration suggests that the $R_iS + HBr$ reaction and reaction 9 are the only processes other than possible impurity reactions which significantly affect the $Br({}^{2}P_{3/2})$ time history (once photolysis and Cl reaction with H₂S and HBr are complete). A typical $Br({}^{2}P_{3/2})$ temporal profile and typical k_a versus [HBr] plot observed in our studies of reactions -1 and -2 are shown in Figures 3 and 4. Kinetic data for reactions -1 and -2 are summarized in Tables IV and V.

As indicated in Tables II–V, pressure dependence studies were carried out for reactions 1, 2, and -2; as expected, no evidence for pressure-dependent rate coefficients was observed over the range investigated (30–300 Torr). Arrhenius plots for reactions 1, 2, -1, and -2 are shown in Figure 5. The solid lines in Figure 5 are obtained from linear least-squares analyses of the ln $k_i(T)$ versus T^{-1} data; these analyses give the following Arrhenius expression in units of cm³ molecule⁻¹ s⁻¹:

$$k_1 = (1.42 \pm 0.34) \times 10^{-11} \exp[(-2752 \pm 90)/T],$$

319-431 K

$$k_{-1} = (4.40 \pm 0.92) \times 10^{12} \exp[(-9/1 \pm 73)/7],$$

299-423 K

$$k_2 = (9.24 \pm 1.15) \times 10^{-12} \exp[(-386 \pm 41)/T],$$

273-431 K

$$k_{-2} = (1.46 \pm 0.21) \times 10^{-12} \exp[(-399 \pm 41)/T],$$

273-426 K

Errors in the above expressions are 2σ and represent precision only. On the basis of observed precision and consideration of possible

TABLE IV: Summary of Kinetic Data for the Reaction SH + HBr \rightarrow Br(²P₄) + H₂S^a

| T | Р | no. of expts ^b | [HBr] _{max} | range of k_a | range of k_9 | $k_{10} \pm 2\sigma^c$ | $k_{-1} \pm 2\sigma^c$ |
|-----|-----|---------------------------|----------------------|----------------|----------------|------------------------|------------------------|
| 299 | 100 | 7 | 161 | 590-2910 | 29-45 | 49 ± 106 | 176 ± 10 |
| 321 | 100 | 6 | 125 | 411-2980 | 24-35 | 64 ± 76 | 209 ± 8 |
| 341 | 100 | 5 | 153 | 626-4050 | 28-39 | 92 ± 140 | 253 ± 14 |
| 402 | 100 | 7 | 117 | 1100-4740 | 31-37 | 302 ± 286 | 385 ± 34 |
| 423 | 100 | 12 | 91.2 | 622-4330 | 23-43 | 112 ± 143 | 457 ± 22 |

^aUnits are T (K); P (Torr); [HBr] (10¹⁴ molecules cm⁻³); k_a , k_9 , k_{10} (s⁻¹); k_{-1} (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). ^bExpt = measurement of a single Br(²P_{3/2}) temporal profile. ^cErrors represent precision only.

| TABLE V: | Summary of | 'Kinetic Data i | for the Reaction | n CH ₃ S + HBr - | → Br(² P _J) + CH ₃ SH ^a |
|----------|------------|-----------------|------------------|-----------------------------|---|
|----------|------------|-----------------|------------------|-----------------------------|---|

| <i>T</i> | Р | no. of expts ^b | [HBr] _{max} | range of k_a | range of k_9 | $k_{10} \pm 2\sigma^c$ | $k_{-2} \pm 2\sigma^{c}$ |
|----------|-----|---------------------------|----------------------|----------------|----------------|------------------------|--------------------------|
| 273 | 100 | 10 | 77.9 | 261-2870 | 11-29 | 99 ± 114 | 347 ± 29 |
| 295 | 200 | 10 | 82.1 | 419-3360 | 17-61 | 247 ± 116 | 383 ± 25 |
| 297 | 30 | 11 | 72.4 | 334-2700 | 20-32 | 81 ± 50 | 363 ± 12 |
| 297 | 100 | 14 | 66.2 | 439-2570 | 10-19 | 56 ± 82 | 382 ± 20 |
| 297 | 300 | 10 | 69.4 | 436-2770 | 9-23 | -18 ± 130 | 385 ± 28 |
| 330 | 100 | 6 | 65.9 | 473-2970 | 14-20 | 49 ± 82 | 438 ± 21 |
| 366 | 100 | 7 | 56.4 | 252-2690 | 25-48 | 65 ± 26 | 468 ± 8 |
| 403 | 100 | 8 | 56.0 | 294-3120 | 30-37 | 55 ± 42 | 546 ± 12 |
| 426 | 100 | 12 | 54.7 | 287-3341 | 24-44 | 22 ± 77 | 592 ± 25 |

^a Units are T (K); P (Torr); [HBr] (10¹⁴ molecules cm⁻³); k_a , k_9 , k_{10} (s⁻¹); k_{-2} (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). ^b Expt = measurement of a single Br(²P_{3/2}) temporal profile. ^c Errors represent precision only.



Figure 3. Typical Br(${}^{2}P_{3/2}$) atom temporal profile observed in the studies of RS + HBr reactions (R = H,CH₃). Reaction: CH₃S + HBr. Experimental conditions: T = 330 K, P = 100 Torr, [CH₃SSCH₃] = 3.29 × 10¹³ molecules cm⁻³, [HBr] = 5.12 × 10¹⁵ molecules cm⁻³, [CH₃S]₀ ~ 1.2 × 10¹¹ molecules cm⁻³, number of laser shots averaged = 5000. The solid line is obtained from a nonlinear least-squares analysis and gives the following best fit parameters: $k_a = 2270 \text{ s}^{-1}$, $k_9 = 15 \text{ s}^{-1}$, C_1 = 7470, $C_2 = 396$.

systematic errors (see below), we estimate the absolute accuracy of each measured bimolecular rate coefficient to be $\pm 15\%$ for the Br($^{2}P_{3/2}$) + R_iSH reactions and $\pm 20\%$ for the R_iS + HBr reactions.

Reaction Mechanisms. One important question one can ask about reactions 1, -1, 2, and -2 concerns the identity of the reaction products. Can we be sure that $Br({}^{2}P_{3/2}) + R_{i}SH$ produces $R_{i}S + HBr$ with unit yield and that $R_{i}S + HBr$ produces $Br + R_{i}SH$ with unit yield? The answer to this question appears to be yes for reactions -1 and -2. We have investigated the possibility of adduct formation in the $Br({}^{2}P_{3/2}) + H_{2}S$ reaction and find no evidence for the occurrence of an addition reaction, even at temperatures as low as 190 K. Hence, it appears that reaction 1 must produce SH + HBr with unit yield. However, there are a number of possible channels via which reaction 2 could proceed:

$$Br(^{2}P_{3/2}) + CH_{3}SH \rightarrow CH_{3}S + HBr \qquad (2a)$$

--- ---

$$\rightarrow CH_2SH + HBr$$
 (2b)

$$\rightarrow$$
 CH₃ + HSBr (2c)

$$\rightarrow H + CH_3SBr \qquad (2d)$$

.....

$$\rightarrow$$
 SH + CH₃Br (2e)

$$\longrightarrow$$
 CH₃S(Br)H (2f)



Figure 4. Typical plot of k_a versus [HBr] observed in the studies of the RS + HBr reactions (R = H,CH₃). Reaction: CH₃S + HBr. T = 330 K, P = 100 Torr. The solid line is obtained from a linear least-squares analysis and gives the bimolecular rate coefficient shown in the figure. The open circle is the data point obtained from the temporal profile shown in Figure 3.



Figure 5. Arrhenius plots. Solid lines are obtained from least-squares analyses which yield the Arrhenius expressions given in the text.

The occurrence of reaction 2b seems unlikely since the C-H bond in CH₃SH is thought to be about 6 kcal mol⁻¹ stronger than the S-H bond.^{19,20} For the similar though considerably more exothermic reactions of Cl and OH radicals with CH₃SH, abstraction of a methyl hydrogen is known to be a very minor reaction channel;^{21,22} since channel 2b is probably significantly endothermic, the yield of CH_2SH from reaction 2 is probably smaller than the (very small) yields of CH₂SH from the reactions of Cl and OH with CH₃SH. Assuming the RS-Br bond strength to be 57 kcal mol⁻¹, i.e., intermediate between published estimates of the RS-Cl²³ and RS-I²⁰ bond strengths, reactions 2c and 2d are highly endothermic. Using the CH₃S and SH heats of formation derived from our data (see below) to calculate the enthalpy change for reaction 2c leads to the conclusion that this reaction is endothermic by 4.6 kcal mol⁻¹; assuming an A factor of 1×10^{-11} cm³ molecule⁻¹ s⁻¹ for k_{2e} and an activation energy equal to the endothermicity suggests that reaction 2e could contribute no more than 1% to the measured k_2 at 431 K and much less at lower temperatures. Recent unpublished experiments in our laboratory have obtained kinetic evidence for reversible adduct formation in the Br + CH₃SH reaction at temperatures below 235 K. A $T \ge 273$ K, the temperature range of interest for this study, our results suggest that the adduct lifetime is too short for its existence to be kinetically important.

As an experimental check on the above conclusions, experiments were carried out where $Br(^{2}P_{3/2})$ kinetics were observed following 355-nm laser flash photolysis of Br₂/CH₃SH/HBr/H₂/N₂ mixtures. To avoid complications from a heterogeneous dark reaction between Br₂ and CH₃SH, it was necessary to inject Br₂ into the gas flow just upstream from the reaction zone. Long-wavelength photolysis was necessary in order to completely avoid production of CH₃S and H via photodissociation of CH₃SH. Following $Br({}^{2}P_{3/2})$ production by the laser flash, the following reactions occur:

$$Br(^{2}P_{3/2}) + CH_{3}SH \rightarrow X^{*} + Y$$
 (2)

$$\mathbf{X}^{\bullet} + \mathbf{Br}_2 \rightarrow \mathbf{X}\mathbf{Br} + \mathbf{Br}(^2\mathbf{P}_J) \tag{11}$$

$$X^{\bullet} + HBr \rightarrow XH + Br(^{2}P_{J})$$
(12)

$$Br(^{2}P_{1/2}) + H_{2} \rightarrow Br(^{2}P_{3/2}) + H_{2}$$
(4)

 $Br({}^{2}P_{3/2}) \rightarrow loss$ by diffusion from the detector field of view and reaction with background impurities (9)

 $X^* \rightarrow$ first-order loss by processes which do not produce Br (13)

Assuming that all reactions are first order or pseudo first order and that $Br({}^{2}P_{1/2})$ deactivation to $Br({}^{2}P_{3/2})$ is instantaneous on the time scale for the occurrence of reactions 2, 11, and 12, the rate equations for the above reaction scheme can be solved analytically:

$$\begin{bmatrix} \mathbf{Br}({}^{2}\mathbf{P}_{3/2}) \end{bmatrix}_{t} / \begin{bmatrix} \mathbf{Br}({}^{2}\mathbf{P}_{3/2}) \end{bmatrix}_{0} = \\ \{(\mathcal{Q} + \lambda_{1}) \exp(\lambda_{1}t) - (\mathcal{Q} + \lambda_{2}) \exp(\lambda_{2}t) \} (\lambda_{1} - \lambda_{2})^{-1} \quad (\text{VII}) \end{cases}$$

where

$$\lambda_1 = 0.5\{(a^2 - 4b)^{1/2} - a\}$$
(VIII)

$$\lambda_2 = -0.5\{(a^2 - 4b)^{1/2} + a\}$$
(IX)

$$Q = k_{11}[Br_2] + k_{12}[HBr] + k_{13}$$
(X)

$$O + k_{2}[CH_{2}SH] + k_{2} = -(\lambda_{1} + \lambda_{2})$$
(XI)

$$b = k_9 Q + k_{13} k_2 [CH_3 SH] = \lambda_1 \lambda_2$$
(XII)

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Figure 6. Typical $Br(^{2}P_{3/2})$ temporal profile observed following 355-nm laser flash photolysis of $Br_2/CH_3SH/HBr/H_2/N_2$ mixtures. Experimental conditions: T = 298 K, P = 30 Torr, $[Br_2] = 5.3 \times 10^{12}$ molecules cm⁻³, [CH₃SH] = 3.50×10^{15} molecules cm⁻³, [HBr] = 2.99×10^{15} molecules cm⁻³, $[Br({}^{2}P_{3/2})]_{0} \approx 4 \times 10^{10}$ atoms cm⁻³, number of laser shots averaged = 10000. The solid line is obtained from a nonlinear least-squares analysis and gives the best fit parameters $Q = 2540 \text{ s}^{-1}, -\lambda_1$ = 67.1 s⁻¹, and $-\lambda_2 = 10250$ s⁻¹.

Observed $Br(^{2}P_{3/2})$ temporal profiles were fitted to the predicted double-exponential functional form (eq VII) using a nonlinear least-squares procedure to obtain values for λ_1 , λ_2 , and Q. The rate coefficient k_9 was directly measured and was always small (10-40 s⁻¹). Hence, the elementary rate coefficients k_2 and k_{13} could be obtained from the relationships

$$k_2 = -(Q + k_9 + \lambda_1 + \lambda_2) / [CH_3SH] \qquad (XIII)$$

$$k_{13} = (k_9 Q - \lambda_1 \lambda_2) / (Q + k_9 + \lambda_1 + \lambda_2) \qquad (\text{XIV})$$

Values for k_{13} were always found to be relatively small, ranging from 14 to 127 s⁻¹ for the 45 double-exponential decays which were analyzed. For a set of experiments where [HBr] is varied at constant (low) [Br₂], a plot of $(Q - k_{13})$ versus [HBr] should, according to eq X, be linear with slope = k_{12} and intercept = $k_{11}[Br_2]$. With the exception of CH₂SH, 298 K rate coefficients for reactions of all possible radicals X* with HBr are known and are significantly different from each other; in units of 10⁻¹³ cm³ molecule⁻¹ s⁻¹ the rate coefficients of interest are 1.7 for $X^* =$ SH (this work), 3.9 for $X^{\bullet} = CH_3S$ (this work), 30 for $X^{\bullet} = CH_3^{24}$ and 65 for $X^{\bullet} = H^{.25}$ Hence, determination of k_{12} as described above should provide strong evidence concerning the identity of X^{*}.

A typical $Br(^{2}P_{3/2})$ temporal profile observed following 355-nm laser flash photolysis of Br₂/CH₃SH/HBr/H₂/N₂ mixtures is shown in Figure 6, while typical plots of $(Q - k_{13})$ versus [HBr] are shown in Figure 7. The data in Figure 7 suggest that $k_{12}(298)$ K) $\approx 4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; considering the nature of the fitting procedure, we estimate the uncertainty in $k_{12}(298 \text{ K})$ to be $\pm 30\%$. This determination of $k_{12}(298 \text{ K})$ strongly supports the contention that the dominant reaction channel for the $Br(^{2}P_{3/2})$ + CH₃SH reaction is production of CH₃S + HBr. The intercepts of the plots in Figure 7 indicate that the $CH_3S + Br_2$ reaction is very fast, i.e., $k_{14} = (1.7 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To our knowledge there are no measurements of k_{14} reported in the literature.

$$CH_3S + Br_2 \rightarrow CH_3SBr + Br(^2P_J)$$
 (14)

However, very fast rate coefficients have recently been reported for the reactions of alkyl radicals²⁶ and SD radicals²⁷ with Br₂.

⁽¹⁹⁾ Dill, B.; Heydtmann, H. Chem. Phys. 1978, 35, 161.

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⁽²⁵⁾ Umemoto, H.; Wada, Y.; Tsunashima, S.; Takayanagi, T.; Sato, S. Chem. Phys. 1990, 143, 333.

⁽²⁶⁾ Timonen, R. S.; Seetula, J. A.; Gutman, D. J. Phys. Chem. 1990, 94, 3005.



Figure 7. Plots of $(Q - k_{13})$ versus [HBr]. Experimental conditions: T = 298 K; P (Torr) = (a) 100, (b) 30, (c) 30; [Br₂] (10¹² molecules cm⁻³) = (a) 2.15, (b) 3.25, (c) 5.3; [CH₃SH] (10¹⁵ molecules cm⁻³) = (a) 1.24, (b) 1.33, (c) 3.61. The lines are obtained from linear least-squares analyses; the slopes give the following values for $k_{12} \pm 2\sigma$ in units of 10^{-13} cm³ molecule⁻¹ s⁻¹: (a) 4.60 ± 0.19 , (b) 4.51 ± 0.26 , (c) 4.81 ± 0.28 ; the intercepts suggest a gas kinetic value for k_{14} . The filled square is the data point obtained from the temporal profile shown in Figure 6.

Reactivity in these systems seems to correlate with properties that reflect the strength of long-range attractive forces, particularly those associated with stabilization of transition states via charge separation. The highly polarizable nature of both CH₃S and Br₂, the low ionization potential of CH_3S (8.06 eV²⁸), and the large electron affinity of Br₂ ($\sim 2.55 \text{ eV}^{28}$) are electronic properties which contribute to the very fast rate of reaction 14.

Potential Systematic Errors. As discussed briefly above, a number of potential systematic errors in our kinetic measurements can be ruled out based on the observed invariance of $Br({}^{2}P_{3/2})$ temporal profiles to variations in laser photon fluence, photolyte concentrations, flow velocity through the reactor, and laser pulse repetition rate; these include contributions to $Br(^{2}P_{3/2})$ kinetics from radical-radical side reactions, from radical-photolyte side reactions, from reactions involving radicals which are produced by reactant photolysis (H and CH₃S from CH₃SH photolysis, for example) or from reactions involving stable products which build up in concentration with successive laser flashes. In situ measurements of stable reactant (i.e., H₂S, CH₃SH, HBr) concentrations greatly reduce another potential source of systematic error.

One type of kinetic interference which needs to be addressed is the potential contribution to measured rate coefficients from impurity reactions. The relatively unreactive nature of Br atoms makes it unlikely that impurity reactions were a problem in our studies of reactions 1 and 2. Gas chromatographic analyses of the H₂S and CH₃SH samples were carried out using a flame photometric detector to search for sulfur-containing impurities; none were observed, lending further confidence that impurity reactions were not a problem. The most likely impurity problem in our studies of reactions -1 and -2 is from Br_2 . Potential sources of Br₂ are impurity in the HBr sample, residual Br₂ (from Br recombination) not swept out of the reaction zone between laser flashes, and catalytic formation of Br2 from heterogeneous reactions of HBr (presumably on the metal surfaces of valves and fittings). As discussed above, reactions 14 and 15 are very fast (the 298 K rate coefficient for the SD + Br₂ reaction has recently been reported to be 9.8 \times 10⁻¹¹ cm³ molecule⁻¹ s^{-1 27}).

$$HS + Br_2 \rightarrow HSBr + Br(^2P_1)$$
(15)

(28) 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.

Since SH and CH₃S react with Br₂ several hundred times faster than with HBr, the HBr concentration must be several thousand times larger than the Br₂ concentration before Br₂ interference can be considered to be unimportant. To investigate the Br₂ interference problem, a 2-m absorption cell was positioned in the slow flow system downstream from the reaction cell and employed to monitor Br₂ photometrically (at 404.7 nm) with typical Cl₂CO/H₂S/HBr/N₂ or CH₃SSCH₃/HBr/H₂/N₂ mixtures flowing through the system. No absorption was observed (i.e., $I/I_0 > 0.998$) even at HBr levels as high as 1×10^{17} molecules cm⁻³. Since the Br_2 absorption cross section at 404.7 nm is about $6 \times 10^{-19} \text{ cm}^{2,17}$ these experiments suggest that [Br₂] < 0.0002[HBr].

Another potential systematic error in our studies of reactions -1 and -2 concerns the possibility that SH and CH₃S are produced in vibrationally or electronically excited states and do not relax much more rapidly than they react. The spin-orbit splittings in SH and CH₃S are 377 cm^{-1 29} and 257 cm⁻¹, ^{30,31} respectively, i.e., only slightly larger than the average collision energy at 298 K $(kT = 207 \text{ cm}^{-1} \text{ at } 298 \text{ K})$. Hence, extremely rapid equilibration of the SH and CH₃S spin orbit states via collisions with the nitrogen buffer gas can be safely assumed. It is known from infrared chemiluminescence experiments that much of the available exothermicity of the $Cl + H_2S$ reaction appears as vibrational excitation in the HCl product, but that the SH product is formed with little or no internal excitation.¹⁹ Furthermore, vibrational relaxation of SH by H_2S is expected to be a very efficient process due to the near resonance ($\Delta \tilde{\nu} \sim 40 \text{ cm}^{-1}$) between the SH vibrational frequency²⁹ and the S-H stretch frequencies in H_2S .³² Hence, it seems safe to conclude that SH was thermalized in our study of reaction -1. Black and Jusinski have studied the time dependence for populating the ground vibrational level of CH₃S following 248-nm pulsed laser photolysis of CH₃SSCH₃ in the presence of a number of inert collision partners.³³ They find that nearly all CH₃S is produced in excited vibrational levels, but that relaxation is very efficient. A phenomenological rate coefficient of 5.1×10^{-12} cm³ molecule⁻¹ s⁻¹ was measured for populating the ground vibrational level (from the unknown initial vibrational state distribution) via collisions with N_2 . Hence, under our experimental conditions (Table V), CH₃S relaxation times ranged from 0.02 to 0.2 μ s while CH₃S reaction times ranged from 300 to 4000 μ s.

As mentioned above, the SH + HBr experiments were carried out with no H₂ added to the reaction mixtures in order to avoid potential complications from the $Cl + H_2$ reaction. This variation in experimental conditions does, however, introduce a different possible complication. As mentioned in the Experimental Section, the resonance fluorescence detection technique is sensitive to both bromine atom spin-orbit states, and the relative sensitivies for detecting the two states are different and difficult to quantify. If $Br({}^{2}P_{1/2})$ was generated in significant quantity, and if its relaxation to $Br(^{2}P_{3/2})$ occurred on the same time scale as the SH + HBr reaction, then temporal profiles for appearance of the fluorescence signal would deviate systematically from the quantity we actually want to measure-the temporal profile for appearance of bromine atoms. Rate coefficients for deactivation of $Br({}^{2}P_{1/2})$ by N₂ and HBr are, in units of cm³ molecule⁻¹ s⁻¹, 2.5 × 10^{-15 34} and $\sim 1 \times 10^{-12,34,35}$ respectively. Hence for the N_2 and HBr levels employed (Table IV), any $Br({}^{2}P_{1/2})$ generated via HBr photolysis, via reaction 7, or via reaction -1, was deactivated to $Br({}^{2}P_{3/2})$ on a time scale which was faster by factors of 3-20 than the time scales for the occurrence of reaction -1. Although the rate coefficient for $Br({}^{2}P_{1/2})$ deactivation by H_2S does not appear to

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TABLE VI: Kinetic Parameters, Enthalpy Changes, and IP - EA Values for a Series of Hydrogen Transfer Reactions R + XH -> RH + X

| | | | kinetic parameters ^a | | | | electronic properties ^c | |
|-------------------|-------------------|-----|---------------------------------|----------|----------------------------|-----------------------|------------------------------------|----------------|
| R | Х | A | Eact | k(298 K) | ref | $-\Delta H_{298}{}^b$ | $\overline{IP(R)} - EA(XH)$ | IP(XH) - EA(R) |
| Br | HS | 140 | 5.5 | 0.013 | TW^d | -3.6 | 10.70 | 7.08 |
| Cl | HS | 360 | -0.4 | 710 | 11 | 11.9 | 11.86 | 6.83 |
| ОН | HS | 60 | 0.15 | 47 | 68 | 28.0 | 12.57 | 8.62 |
| Br | CH ₃ S | 92 | 0.8 | 24 | TW^d | 0.1 | 11.6" | 6.08 |
| Cl | CHS | 120 | -0.3 | 2000 | 11 | 15.7 | 12.8 ^e | 5.82 |
| ОН | CHS | 99 | -0.7 | 320 | 68 | 31.8 | 13.5" | 7.61 |
| Cl | Br | 230 | 0.8 | 60 | 12 | 15.6 | 12.8 ^e | 8.04 |
| ОН | Br | 110 | 0 | 110 | 68 | 31.7 | 13.5 ^e | 9.83 |
| SH | Br | 44 | 1.9 | 1.8 | $\mathbf{T}\mathbf{W}^{d}$ | 3.6 | 10.2 ^e | 9.36 |
| CH ₃ S | Br | 15 | 0.8 | 3.9 | $\mathbf{T}\mathbf{W}^{d}$ | -0.1 | 7.9 ^e | 9.78 |
| CH ₃ | Br | 14 | -0.5 | 32 | 24 | 17.8 | 9.6° | 10.5 |
| C,H, | Br | 13 | -1.1 | 83 | 24 | 13.7 | 7.9° | 10.7 |
| t-Č₄H, | Br | 11 | -1.9 | 270 | 24 | 8.9 | 6.5 ^e | 11.0 |

^a Units for A and k(298 K) are 10^{-13} cm^3 molecule⁻¹ s⁻¹ and units for E_{act} are kcal mol⁻¹. ^b Units are kcal mol⁻¹; values are computed using heats of formation from this work (SH and CH₃S), ref 24 (CH₃, C₂H₅, t-C₄H₉), ref 28 (*i*-C₄H₁₀), and ref 68 (all others). ^c Units are electronvolts; ionization potentials and electron affinities taken from ref 28. ^dTW = this work. ^eThe unknown (but presumably very small) EA(XH) is assumed to be 0.2 eV.

be known, it appears likely (based for example on analogy with the known fast rate for $Br(^{2}P_{1/2})$ deactivation by $H_{2}O^{36}$) that $H_{2}S$ levels of 1×10^{16} molecules cm⁻³ were sufficient to contribute significantly to the overall rate of $Br({}^{2}P_{1/2})$ deactivation

Comparison of Reaction Rates for a Series of Radical + H₂S, CH₃SH, HBr Reactions. To our knowledge, there are no previous kinetics studies of reactions 1, -1, 2,or -2 with which to compare our results. However, kinetic data are available for many "similar" reactions. Kinetic parameters, reaction enthalpies, and relevant electronic properties for a series of hydrogen-transfer reactions involving free-radical attack on H₂S, CH₃SH, and HBr are summarized in Table VI.

When one considers series of similar reactions such as those in Table VI, a correlation between the activation energy (in the exothermic direction) and the reaction exothermicity is often observed. Such correlations were clearly established by Evans and Polanyi in the 1930s³⁷ and are heavily documented in the Examination of Table VI, however, shows the literature.38 correlation between activation energy and reaction exothermicity to be rather poor. Only the small subset of reactions Cl, OH, SH + HBr appear to follow such a trend.

As mentioned above when considering the very fast rate observed for the $CH_3S + Br_2$ reaction, it is often possible to correlate reactivity with properties that reflect the strength of long-range attractive forces, particularly those associated with stabilization of transition states via charge separation. For some classes of reactions, reactivity is found to be strongly correlated with the parameter IP - EA, the difference between the ionization potential of one reactant and the electron affinity of the other reactant. Bayes and co-workers have observed that low values of IP - EA correlate with enhanced reactivity in the alkyl + O_2 , O_3 reactions.^{39,40} Gutman and co-workers have observed a similar reactivity trend for the reactions of alkyl radicals with Cl₂,⁴¹ Br₂,²⁶ HI,⁴² and HBr;⁴³⁻⁴⁵ recent work in our laboratory has confirmed the reactivity trend in the alkyl + HBr series²⁴ (Table VI). Anderson and co-workers have observed correlations between IP - EA and reactivity in reactions of OH and SD radicals with

- (38) see for example, Semenov, W. N. Some Problems in Chemical Kinetics and Reactivity, Princeton University Press: Princeton, NJ, 1958.
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halogen molecules^{27,46} and in the reactions of Br, Cl, F, O, N, and OH radicals with ClNO⁴⁷ and with O₃.⁴⁸ The property IP - EA has been found to correlate with both activation energies^{24,26,42-48} and A factors.³⁹⁻⁴¹ As discussed by Abbatt et al.,⁴⁷ the barrier (i.e., activation energy) to reaction can be lowered through an interaction with low-lying ionic states. Presumably, the ionic character of the reaction potential energy surface in the region of the transition state is enhanced when IP - EA is relatively small; this ionic character presumably lowers the barrier by increasing the stability of charge separation at the transition state. The long-range electronic interaction which can occur when IP - EA is relatively low can result in formation of highly polar, loose transition states, an effect which leads to abnormally large Afactors.

Examination of the kinetic parameters and IP - EA values in Table VI leaves little doubt that ionic interactions exert an important influence on reactivity in the reactions considered. The low ionization potential of CH₃SH and high electron affinity of Cl allow these reactants to interact via a charge-transfer mechanism at large separation, thus leading to a very large A factor and very fast reaction rate. Differences in reactivity of H_2S and CH₃SH toward Cl and OH correlate very well with the value of IP(RSH) - EA(X), X = Cl,OH. For $Br(^{2}P_{3/2})$ reactions with H₂S and CH₃SH, however, the above correlation would predict faster rate coefficients than are actually observed as a result of the high electron affinity of Br. The reactions of Cl and OH with H₂S and CH₃SH, all of which are significantly exothermic, are barrierless processes. However, the thermoneutral $Br(^{2}P_{3/2})$ + CH₃SH reaction has an activation energy of 0.8 kcal mol⁻¹ and the endothermic $Br({}^{2}P_{3/2}) + H_{2}S$ reaction has an activation energy 1.9 kcal mol⁻¹ larger than the endothermicity. It seems clear that $Br({}^{2}P_{3/2})$ can form (very weakly bound) long-range polar complexes with H₂S and CH₃SH. However, the unfavorable thermochemistry of the Br + RSH reactions apparently leads to significant barriers for H atom transfer within the complexes, such that complex dissociation back to reactants can compete effectively with the H-transfer reaction.

Observed A factors for the radical + HBr reactions in Table VI follow the well-established trend of decreasing with increasing complexity of the reactant radical (i.e., atomic > diatomic > polyatomic).⁴⁹ As mentioned above, alkyl + HBr reactivity correlates well with the alkyl radical ionization potential, i.e., the lower the radical ionization potential, the faster the reaction; alkyl + HBr reactivity does not correlate with reaction exothermicity.

⁽³⁶⁾ Taatjes, C. A.; Lovejoy, C. M.; Opansky, B. J.; Leones, S. R. Chem. Phys. Lett. 1991, 182, 39.

⁽³⁷⁾ Evans, M. G.; Polanyi, M. Trans. Faraday Soc. 1938, 34, 11.

⁽⁴⁶⁾ Loewenstein, L. M.; Anderson, J. G. J. Phys. Chem. 1985, 89, 5371. (47) Abbatt, J. P. D.; Toohey, D. W.; Fenter, F. F.; Stevens, P. S.; Brune,
W. H.; Anderson, J. G. J. Phys. Chem. 1989, 93, 1022.
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^{1988, 20, 131.}

⁽⁴⁹⁾ see for example, Johnston, H. S. Gas Phase Reaction Rate Theory; Ronald Press Co.: New York, 1966; Chapter 12.

TABLE VII: Thermochemical Parameters for the Reactions $Br(^{2}P_{3/2}) + H_{2}S \rightarrow SH + HBr$ (1) and $Br(^{2}P_{3/2}) + CH_{3}SH \rightarrow CH_{3}S + HBr$ (2)

| | | | ΔH , ^{<i>a</i>} ko | ΔH , ^{<i>a</i>} kcal mol ⁻¹ | | $\Delta S,^a$ cal mol ⁻¹ deg ⁻¹ | | |
|----------|----------|--------------|-------------------------------------|---|-----------------|---|--|--|
| reaction | reaction | <i>T</i> , K | 2nd law | 3rd law | 2nd law | 3rd law | | |
| | 1 | 360 | 3.54 ± 0.32 | 3.96 ± 0.21 | 2.33 ± 0.60 | 3.50 ± 0.15 | | |
| | | 298 | 3.46 ± 0.33 | 3.82 ± 0.17 | 2.04 ± 1.56 | 3.24 ± 0.12 | | |
| | | 0 | 3.08 ± 0.35 | 3.44 ± 0.19 | | | | |
| | 2 | 333 | -0.03 • 0.17 | -0.17 ± 0.32 | 3.67 ± 0.44 | 3.23 ± 0.53 | | |
| | | 298 | -0.08 ± 0.19 | -0.20 ± 0.28 | 3.48 ± 1.09 | 3.07 ± 0.51 | | |
| | | 0 | -0.59 ± 0.27 | -0.71 ± 0.36 | | | | |
| | | U | 0.57 ± 0.27 | 0.71 ± 0.50 | | | | |

^{*a*} Errors are 2σ and represent best estimates of absolute accuracy.

On the other hand, for the Cl, OH, and SH reactions with HBr, a reasonable correlation of activation energy with reaction exothermicity is observed. These reactions apparently proceed through transition states which are not strongly influenced by ionic interactions. The thermoneutral $CH_3S + HBr$ reaction appears to be an intermediate case. Unlike the alkyl + HBr reactions, the $CH_3S + HBr$ reaction does have a positive activation energy. However, the barrier is much smaller than one would predict based on the ΔH versus E_{act} trend observed for the Cl, OH, SH + HBr reactions. Apparently, the low ionization potential of CH₃S facilitates ionic interactions which reduce but do not eliminate the barrier.

SH and CH₃S Thermochemistry. From the Arrhenius parameters determined in this study we can obtain the enthalpy changes and entropy changes associated with reactions 1 and 2. One approach, the "second law method", employs the following relationships to obtain thermochemical parameters for reaction i:

$$\Delta H_i = E_i - E_{-i} \tag{XV}$$

$$\Delta S_i = R \ln \left(A_i / A_{-i} \right) \tag{XVI}$$

where A_i and E_i are the A factor and activation energy for reaction i. Thermochemical parameters for reactions 1 and 2 obtained from the second law analyses are tabulated in Table VII. The temperature, 360 K for reaction 1 and 333 K for reaction 2, is defined as the arithmetic mean of the T^{-1} ranges employed in the determinations of k_i and k_{-i} . Values for ΔH at 298 and 0 K were computed using heat capacity corrections obtained from the JA-NAF tables⁵⁰ for Br, HBr, SH, and H₂S, and calculated from available spectroscopic data for CH₃S^{30,31} and CH₃SH.^{32,51,52} Second law values for ΔS at 298 K were computed from the relationship

$$\Delta G_{298} = \Delta H_{298} - T \Delta S_{298} = RT \ln K_{eq}(298 \text{ K}) = RT \ln [k_{-i}(298 \text{ K})/k_i(298 \text{ K})] \text{ (XVII)}$$

Values for $k_i(298 \text{ K})$ and $k_{-i}(298 \text{ K})$ were computed from the Arrhenius expressions reported above.

An alternate procedure for obtaining thermochemical parameters is the "third law method" where the entropy change is calculated using standard statistical mechanical methods⁵³ and employed in conjunction with experimental values for $K_{eq}(T)$ to obtain ΔH_T (from eq XVII). Absolute entropies as a function of temperature were obtained from the JANAF tables⁵⁰ for Br, HBr, SH, and H_2S , and calculated from available spectroscopic data for $CH_3S^{30,31}$ and $CH_3SH^{32,51,52}$ Uncertainties in the third law ΔS values are estimated based on uncertainties in key structural parameters. For reaction 1, the calculated ΔS appears to be quite accurate. For reaction 2, a significant uncertainty in the calculated ΔS arises from uncertainty in the frequency of the doubly degenerate ν_6 mode of CH₃S, which was recently assigned a value of 586 cm⁻¹ by Lee and Chiang;³¹ we "guesstimate" the error in this assignment to be ± 100 cm⁻¹. In units of cal mol⁻¹

deg⁻¹, the 298 K entropies of SH and CH₃S used in our third law determinations are 46.77 and 58.32, respectively. Results of the third law determinations are summarized in Table VII.

The analysis presented above is based on the idea that reactions -1 and -2 are the reverse of reactions 1 and 2. In the case of reactions 1 and 2 we know that the reacting bromine atom was in the ${}^{2}P_{3/2}$ ground state because sufficient H₂ was present in the reaction mixtures to instantaneously (on the time scale for Br reaction) deactivate any photolytically generated $Br(^{2}P_{1/2})$. Hence, the reverse reactions we wish to determine the rates of are

$$SH + HBr \rightarrow H_2S + Br(^2P_{3/2})$$
 (-1a)

$$CH_3S + HBr \rightarrow CH_3SH + Br(^2P_{3/2})$$
 (-2a)

Our method, however, actually measures $k_{-1} = k_{-1a} + k_{-1b}$ and $k_{-2} = k_{-2a} + k_{-2b}$ where reactions -1b and -2b are the channels producing $Br(^{2}P_{1/2})$:

$$SH + HBr \rightarrow H_2S + Br(^2P_{1/2})$$
 (-1b)

$$CH_{3}S + HBr \rightarrow CH_{3}SH + Br(^{2}P_{1/2}) \qquad (-2b)$$

Clearly, if reactions -1 and/or -2 proceed exclusively or a significant fraction of the time via channels -1b and/or -2b, then we would be overestimating the rate of the true reverse reaction(s) and our reported enthalpy changes would be in error. Simple thermochemical arguments based on the measured activation energies for reactions 1 and 2 can be used to place reasonable upper limits on k_{-1b} and k_{-2b} . Our measured activation energy for reaction 1 is 5.5 kcal mol⁻¹. It is reasonable to assume that the activation energy for reaction -1a is greater than -1.0 kcal mol⁻¹. Since the bromine atom spin-orbit splitting is 10.5 kcal mol⁻¹, reaction -1b must be endothermic by at least 4.0 kcal mol⁻¹. Taking 1×10^{-11} cm³ molecule⁻¹ s⁻¹ as an upper limit A factor for reaction -1b and 4.0 kcal mol⁻¹ as a lower limit activation energy for reaction -1b leads to the result $k_{-1b}(299 \text{ K}) \le 1.2 \times$ $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k_{-1b}(423 \text{ K}) \le 8.6 \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹, i.e., $k_{-1b}/k_{-1} \le 0.068$ at 299 K and $k_{-1b}/k_{-1} \le 0.19$ at 423 K. We have repeated the second and third law analyses of the reaction 1 data assuming that the above upper limits were the correct values for k_{-1b} . Under this scenario, the second law ΔH values for reaction 1 which are given in Table VII would be increased by 0.29 kcal mol⁻¹ while the third law ΔH values for reaction 1 would be decreased by 0.09 kcal mol⁻¹. Our measured activation energy for reaction 2 is 0.8 kcal mol⁻¹. If we assume as above that the activation energy for reaction -2a is greater than -1.0 kcal mol⁻¹, then we are led to the conclusion that reaction -2b must be endothermic by at least 8.7 kcal mol⁻¹. Taking 1 $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ as an upper limit A factor for reaction -2b and 8.7 kcal mol⁻¹ as a lower limit activation energy for reaction -2b leads to the result $k_{-2b}(273 \text{ K}) \le 1.1 \times 10^{-18} \text{ cm}^3$ molecule⁻¹ s⁻¹ and $k_{-2b}(426 \text{ K}) \le 3.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, i.e., $k_{-2b}/k_{-2} \le 3.1 \times 10^{-6}$ at 273 K and $k_{-2b}/k_{-2} \le 5.7 \times 10^{-4}$ at 426 K. Clearly, the contribution of channel -2b to our measured values for k_{-2} must be negligible over the entire temperature range investigated.

The enthalpy changes for reactions 1 and 2 determined in this study can be combined with the accurately known heats of formation of Br, HBr, H₂S, and CH₃SH^{28,50} (Table VIII) to obtain SH and CH₃S heats of formation. Values for $\Delta H_{f_0}^{\circ}(\mathbf{R}_i \mathbf{S})$ and

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TABLE VIII: Gas-Phase Heats of Formation

| species | $\Delta H_{\rm f}^{\rm o}{}_0$ | $\Delta H_{f}^{\circ}{}_{298}$ | ref |
|-----------------------------------|--------------------------------|--------------------------------|-----------|
| Н | 51.634 ± 0.001 | 52.103 ± 0.001 | 50 |
| S | 65.662 ± 0.060 | 66.200 ± 0.060 | 50 |
| Br | 28.184 ± 0.014 | 26.735 ± 0.014 | 50 |
| HBr | -6.836 ± 0.060 | -8.710 ± 0.040 | 50 |
| H_2S | -4.203 ± 0.191 | -4.900 ± 0.191 | 50 |
| CH, | 35.62 ± 0.19 | 34.82 ± 0.19 | 50 |
| CH ₃ SH | -2.89 ± 0.14 | -5.47 ± 0.14 | 28 |
| CH ₃ SCH ₃ | -5.09 ± 0.12 | -8.96 ± 0.12 | 28 |
| CH ₃ SSCH ₃ | -1.63 ± 0.24 | -5.78 ± 0.24 | 28 |
| SH | 34.07 ± 0.72 | 34.18 ± 0.68 | this work |
| | | 33.3 ± 1.2 | 50 |
| | | 33.6 ± 1.1 | 57 |
| | 33.9 ± 1.5 | | 58 |
| CH₃S | 31.44 ± 0.54 | 29.78 ± 0.44 | this work |
| | | $29.4 \pm 2.1^{b,c}$ | 28 |
| | | 34.2 ± 2.0^{b} | 59 |
| | | 31.4 ± 2.0^{b} | 60 |
| | | $33.2 \pm 1.5^{b,c}$ | 61 |
| | | 30.5 ± 2.0 | 63 |
| | | ≥29.5 ± 2.0 | 20 |
| | 35.4 ± 1.5 | | 65 |
| | 35.5 ± 2 | | 58 |
| | 34.2 ± 1.5 | | 66 |

^a Units are kcal mol⁻¹. ^b These values are obtained by coupling the kinetic data of Colussi and Benson (ref 59) with different values (ranging from 44 to 49 kcal mol⁻¹) for the benzyl radical heat of formation. Critical review.

TABLE IX: Bond Strengths Derived Using the SH and CH₃S Heats of Formation Determined in This Study in Conjunction with Other Heats of Formation Given in Table VIII^a

| bond | D° ₀ | D° 298 | |
|------------------------------------|------------------|----------------------|--|
| S-H | 83.23 ± 0.78 | 84.12 ± 0.74 | |
| HS-H | 89.91 ± 0.91 | 91.18 ± 0.87 | |
| H ₃ C–SH | 72.58 ± 1.05 | 74.47 ± 1.01 | |
| | | $(75.0 \pm 1.3)^{b}$ | |
| H ₃ C–S | 69.84 ± 0.79 | 71.24 ± 0.69 | |
| | | $(71.7 \pm 1.0)^{b}$ | |
| H ₃ CS–H | 85.96 ± 0.68 | 87.35 ± 0.58 | |
| H ₃ CS-CH ₃ | 72.15 ± 0.85 | 73.56 ± 0.75 | |
| | | $(74.0 \pm 1.1)^{b}$ | |
| H ₃ CS-SCH ₃ | 64.51 ± 1.32 | 65.34 ± 1.00 | |
| | | | |

^a Units are kcal mol⁻¹. ^b Computed using $\Delta H_{f,298}(CH_3) = 35.3 \pm 0.5$ kcal mol⁻¹ as reported in ref 24.

 $\Delta H_{f^{\circ}_{298}}(\mathbf{R}_{i}\mathbf{S})$ are given in Table VIII. Simple averages of the second and third law enthalpies of reaction have been employed to obtain our reported R,S heats of formation; this approach seems reasonable since (a) estimated uncertainties in the second and third law determinations do not differ greatly and (b) the second and third law values for $\Delta H_{f}^{o}_{T}(\mathbf{R}_{i}\mathbf{S})$ agree to within a few tenths of a kcal mol⁻¹ for both SH and CH₃S. The reported uncertainties in $\Delta H_f^{\circ}(\mathbf{R},\mathbf{S})$ represent 2σ estimates of absolute accuracy; since the 2σ error estimates for the individual second and third law determinations are significantly larger than the deviation of the two determinations from their mean, we take the larger of the (second and third law) error estimates to be the error estimate for the mean. In the case of SH, we increase the uncertainty by an additional 0.1 kcal mol⁻¹ to account for the fact that reaction -1 could have a small but not negligible channel forming $Br(^{2}P_{1/2})$ (see above). Our estimated uncertainties in $\Delta H_{f}^{\circ}_{T}(\mathbf{R}_{i}\mathbf{S})$ of 0.44-0.72 kcal mol⁻¹ are substantially smaller than those reported previously (Table VIII). The SH or CH₃S heat of formation represents the least well-known parameter required for evaluation of a number of bond dissociation energies (BDEs); in Table IX we give values for these BDEs derived using our reported values for $\Delta H_1^{\circ}(\mathbf{R}, \mathbf{S})$ in conjunction with the other heats of formation given in Table VIII. For consistency, we employ the JANAF⁵⁰ value of 34.82 \pm 0.19 kcal mol⁻¹ for $\Delta H_{f,298}(CH_3)$ to derive H₃C-SH, H₃C-S, and H₃C-SCH₃ bond strengths. It should be pointed out, however, that combining our recent measurement of the $CH_3 + HBr$ rate coefficient with the literature value for the

Br + CH₄ rate coefficient leads to a value of 35.3 ± 0.5 kcal mol⁻¹ for $\Delta H_{f,298}(CH_3)$;²⁴ bond strengths derived using this value for the methyl heat of formation are given in parentheses in Table IX.

Values for $\Delta H_{f}^{o}_{T}(SH)$ reported in this study are compared with literature values in Table VIII. The current JANAF recommendations⁵⁰ are based on measurements of the SH ionization potential^{54,55} and the appearance potential of SH^+ from photoionization of H_2S .⁵⁶ Hwang and Benson have obtained a value for $\Delta H_{f,298}(SH)$ based on a study of the $I_2 + H_2S$ reaction at 555-595 K;⁵⁷ derivation of $\Delta H_{f,298}(SH)$ from their kinetic data required the assumption that the activation energy for the SH + HI reaction is 1 ± 1 kcal mol⁻¹. A value for $\Delta H_{f,0}(SH)$ has recently been obtained by Nourbakhsh et al. based on time-offlight measurements of CH₃ and SH photofragments from 193-nm photodissociation of CH₃SH in a supersonic molecular beam.⁵⁸ Within combined uncertainties, the results reported in this study agree with all three literature values mentioned above. However, the error limits in the present study are somewhat smaller than those reported previously.

Values for $\Delta H_1^{\circ}(CH_3S)$ reported in this study are compared with literature values in Table VIII. An early determination of $\Delta H_{f,298}(CH_3S)$, reported by Colussi and Benson,⁵⁹ involved studying the kinetics of benzylmethyl sulfide pyrolysis; their data analysis required knowledge of the benzyl radical heat of formation. A number of subsequent evaluations of $\Delta H_{f,298}(CH_3S)$ have appeared in the literature^{28,60,61} which involve reevaluation of Colussi and Benson's results based on different assumed values for $\Delta H_{f,298}$ (benzyl); the recommendation of Lias et al.,²⁸ which shows the best agreement with our results, is based on an assumed benzyl heat of formation of 49 kcal mol⁻¹, as recommended by Tsang.⁶² Janousek et al.⁶³ have measured the electron affinity of CH_3S and combined their result with gas-phase acidity data for CH_3SH^{64} to derive a value for $\Delta H_{f,298}(CH_3S)$ which agrees quite well with our findings. Shum and Benson²⁰ have studied the kinetics of the I_2 + CH₃SH reaction over the temperature range 476-604 K and obtain a lower limit value for $\Delta H_{f,298}(CH_3S)$ which is consistent with our findings. Hence, the value for $\Delta H_{f,298}(CH_3S)$ which we obtain from kinetics studies of reactions 2 and -2 seems to be consistent with (but more precise than) most earlier work, although uncertainties in the heat of formation of benzyl radical^{61,62} somewhat hinders the comparison. However, an interesting discrepancy exists between our results and the recent molecular beam photofragmentation studies of Nourbakhsh et al.^{58,65,66} These authors have obtained three independent measurements of $\Delta H_{10}(CH_3S)$ based on time-of-flight measurements of photofragments from 193-nm photodissociation of CH₃SH,⁵⁸ CH_3SSCH_3 ,⁶⁵ and CH_3SCH_3 ,⁶⁶ they report values for $\Delta H_{f,0}$ -(CH₃S) (with uncertainties of 1.5-2 kcal mol⁻¹) which are all 3-4

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kcal mol⁻¹ higher than the value of 31.44 ± 0.54 kcal mol⁻¹ obtained in this study. The error in our determination of k_2/k_{-2} needed to rationalize a 3-4 kcal mol⁻¹ increase in $\Delta H_{f,0}$ (CH₃S) is a factor of several hundred in the direction where k_2 would have to be slower or k_{-2} would have to be faster; errors of this magnitude seem unlikely.

Summary

Time-resolved resonance fluorescence detection of $Br(^{2}P_{3/2})$ disappearance following 266-nm laser flash photolysis of $CF_2Br_2/H_2S/H_2/N_2$, $CF_2Br_2/CH_3SH/H_2/N_2$, $Cl_2CO/H_2S/$ HBr/N₂, and CH₃SSCH₃/HBr/H₂/N₂ mixtures has been employed to study the kinetics of reactions 1, 2, -1, and -2 as a function of temperature. In units of 10^{-12} cm³ molecule⁻¹ s⁻¹, Arrhenius expressions which describe our results are $k_1 = (14.2)$ \pm 3.4) exp[(-2752 \pm 90)/T], $k_{-1} = (4.40 \pm 0.92) \exp[(-971 \pm$ 73)/T], $k_2 = (9.24 \pm 1.15) \exp[(-386 \pm 41)/T]$, and $\hat{k}_{-2} = (1.46)$ \pm 0.21) exp[(-399 \pm 41)/T]. By examining Br(²P_{3/2}) equilibration kinetics following 355-nm laser flash photolysis of Br₂/ $CH_3SH/H_2/N_2$ mixtures, a 298 K rate coefficient of (1.7 ± 0.5) $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ has been obtained for the CH₃S + Br₂ reaction. To our knowledge, these are the first kinetic data reported for each of the reactions studied. Comparison of A factors and activation energies for reactions 1, -1, 2, and -2 with known kinetic parameters for other radical + H₂S, CH₃SH, HBr hydrogen-transfer reactions suggests that both thermochemistry and electronic properties (i.e., IP - EA) exert important influences on observed reaction rates.

Second and third law analyses of the equilibrium data, i.e., k_1/k_{-1} and k_2/k_{-2} , have been employed to obtain the enthalpy changes associated with reactions 1 and 2. At 298 K, reaction 1 is endothermic by 3.64 kcal mol⁻¹ while reaction 2 is exothermic by 0.14 kcal mol⁻¹. Combining the experimentally determined enthalpies of reaction with the well-known heats of formation of Br, HBr, H₂S, and CH₃SH gives the following heats of formation for RS radicals in units of kcal mol⁻¹: $\Delta H_{f_0}^{\circ}(SH) = 34.07 \pm 0.72$, $\Delta H_{\rm f}^{\circ}{}_{298}(\rm SH) = 34.18 \pm 0.68, \ \Delta H_{\rm f}^{\circ}{}_{0}(\rm CH_{3}S) = 31.44 \pm 0.54;$ $\Delta H_{\rm f}^{\circ}_{298}(\rm CH_3S) = 29.78 \pm 0.44$; errors are 2σ and represent estimates of absolute accuracy. The SH heat of formation determined from our data agrees well with literature values but has reduced error limits compared to other available values. The CH₃S heat of formation determined from our data is near the low end of the range of previous estimates and is 3-4 kcal mol⁻¹ lower than values derived from recent molecular beam photofragmentation studies. 58,64,65

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Comparison of Heterogeneous and Homogeneous Electron-Transfer Rates for Some Nitroalkanes and Diketones

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Redox catalysis has been used to investigate the homogeneous electron-transfer reactions between the substrates (nitroalkane or diketone) and the reduced form of the catalyst, which was terephthalonitrile. The substrates were RNO₂ (R = Me, Et, *i*-Pr, and *t*-Bu) and RC(O)C(O)R (R = Me, Et, and *t*-Bu). The experiments were conducted in acetonitrile solvent at 298 K with three different electrolytes, R_4NClO_4 (R = Et, *n*-Bu, and *n*- C_7H_{15}). The effect of added water and alcohols (methanol, ethanol, and *s*-butanol) was investigated. Formal potentials and standard heterogeneous electron-transfer rate constants, k_s , were also determined. It was found that increasing the size of the cation of the electrolyte resulted in a decrease in k_s but did not affect the rate of the homogeneous electron-transfer reactions. The result is interpreted as a decrease in influence the homogeneous reaction. Addition of the hydroxylic solutes, S, caused diminution of both k_s and the rate constant for homogeneous electron transfer from the anion radical of the substrate to the catalyst. This result is discussed in terms of two models, viz., complexation or adduct formation between the anion radical and S or increasing solvation energy of the anion radical.

Introduction

Factors governing the rates of heterogeneous and homogeneous electron-transfer reactions continue to be of fundamental interest. It has recently been demonstrated¹ that the technique of homogeneous redox catalysis² can be used to determine rate constants for solution electron-transfer reactions between a catalyst redox couple and a substrate couple even when there are no irreversible chemical steps to drive the catalysis reaction. In this way, the rate constant for electron transfer from the radical anion of terephthalonitrile to 2-methyl-2-nitropropane was measured under a variety of conditions. From the known self-exchange rate constant for terephthalonitrile and its radical anion, the self-exchange rate constant for 2-methyl-2-nitropropane and its radical anion was estimated for the first time.

In this technique, mixtures of the catalyst (P) and the substrate (A) are investigated by cyclic voltammetry. The catalyst couple is chosen so that its formal potential, E° _{PO}, is close to that of the

$$\mathbf{A} + \mathbf{e} = \mathbf{B} \qquad E^{\mathbf{e}'}{}_{\mathbf{A}\mathbf{B}} \tag{1}$$

$$P + e = Q \qquad E^{\circ'}{}_{PQ} \tag{2}$$

$$A + Q \stackrel{\kappa_{f_{A}}}{\underset{k_{b}}{\leftarrow}} B + P \qquad \ln K_{3} = (F/RT)(E^{\circ'}{}_{AB} - E^{\circ'}{}_{PQ}) \qquad (3)$$

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