Kinetics and Thermochemistry of R + HBr \rightleftharpoons RH + Br Reactions: Determinations of the Heat of Formation of C₂H₅, /-C₃H₇, sec-C₄H₉, and t-C₄H₉

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The reactions of alkyl radicals ($R = CH_3$, C_2H_5 , *i*- C_3H_7 , and *t*- C_4H_9) with HBr have been studied by excimer laser flash photolysis coupled with photoionization mass spectrometry. Rate constants were obtained in the following temperature ranges and provided Arthenius parameters for each reaction ($A/(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$, $E_a/(\text{kJ mol}^{-1})$): R = CH₃, 299–536 K ((-1.57 ± 0.26) × 10⁻¹², 1.6 ± 0.6); R = C₂H₅, 297–530 K ((1.70 ± 0.55) × 10⁻¹², -4.2 ± 1.2); R = *i*-C₃H₇, 298–530 K ((1.58 ± 0.38) × 10⁻¹², -6.4 ± 0.9); R = *t*-C₄H₉, 298–530 K ((1.37 ± 0.47) × 10⁻¹², -7.8 ± 1.4). R + HBr rate constants are approximately a factor of 2 higher than previously reported. The source of this disparity is explained. The kinetics of reverse reactions, Br + RH (R = C_2H_6 , C_3H_8 , $n-C_4H_{10}$, $i-C_4H_{10}$), have also been investigated using laser flash photolysis/resonance fluorescence methods. Rate constants were obtained in the following temperature ranges and provided Arrhenius parameters for each reaction (same units): $RH = C_2H_6$, 473–621 K ((2.35 ± 1.12) × 10⁻¹⁰, 53.3 ± 2.1); $RH = C_3H_8$, 476–667 K ((8.78) ± 3.00 × 10⁻¹¹, 36.0 ± 2.0 ; RH = *n*- $\tilde{C}_4\tilde{H}_{10}$, 447–625 K ((2.86 ± 0.90) × 10⁻¹⁰, 37.7 ± 2.0); RH = *i*- C_4H_{10} , 423–621 K $((1.61 \pm 0.60) \times 10^{-10}, 28.8 \pm 1.5)$. These results, combined with previously obtained kinetic information, were used in second- and third-law thermochemical calculations to obtain accurate determinations of the heats of formation of the C_2-C_4 alkyl radicals involved. Second- and third-law determinations agreed extremely closely (differences were under 1.3 kJ mol⁻¹). The heats of formation of the radicals thus obtained are in excellent agreement with values obtained from studies of dissociation/association equilibria, within 2.6 kJ mol⁻¹. Recommended alkyl-radical heats of formation (with uncertainties) at 298 K are provided that are based on an assessment of all the results of the current study and a review of other recent determinations (kJ mol⁻¹): C_2H_5 , 121.0 ± 1.5 ; $i-C_3H_7$, 90.0 ± 1.7 ; sec- C_4H_9 , 67.5 ± 2.2 ; $i-C_4H_9$, 51.3 ± 1.8 . Accurate determinations of carbon-hydrogen bond enthalpies (298 K) are provided that are based on these heats of formation (kJ mol⁻¹): primary C-H in C₂H₆ (422.8 ± 1.5); secondary C-H in C₃H₈ (412.7 ± 1.7) and in n-C₄H₁₀ (411.1 ± 2.2); tertiary C-H in *i*-C₄H₁₀ (403.5 \pm 1.8).

Introduction

Disparities in the heats of formation of the smaller alkyl radicals (R) derived from studies of different kinds of chemical equilibria have largely been reconciled. Until recently, investigations of equilibria involving hydrogen halides (HX)

$$\mathbf{R} + \mathbf{H}\mathbf{B}\mathbf{r} \rightleftharpoons \mathbf{R}\mathbf{H} + \mathbf{B}\mathbf{r} \tag{1}$$

$$\mathbf{R} + \mathbf{H}\mathbf{I} \rightleftharpoons \mathbf{R}\mathbf{H} + \mathbf{I} \tag{2}$$

have yielded lower heats of formation¹⁻³ (by 8–12 kJ mol⁻¹) than studies of dissociation/association equilibria,^{4,5} e.g.,

$$\mathbf{R} \rightleftharpoons \mathbf{R}_{-\mathrm{H}} + \mathbf{H} \tag{3}$$

$$R \rightleftharpoons R_{-CH_3} + CH_3 \tag{4}$$

The large uncertainties in the heats of formation of the alkyl radicals created by these disparities provided corresponding uncertainties in the primary, secondary, and tertiary C-H bond energies, whose values are derived largely from the heats of formation of the smaller alkyl radicals.

In the older thermochemical studies of the equilibria involving the hydrogen halides, the heats of formation were derived from reaction enthalpies which were obtained by combining *measured* activation energies of I + RH or Br + RH reactions with *assumed* activation energies of the reverse reactions.² In more recent investigations, the kinetics of R + HBr and R + HI reactions were isolated for direct investigation, and it was discovered that the activation energies of these ostensible metathesis reactions are all negative,⁶⁻¹⁰ decreasing from -1.2 to about -6.3 kJ mol⁻¹ as the complexity of R increases from CH₃ to *t*-C₄H₉ (in the case of the R + HI reactions).¹⁰ In the thermochemical calculations associated with earlier studies of reactions 1 and 2, assumed generic activation energies of R + HX reactions had been used (8 kJ mol⁻¹ for all R + HBr reactions and 4 kJ mol⁻¹ for all R + HI reactions).² The errors in these assumed activation energies largely account for the disparities in the alkyl-radical heats of formation described above.⁶⁻¹⁰

Additional reconciliations of formerly disparate heats of formation of other free radicals have followed for similar reasons based on direct measurements of rate constants and activation energies of reactions of these radicals with HBr and HI. They include heats of formation for the radicals SiH_3 ,¹¹ CH₃CO,¹² and CH₂OH.¹³

In our earlier kinetic and thermochemical studies of reaction 1 involving alkyl radicals (CH₃, C₂H₅, *i*-C₃H₇, *sec*-C₄H₉, and *t*-C₄H₉),⁶⁻⁸ it was necessary to pool information from more than one source to obtain the Br + RH rate constants and activation energies needed to calculate the alkyl-radical heats of formation with one exception. For the *t*-C₄H₉ radical, absolute rate constants and activation energies were obtained for both the forward and reverse reactions, Br + *i*-C₄H₁₀ and *t*-C₄H₉ + HBr. In the other cases, the Br + RH rate constants were available only from ratios of Br + RH rate constants combined with the new determinations of the Br + *i*-C₄H₁₀ reaction rate constant.^{7,8} The results obtained from the thermochemical calculations were in very good agreement

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with those obtained from studies of reactions 3 and 4.

We have now returned to the study of equilibria involving the alkyl radicals and HBr, in particular the following systems:

$$C_2H_5 + HBr \rightleftharpoons C_2H_6 + Br$$
 (5,-5)

$$i-C_3H_7 + HBr \rightleftharpoons C_3H_8 + Br$$
 (6,-6)

$$sec-C_4H_9 + HBr \rightleftharpoons n-C_4H_{10} + Br$$
 (7,-7)

$$t-C_4H_9 + HBr \Rightarrow i-C_4H_{10} + Br$$
 (8,-8)

Rate constants for forward and reverse reactions were determined as a function of temperature¹⁴ and used in new thermochemical calculations to obtain the heats of formation of the four alkyl radicals involved more directly than has been possible to date.

This study was motivated by two developments. First, at Oxford University procedures were developed to allow direct measurement of Br + RH rate constants at elevated temperatures.¹⁵ In the current study, rate constants were obtained as a function of temperature for reactions -5 to -8. In the cases of reactions of -5 to -7, this study is the first to isolate these Br-atom reactions for direct investigation of their kinetic behavior.

Second, indications appeared that our original thermochemical study of the kinetics of R + HBr reactions (our first kinetic investigation of any R + HX reaction) involved an experimental oversight. Very recent additional studies of the kinetics of these R + HBr reactions, by Nicovich et al.¹⁶ and by Seakins and Pilling,¹⁵ while finding the same negative activation energies that we reported, also obtained absolute values for the rate constants that were, in each case, about a factor of 2 higher than those we had reported.

A possible explanation for this systematic difference in rate constants was offered by Nicovich et al.,¹⁶ which now appears to be correct in light of the results obtained in the current study. They suggested that the HBr used by us in this initial investigation of reactions 5, 6, 8, and 9 was in fact contaminated with large

$$CH_3 + HBr \rightarrow CH_4 + Br$$
 (9)

amounts of H_{2} , an HBr decomposition product, which acted simply as an unkown diluent of the HBr. In our original investigation of R + HBr reactions (as stated in the published papers^{6,7}), HBr (Matheson, stated purity >99.8%) was used as provided. Since it was found to be free of the decomposition product we could detect, Br_2 , it was presumed to have the stated purity.

After this initial study of R + HX reactions, a special all-glass gas handling system for purifying, storing, and handling hydrogen halide gases was constructed. It has been used in all our subsequent investigations of R + HX reaction kinetics.⁸⁻¹³ HBr and HI are now purified by multiple distillations which are repeated daily to maintain a very high level of purity. Hence, none of our subsequent kinetic studies of R + HBr or HI reactions was similarly affected. The former gas handling equipment was largely metal. Presumably Br_2 from the decomposition of HBr was lost (and hence escaped undetected) in the earlier reported study due to reactions on the metal surfaces.

We have now redetermined all the R + HBr rate constants reported in this initial investigation, those of reactions 5, 6, 8, and 9. In these new experiments, the now carefully purified HBr was used. The new results, reported here, are in excellent agreement with the recent determinations mentioned above. They replace our earlier reported R + HBr rate constants.

The results of this investigation of the kinetics of R + HBr and Br + RH reactions involving the smaller alkyl radicals as well as new thermochemical calculations conducted to obtain the heats of formation of C_2H_5 , *i*- C_3H_7 , *sec*- C_4H_9 , and *t*- C_4H_9 based on these results are presented here. The heats of formation obtained are compared to other values based on kinetic studies of other equilibria, (2,-2) to (4,-4). It is shown that there is essentially complete agreement between values obtained from studies of the different kinds of chemical equilibria described above. Recommendations are provided for the heats of formation of C_2H_5 , *i*- C_3H_7 , *sec*- C_4H_9 , and *t*- C_4H_9 based on an assessment of all recent determinations.

TABLE I: Free-Radical Precursors, Laser Photolysis Wavelengths, and Photoionization Energies Used in the Study of R + HBr Reactions

R	free-radical precursor	photolysis wavelengths (nm)	photoionization energies (eV)
CH ₃	acetone	193	10.2
	2-butanone	248	
C ₂ H ₅	3-pentanone	193	8.9-9.1
	2-butanone	248	
i-C ₃ H ₇	2,4-dimethyl-3-pentanone	193	8.9-9.1
•	2-bromopropane	248	
t-C₄H ₉	4,4-dimethyl-1-pentene	193	8.9-9.1
	3,3-dimethyl-2-butanone	248	

Kinetic Studies of Reactions 5-9

Studies of the R + HBr reactions were conducted at The Catholic University of America, and those of the Br + RH were conducted at Oxford University. They are presented below separately. Kinetic studies of these kinds have been conducted before at both laboratories and hence are described here only briefly except for the special data analysis that was required in the study of the Br + RH reactions.

A. Kinetic Study of the R + HBr Reactions. The apparatus¹⁷ and experimental procedures⁶⁻⁸ used have been described previously. Briefly, gas flowing through the 1.05-cm- (or 2.20-cm) i.d. heatable Pyrex tubular reactor contained the radical precursor (see below), HBr in varying amounts, and an inert carrier gas in large excess (He, >99%). Reaction was initiated by pulsed, unfocused radiation from a Lambda Physik 201 MSC laser (193 or 248 nm) directed along the axis of the tubular reactor. The flow velocity ($\approx 5 \text{ m s}^{-1}$ when the small reactor was used and $\approx 3 \text{ m s}^{-1}$ when the larger one was employed) was adequate to completely replace gases in the reactor between laser pulses. The free-radical precursors and photolysis wavelengths used are given in Table I.

Gas emerging from a small sampling orifice in the wall of the reactor is formed into a molecular beam and analyzed continuously using a photoionization mass spectrometer. The photoionizing energies used to detect and monitor the alkyl radicals of interest in this study are also given in Table I.

The decay of the radicals was monitored in time-resolved experiments in the absence and presence of HBr (whose concentration was varied) to obtain the reaction rate constant. Experiments were conducted under pseudo-first-order conditions (HBr in large excess). Initial conditions were chosen to essentially isolate the reaction of interest. By keeping the initial concentration of the radical low (typically $< 5 \times 10^{10}$ molecules cm⁻³), radical-radical and radical-atom reactions had negligible rates compared to the elementary reaction of interest.

Under the conditions used, the alkyl radical was lost by only two reactions, the R + HBr reaction under study and a heterogeneous loss process which was kinetically first order:

$$R \rightarrow heterogeneous loss$$
 (10)

Measurements of the radical exponential decay constant (k') as a function of the concentration of the second reactant yielded the rate constant of interest. Sample decay profiles of alkyl radicals and examples of plots of k' vs [HX] have been published.^{6,7}

To test for the presence of interfering heterogeneous bimolecular reactions involving HBr, experiments were conducted using two different diameter reactors (to vary the surface/volume ratio) and two wall-coating materials (Halocarbon Wax and polytetra-fluoroethylene (PTFE)).¹⁸ Use of either reactor or wall coating yielded the same results indicating that such reactions, if they occurred, were of negligible importance in these experiments. Other experimental parameters not expected to affect the rate constant determination were varied at selected temperatures. They include the total gas density, the flow velocity, and the laser photolysis wavelength. The measured rate constants were also independent of these variables as expected from the two-step mechanism for alkyl-radical loss used to reduce the data. The conditions used in all experiments and a summary of the results



Figure 1. Arrhenius plot of R + HBr rate constants: closed circles, current study; open circles, Nicovich et al.;¹⁶ open squares, Seakins and Pilling;¹⁵ open triangle, Donaldson and Leone.³¹ Solid lines are Arrhenius fits to the current results. The Arrhenius parameters are given in Table II. Dotted lines indicate prior R + Br rate constants reported by Russell et al.^{6,7}

obtained (rate constants of reactions 5, 6, 8, and 9 in Arrhenius form) are presented in Table II. The rate constants are plotted in Figure 1 together with the other recent determinations.

The reagent gases used were obtained from Aldrich (acetone, >99%; 2-butanone, 99.7%; 3-pentanone, >96%; 2,4-dimethyl-3-pentanone, 98%; 2-bromopropane, >99%; 4,4-dimethyl-1-pentene, >99%; 3,3-dimethyl-2-butanone, 98%; HBr, >99%). Helium (99.995%) came from Matheson. The free-radical precursors were degassed using freeze-pump-thaw cycles and used without further purification. HBr was passed through two ethanol traps (156 K) to remove Br₂ and distilled daily to remove residual Br₂ and H₂ as well as other possible impurities. The Br₂ impurity in HBr was measured regularly and found to be $\leq 0.04\%$. Helium was used as provided.

B. Kinetic Study of Br + RH Reactions. The laser flash photolysis resonance fluorescence apparatus used to determine absolute rate coefficients of the reactions of Br atoms has been described.¹⁵ In these experiments, CF_2Br_2 (the Br-atom source), the alkane, and helium bath gas were flowed through the heatable Pyrex reactor, typically at 100 Torr of total pressure.

Bromine atoms were produced by pulsed excimer laser (Lumonics TE861S) photolysis, at either 193 or 248 nm, of CF_2Br_2 . There is now evidence that the principal photolysis channel at 248 nm is

$$CF_2Br_2 \xrightarrow{248 \text{ nm}} CF_2Br + Br$$
 (11a)

while at 193 nm it is

$$CF_2Br_2 \xrightarrow{193 \text{ nm}} CF_2 + 2Br$$
 (11b)

Talukdar et al.¹⁹ have recently measured the Br yield at the photolysis wavelengths used and report that at 193 nm it is 1.96 \pm 0.27 while at 248 nm it is 1.01 \pm 0.15.

Bromine atom decays were monitored by recording its resonance fluorescence in time-resolved experiments. The bromine atom resonance radiation was generated by flowing a premixed Br_2 (0.2%)-He mixture at 0.5 Torr through a microwave discharge. The scattered resonance radiation was detected perpendicular to both the photolysis and resonance lamp beams by using a solar-blind photomultiplier (EMI 9413). A CaF₂ window was placed between the cell and the photomultiplier to filter out any impurity Lyman α radiation. The fluorescence signal was digitized and stored in a Gould Biomation wave form recorder. Signals from 200-2000 repetitions of the experiment were collected and stored

TABLE II: Reaction Conditions and Rate Constants Obtained in the Study of the R + HBr Reactions

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	10 ⁻¹⁶ [He]	10 ⁻¹² [HBr]		$10^{12}k^{b}$
T°	(molecules	(molecules	k,	(cm ³ molecule ⁻¹
(K)	cm ⁻³)	cm ⁻³)	(s ⁻¹)	s ⁻¹)
<u> </u>	,	$\pm IIP_{-} \rightarrow C$		
1		$_3 \neq HBT \rightarrow C$	$H_4 + BI$	
$\kappa_9 = 0$	(1.57 ± 0.26) X	10 ··· exp((1.6	± 0.6) I	$(J mol^{-1}/RI)^{\circ} cm^{\circ}$
•••		molecule		
299	6.00	9.36-35.6	18	3.05 ± 0.23
322	5.94	9.73-47.2	15	2.79 ± 0.23
346 ^a	17.9	28.0-116	7	2.85 ± 0.19
350	5.97	8.68-34.3	15	2.50 ± 0.32
388	5.95	10.034.8	13	2.43 ± 0.18
428	5.99	8.87-35.5	15	2.48 ± 0.13
482	5.95	7.07-33.6	15	2.50 ± 0.32
536	5.92	15.5-32.2	20	2.21 ± 0.18
	C₂H	$_{s} + HBr \rightarrow C_{s}$	$_2H_6 + B_1$	r j
$k_5 = ($	$(1.70 \pm 0.55) \times$	$10^{-12} \exp((4.2)$	± 1.2)	$J \text{ mol}^{-1}/RT)^c \text{ cm}^3$
		molecule ⁻¹ s	i ⁻¹	
297	6.00	7.07-12.7	21	9.39 ± 0.50
301	6.00	3.22-12.0	24	8.20 ± 1.07
322	5.94	4.04-13.2	23	8.79 ± 0.60
346 ^d	17.9	27.3-147	36	7.16 ± 0.30
350	5.97	4.75-16.6	16	6.77 ± 0.57
388	5.96	875-158	19	6.71 ± 0.57
399	5.95	7 40-18 5	12	6.04 ± 0.51
428	5.00	6 30-24 5	11	5.11 ± 0.05
420	5.05	10 5-26 2	10	5.11 ± 0.95
402	5.95	7 90 24 4	10	5.05 ± 0.36
482	5.95	7.89-24.4	15	4.24 ± 0.40
530	5.92	1.45-27.8	13	4.19 ± 0.71
	4-C.4	$I_1 + HB_r \rightarrow C$.H. + F	l r
k = 0	$(1.58 \pm 0.38) \times$	10^{-12} ern((6 A	- 1 0 0 L	$I mol^{-1} / PT \sim cm^3$
$\kappa_6 = 0$	(1.50 ± 0.50)		± 0.9) I	
200	6.00		40	10 2 + 20
298	6.00	1.81-7.21	42	19.3 ± 3.0
301	6.00	2.48-6.69	39	21.9 ± 4.0
302	6.00	2.65-5.32	37	21.6 ± 2.1
322	5.94	5.50-11.4	39	17.0 ± 1.6
322	5.94	1.83-6.06	32	17.6 ± 1.2
350	5.97	1.95-7.53	25	14.4 ± 1.0
388	5.96	3.48-11.0	22	10.1 ± 1.0
388	5.95	2.51-7.12	36	12.4 ± 1.4
428	5.99	3.42-11.7	17	9.38 ± 0.65
482	5.95	4.72-15.4	15	7.58 ± 0.90
530	5.92	3.93-14.5	9	7.04 ± 0.63
530	5.92	4.02-20.3	29	6.98 ± 0.66
	t-C₄H	$_{9}$ + HBr \rightarrow <i>i</i> -C	$C_4H_{10} + $	Br
$k_8 = ($	$(1.37 \pm 0.47) \times$	$10^{-12} \exp((7.8)$	± 1.4) 1	$J \text{ mol}^{-1}/RT)^c \text{ cm}^3$
		molecule ⁻¹ s	₁ ^{−1}	·
298	6.00	1.16-3.70	58	27.7 ± 3.3
300 ^d	17.8	4.51-21.2	174	25.5 ± 2.3
301	6.00	1.07-4.09	64	31.1 ± 6.6
322	5.94	1.29-3.60	50	29.0 ± 3.8
350	5.97	1.20-4.12	41	19.6 ± 3.5
388	5 95	2.51-7.62	35	16.2 ± 0.84
428	5 99	212-7.05	30	12.2 ± 0.57
480	5.77	2.12-7.03	21	0.27 ± 0.32
404 520	2.73	2.0/-11./	21	7.04 ¥ 1.31 7.55 ¥ 0.07
230	5.92	2.31-10.2	17	1.33 = 0.97

^aTemperature uncertainty \pm 3 K. ^bErrors are 1σ and refer to statistical uncertainties only. ^cErrors are 1σ . ^d248-nm photolysis, 1.05cm-diameter Halocarbon Wax coated reactor; all other experiments used 193-nm photolysis and 2.2-cm-diameter poly(tetrafluoroethylene) coated reactor.

in a microcomputer for data analysis.

Temperatures in the range 400-700 K were produced by a heating tape wrapped around the cell. Both were surrounded by thermal cladding to reduce heat loss and to increase temperature uniformity. The gas temperatures just above and below the reaction zone were monitored with type K thermocouples that also acted as sensors for the controller supplying power to the heating tape.

The alkanes (ethane and propane, Matheson CP grade; *n*-butane and isobutane, BDH CP grade) and helium (BOC CP grade) were used without further purification. Gas chromatographic analysis showed no significant impurities in any of the samples. Mixes



Figure 2. Arrhenius plot of Br + RH rate constants obtained in the current investigation. Solid lines are Arrhenius fits to the experimental data. The Arrhenius parameters are given in Table IV.

of alkanes in helium were made and stored in 5-L Pyrex bulbs. CF_2Br_2 and Br_2 (BDH) were degassed with several freezepump-thaw cycles and stored diluted in helium. Gas mixtures were measured and controlled by Tylan (type FM 360) mass flowmeters and valves linked to a MKS Type 260 flow ratio/ pressure controller. Calibration of the individual flowmeters was performed using a detergent bubble flowmeter, enabling an accuracy limit of $\pm 2\%$ to be placed on the substrate concentrations. Total pressures were monitored by a MKS capacitance manometer (0-1000 Torr; Model 220 BHS 3A1).

All experiments were performed with the alkane substrate in significant excess such that the decay of the bromine atoms was always exponential in character $([Br]_t = [Br]_0 \exp(-k't))$; i.e., experiments were performed under pseudo-first-order conditions. Time-resolved bromine atom decay traces were analyzed using a nonlinear least squares algorithm to extract k'. The experimental decay constant contains two components, a minor loss term to account for diffusion out of the monitoring zone and the major component due to reaction with the alkane substrate. The slope of a plot of k' vs alkane concentration yields the bimolecular rate coefficient at that temperature. Weighted linear least squares analyses were used in the determination of the bimolecular rate coefficients. The intercept of such plots was always within the experimental range for the diffusional loss rate of bromine atoms, measured in the absence of the alkane substrate.

Pseudo-first-order rate coefficients were invariant over a factor of 3 variation in precursor concentration at constant laser flash energy, indicating that secondary reactions were of no significance. The independence of the results with laser repetition rate (1-10 Hz) shows that reactions involving products are also of no importance.

Photolysis of CF_2Br_2 generates both ground-state $Br(^2P_{3/2})$ and spin-orbit excited $Br(^2P_{1/2})$. The resonance fluorescence technique used excites both electronic states. Relaxation of the bromine atoms produced by reaction 11a or 11b to a thermal distribution of spin-orbit states is expected to be very much quicker than the reaction times with the alkanes (by at least a factor of 10) for the experimental conditions used. This being the case, the Br spin-orbit states are also expected to remain in equilibrium during the chemical reaction under study, and the Br + RH rate constants determined in the manner described in this section are the thermal rate constants. These conclusions are based on the known relaxation rate constant for $Br(^2P_{1/2})$ by CH_4 (4.2 × 10⁻¹² cm³ molecule⁻¹ s⁻¹),²⁰ which may be regarded as a lower limit for the unknown $Br(^2P_{1/2})$ rate constants for the relaxation of $Br(^2P_{1/2})$

TABLE III: Reaction Conditions and Rate Constants Obtained in the Study of Br + RH Reactions

	[RH]		k ^a					
T (K)	(molecules cm ⁻³)	no. expts	$(cm^3 molecule^{-1} s^{-1})$					
	$Br + C_2H_4 \rightarrow HBr + C_2H_4$							
473	$(6.4-14.0) \times 10^{16}$	15	$(2.98 \pm 0.32) \times 10^{-16}$					
500	$(3.2-7.5) \times 10^{16}$	15	$(6.43 \pm 0.60) \times 10^{-16}$					
523	$(2.7-10.0) \times 10^{16}$	16	$(1.36 \pm 0.14) \times 10^{-15}$					
546	$(2.4-9.0) \times 10^{16}$	17	$(2.05 \pm 0.15) \times 10^{-15}$					
577	$(1.3-6.8) \times 10^{16}$	22	$(3.63 \pm 0.25) \times 10^{-15}$					
621	$(1.2-6.5) \times 10^{16}$	21	$(7.31 \pm 0.62) \times 10^{-15}$					
	$Br + C_1H_2$	→ HBr + (C,H ₇					
476	$(8.4-100.0) \times 10^{14}$	27	$(1.15 \pm 0.11) \times 10^{-14}$					
500	$(6.6-76.0) \times 10^{14}$	39	$(1.59 \pm 0.10) \times 10^{-14}$					
526	$(13.0-61.0) \times 10^{14}$	36	$(2.43 \pm 0.21) \times 10^{-14}$					
571	$(5.8-40.0) \times 10^{14}$	24	$(4.98 \pm 0.52) \times 10^{-14}$					
625	$(5.3-40.0) \times 10^{14}$	24	$(8.05 \pm 0.73) \times 10^{-14}$					
667	$(2.4-30.0) \times 10^{14}$	27	$(1.33 \pm 0.11) \times 10^{-13}$					
	$Br + n - C_4 H_1$	₀ → HBr +	C₄H₀					
447	$(9.4-63.0) \times 10^{14}$	23	$(1.20 \pm 0.13) \times 10^{-14}$					
476	$(4.3-45.0) \times 10^{14}$	21	$(1.99 \pm 0.22) \times 10^{-14}$					
526	$(2.0-31.0) \times 10^{14}$	32	$(5.08 \pm 0.46) \times 10^{-14}$					
571	$(6.2-27.0) \times 10^{14}$	17	$(1.11 \pm 0.09) \times 10^{-13}$					
625	$(3.2-27.0) \times 10^{14}$	22	$(1.96 \pm 0.14) \times 10^{-13}$					
	$Br + i - C_2 H_1$	₀ → HBr +	C4H					
423	$(5.0-42.0) \times 10^{14}$	24	$(4.20 \pm 0.39) \times 10^{-14}$					
446	$(3.0-15.0) \times 10^{14}$	15	$(8.64 \pm 0.95) \times 10^{-14}$					
473	$(3.8-19.0) \times 10^{14}$	16	$(9.52 \pm 0.87) \times 10^{-14}$					
483	$(3.5-20.0) \times 10^{14}$	18	$(1.24 \pm 0.10) \times 10^{-13}$					
528	$(3.7-18.0) \times 10^{14}$	16	$(1.82 \pm 0.21) \times 10^{-13}$					
545	$(2.2-17.0) \times 10^{14}$	22	$(2.86 \pm 0.22) \times 10^{-13}$					
571	$(3.4-22.0) \times 10^{14}$	20	$(4.11 \pm 0.44) \times 10^{-13}$					
621	$(3.0-14.0) \times 10^{14}$	20	$(6.34 \pm 0.37) \times 10^{-13}$					

^e Errors are 1σ and represent statistical uncertainties only.

TABLE IV: Reported Arrhenius Parameters for Br + RH Reactions

ref	temp range (K)	A factor ^a (cm ³ molecule ⁻¹ s ⁻¹)	activation energy (kJ mol ⁻¹)
	Br + ($C_2H_6 \rightarrow HBr + C_2H_5$	
current study	473-621	$(2.35 \pm 1.12) \times 10^{-10}$	53.3 ± 2.1
35	494-592	$(6.61 \pm 1.70) \times 10^{-10}$	58.6 ± 1.0
26	332-472	$(1.30 \pm 0.10) \times 10^{-10}$	56.0 ± 0.4
34	350-500	$(2.29 \pm 0.34) \times 10^{-10}$	57.2 ± 0.5
7	332-472	$(7.0 \pm 7.0) \times 10^{-10}$	53.4 ± 2.3
	Br +	$C_1H_8 \rightarrow HBr + C_1H_7$	
current study	476-667	$(8.78 \pm 3.00) \times 10^{-11}$	36.0 ± 2.0
26	285-418	$(8.56 \pm 1.36) \times 10^{-11}$	42.4 ± 0.6
7	285-418	$(4.7 \pm 2.2) \times 10^{-10}$	39.8 ± 1.7
	Br + n	$C_4H_{10} \rightarrow HBr + C_4H_0$	
current study	447-625	$(2.86 \pm 0.90) \times 10^{-10}$	37.7 ± 2.0
26	267-371	$(2.76 \pm 1.03) \times 10^{-11}$	42.7 ± 0.9
8	267-371	$(1.54 \pm 0.31) \times 10^{-9}$	40.1 ± 1.2
	Br + i-	$C_4H_{10} \rightarrow HBr + C_4H_9$	
current study	423-621	$(1.61 \pm 0.60) \times 10^{-10}$	28.8 ± 1.5
6	298-710	$(1.83 \pm 0.18) \times 10^{-10}$	28.7 ± 0.9
26	307-421	$(3.34 \pm 0.98) \times 10^{-11}$	31.4 ± 0.8
36, 37	298-363	$(4.2 \pm 4.0) \times 10^{-11}$	28.1 ± 2.5

^a Errors are 1σ and represent only the statistical uncertainty of the Arrhenius fit.

by the larger alkanes used in these experiments.

The conditions used in all experiments and results obtained are presented in Table III, and the rate constants are plotted in Figure 2. Arrhenius parameters were obtained from weighted linear least squares fits of plots of $\ln k vs 1/T$. The Arrhenius parameters for reactions -5 to -8 are given in Table IV together with those values from prior investigations.

In reactions -6 to -8 the primary process of interest is the abstraction of the secondary or tertiary hydrogen atoms. In each of these reactions, there exists the possibility of a complicating parallel reaction, abstraction of primary hydrogens by the bromide

TABLE V: Observed Rate Constants for Br + RH Reactions and Rate Constants for the Removal of Primary and Secondary Hydrogen Atoms from Three Hydrocarbons

т (К)	$\frac{k_o^a}{(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})}$	$\frac{k_p^{b}}{(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})}$	$k_{\rm p}/k_{\rm o}$	$\frac{k_{s} \text{ or } k_{t}^{c}}{(\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1})}$	
		$Br + C_1H_2 \rightarrow HBr + C_1H_7$			
473	$(9.4 \pm 0.9) \times 10^{-15}$	$(3.1 \oplus 0.9) \times 10^{-16}$	0.03	$(9.07 \oplus 1.00) \times 10^{-15}$	
671	$(1.4 \pm 0.1) \times 10^{-13}$	$(1.7 \pm 0.5) \times 10^{-14}$	0.12	$(1.23 \pm 0.20) \times 10^{-13}$	
		$Br + n - C_4 H_{10} \rightarrow HBr + C_4 H_9$			
447	$(1.1 \pm 0.1) \times 10^{-14}$	$(1.4 \oplus 0.4) \times 10^{-16}$	0.01	$(1.13 \pm 0.11) \times 10^{-14}$	
621	$(1.9 \pm 0.2) \times 10^{-13}$	$(7.7 \pm 2.3) \times 10^{-15}$	0.04	$(1.86 \pm 0.20) \times 10^{-13}$	
		$Br + i - C_4 H_{10} \rightarrow HBr + C_4 H_9$			
423	$(4.4 \pm 0.4) \times 10^{-14}$	$(9.2 circle 2.8) \times 10^{-17}$	0.002	$(4.43 \pm 0.44) \times 10^{-14}$	
621	$(6.1 \pm 0.6) \times 10^{-13}$	$(1.2 \bullet 0.5) \times 10^{-14}$	0.02	$(5.98 \pm 0.61) \times 10^{-13}$	

"Observed rate coefficient. "Primary rate coefficient. "Secondary rate coefficients.

atoms. We have assessed the importance of such parallel processes and conclude that, for nearly all the conditions used, the effect is negligible.

Simple principles of additivity and similarity have been useful for characterizing competitive abstraction processes involving a single molecule. The Arrhenius A factor of a bimolecular reaction is associated with the collision frequency for the reactants and a probability or steric term (which includes reaction-path degeneracy considerations). From degeneracy considerations alone, the A factor for the abstraction of a primary hydrogen atom from a hydrocarbon molecule by bromine atoms would be expected to be close to one-sixth of the value for the A factor for reaction -5. $Br + C_2H_6$. The activation barrier associated with a single primary abstraction is expected to be similar to that measured for reaction -5. Such simple concepts have been used to predict overall reaction rate constants for other abstraction processes. Herron and Huie²¹ studied the rate of attack of ground-state oxygen atoms on various alkanes. They showed that, to a good approximation, the overall rate can be expressed as the sum of the rates of attack on the individual hydrogen atoms,

$$k = n_{\rm p}A_{\rm p} \exp(-E_{\rm p}/RT) + n_{\rm s}A_{\rm s} \exp(-E_{\rm s}/RT) + n_{\rm t}A_{\rm t} \exp(-E_{\rm t}/RT)$$
(I)

where the subscripts p, s, and t refer to primary, secondary, and tertiary hydrogens and n_x is the number of hydrogens of type x in the alkane molecule. The technique has been discussed by Walker²² and experimentally verified for the O + *i*-C₄H₁₀ reaction by Washida and Bayes.²³ Bond energy-bond order (BEBO) calculations performed by Michael et al.²⁴ have confirmed that primary hydrogen abstraction in hydrocarbons can be taken to be the same for all such bonds. This concept has also been found very useful for characterizing all the H-atom abstraction channels of OH + hydrocarbon reactions.²⁵

Propane and *n*-butane contain six primary positions for abstraction, and hence the rate constant for secondary abstraction should be calculated by subtracting the appropriately scaled value of k_{-5} from the observed rate coefficient. For example, for isobutane with nine primary hydrogen atoms, a value of $1.5k_{-5}$ is subtracted.

Table V shows the results of these calculations for reactions -6 to -8 at the high- and low-temperature extremes of the experiments performed. Values of k_{-5} at temperatures below that of the experimental study needed for these calculations were obtained using extrapolated values from the Arrhenius expression for k_{-5} in Table IV.

Assuming that this concept of rate constant additivity is valid, the results displayed in Table V show that only for reaction -6, and then only at the highest temperature used to study the kinetics of this reaction, will the abstraction of a primary hydrogen compete to any significant extent with that of a secondary or tertiary hydrogen. The data and calculations for the worst case, reaction -6, are plotted in Figure 3. There is reported evidence that, at slightly lower temperatures than were used in the current investigation, primary abstractions are unimportant in reactions -6to -8. Fettis et al.,²⁶ who analyzed the stable bromides ultimately produced in static systems in which these reactions occurred, found



Figure 3. Plot of the measured rate constant for reaction -6 (solid line) as well as the components of k_{-6} due to the abstraction of secondary hydrogens (dashed line) and primary hydrogens (dotted line).

that the products from abstraction of primary hydrocarbons were of negligible importance (i.e., below detectable limits).

Arguments such as those used above suggest that the A factor for the reaction of bromine atoms with *n*-butane should be twice that for propane (four versus two secondary hydrogen atoms) while the activation barriers should be equal. This appears to be the case. The absolute values for the rate coefficients for reaction -7 are approximately twice those measured for reaction -6. In addition the ratio k_{-7}/k_{-6} remains approximately 2 (within the estimated uncertainty limits) over the range of temperatures covered in this investigation, indicating that the two reactions have comparable activation energies.

A determination of the Arrhenius parameters for the abstraction of a single secondary hydrogen from hydrocarbon molecules by bromine atoms can be made from a composite plot of $k_{-6}/2$ and $k_{-7}/4$ vs 1/T (Figure 4). As would be expected if the above arguments are valid, the plotted data lie together along a line which, when fitted to an Arrhenius expression, yields the result

$$k_{\rm s} = (5.3 \pm 5.0) \times$$

 $10^{-11} \exp(-(36.4 \pm 4.0) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Thermochemical Calculations

Both second-law and third-law calculations were performed to obtain heats of formation of C_2H_5 , $i-C_3H_7$, $sec-C_4H_9$, and $t-C_4H_9$. The procedures used were exactly as described before⁶⁻¹⁰ and will not be repeated here in detail. Basically the second-law method uses the difference of the activation energies determined for the forward and reverse reactions as a direct measure of the enthalpy of reaction at a particular temperature, typically the middle of the overlapping temperature ranges of the studies of the forward and reverse reactions (more exactly the middle of the overlapping 1/T ranges, described here as the mean temperature, T_m). This

TABLE VI: Experimental Determinations of Alkyl-Radical Thermodynamic Properties from Studies of Chemical Equilibria^a

		$R + HBr \rightleftharpoons RH + Br (current study)$						$R + HI \rightleftharpoons RH + I$ (Sectula et al.) ^b third law ^d	dissoc/recomb equilib (Tsang) ^c third law ^d	other
radical	third law		second law							
(recommended $\Delta H_{\rm f}$)	$\overline{\Delta G_{\mathrm{T}}}^{\circ e}$	$T_{\rm m}^{f}$	$\Delta H_{\rm f}^{\circ}{}_{298}$	$\overline{E_{\rm f} - E_{\rm r}}$	$T_{\rm m}^{f}$	$\Delta H_{\rm f}^{\rm o}{}_{298}$	S°	$\Delta H_{\rm f}^{\circ}{}_{298}$ $\Delta H_{\rm f}^{\circ}{}_{298}$	$\Delta H_{f}^{\circ}{}_{298}$	
$\overline{C_2H_5}$ (121.0 ± 1.5)	-36.9	503	122.0 ± 1.7	-57.5	367	121.8 ± 1.7	256 ± 7	117	119 ± 2	$ \begin{array}{c} \{118.5,^{g} 120.2 \pm \\ 0.8,^{h} 118,^{i} \\ 119,^{j} 122^{k}\} \end{array} $
$i-C_{3}H_{7}$ (90.0 ± 1.7)	-25.6	502	90.5 ± 1.9	-46.2	367	89.1 ± 1.4	292 ± 5	91, 88	88 ± 2.5	. ,
$sec-C_4H_9'$ (67.5 ± 2.2)	-21.8	486	67.5 ± 2.3	-44.9	306	67.6 ± 3.0	343 ± 9	75	70.6 ± 1.6	
$t - C_4 H_9 (51.3 \pm 1.8)$	-22.4	359	51.3 ± 1.8	-36.6	359	51.3 ± 1.7	313 ± 5	50, 47, 48	50.1 ± 2	{48.6 ± 1.7, ^m 47.3 ± 3.5, ⁿ 50.6°}

^aUnits: energy, kJ mol⁻¹; entropy, J mol⁻¹ K⁻¹. ^bReference 10. ^cReferences 4 and 5. ^dRecalculated heats of formation using same entropies used for third law HBr equilibrium calculations. [•] ΔG_T° for $T_m^{f, f}T_m$ is the mean temperature (K) of studies of forward and reverse reactions. [#]Reference 27. ^bReference 37. ⁱReference 38. ^jReference 39. ^kReference 16. ⁱSome entropies in table from ref 8. ^mReference 6. ⁿReference 15. ^oReference 16.



Figure 4. Composite Arrhenius plot for the abstraction of a single secondary hydrogen from C_3H_8 ($k_{-6}/2$, closed circles), and from n- C_4H_{10} , ($k_{-7}/4$, closed squares).

reaction enthalpy change (typically at $T_{\rm m}$) is corrected using available heat capacities to obtain its value at 298 K. The entropy change for the reaction is also obtained in the second-law calculations since the free energy change at the selected temperature is obtained directly from the ratio of the forward and reverse rate constants. Again the reaction entropy change is corrected to 298 K using the heat capacity functions of reactants and products. The radical heat of formation and entropy are obtained from the reaction enthalpy and entropy using known molar heats of formation and entropies of RH, Br, and HBr.

In the third-law procedure, only the free energy change is taken directly from the kinetic results as described above (again at T_m). The reaction entropy change comes from calculated entropies of reactants and products obtained from partition functions. This latter procedure can be preferable if the activation energies are not very accurately determined (e.g., because the kinetic study could be conducted over only a limited temperature range, more exactly over a limited 1/T range) and/or because the structures and vibration frequencies of reactants and products are sufficiently well-known to make calculated reaction entropy changes more accurate than those obtained from experiments of this kind. Again, as described above, thermodynamic properties are corrected to their values at 298 K using tabulated heat capacities.

The thermochemical information used in the second- and third-law calculations and/or its origins (heat capacities, heats of formation, and entropies) are given in Table VIII.

Third-law determinations of the alkyl-radical heats of formation were performed using the R + HBr and Br + RH rate constants obtained in the current study (Tables II and III). In the limited high-temperature ranges that could be used for the studies of the Br + RH reactions, only a relatively small range of the variable 1/T could usually be covered. Hence, while the absolute values of the Br + RH rate constants are rather accurately known, the activation energies are not so well established. For each of the reactions studied, the values of ΔG_T° [-RT ln ($k_{forward}/k_{reverse}$]] obtained directly from the results of the current study at a designated elevated temperature are given in Table VI.

The error limits of the third-law heats of formation include estimated errors in the calculated reaction entropies which are largely determined by the uncertainties of the radical entropies. The values of these entropies at 298 K and our assessments of the uncertainty in each value are as follows (units are J mol⁻¹ K⁻¹): 247 ± 3 for C₂H₅,²⁷ 288 ± 4 for *i*-C₃H₇,²⁸ 334 ± 6 for sec-C₄H₉,²⁹ and 313 ± 6 for *t*-C₄H₉.^{6,9} The rising uncertainty with radical complexity reflects the increasing number of low vibrational frequencies and internal rotations which make significant contributions to the molecular entropy and the fact that knowledge about these motions from theory (barriers to internal rotation and frequencies) also becomes less accurate as the size of the radical increases.

Second-law heats of formation of the alkyl-radical heats were also obtained. Arrhenius activation energies of the R + HBr reactions (5, 6, 8) obtained in the current study (Table II) were combined with activation energies of the Br + RH reactions to obtain reaction enthalpies at the mean temperatures discussed above, which were corrected to obtain their values at 298 K. There is confidence that the activation energy of reaction -8 was very accurately determined (28.8 \pm 1.0 kJ mol⁻¹ at $T_m = 359$ K) in the current investigation. It was studied at lower temperatures (and therefore over a larger 1/T range) than the other reactions, and there is perfect agreement between this activation energy and that obtained previously in another extensive study of the kinetics of this reaction.⁶ Hence it is used here in the second-law calculation of the $t-C_4H_9$ heat of formation. The activation energies of reactions -5 and -6 used in these calculations were obtained less directly, from activation energies of rate constant ratios, combined with the activation energy of reaction -8. To obtain E_{-5} (53.3 ± 1.5 kJ mol⁻¹ at 367 K), the activation energies of two ratios were required, those of k_{-6}/k_{-8} and k_{-5}/k_{-6} . To obtain E_{-6} (39.7 ± 2.1 kJ mol⁻¹ at 367 K), only one activation energy of a rate constant ratio was required, that of k_{-6}/k_{-8} . The ratios used and their activation energies are those reported by Fettis and Knox.³⁰ The second-law calculation for reaction (7,-7) using comparable ratios was reported previously.8

The results of all these second- and third-law thermochemical calculations are given in Table VI.

Discussion

A. Kinetics of \mathbf{R} + HBr Reactions. The rate constants obtained from the kinetic studies of the four \mathbf{R} + HBr reactions (reactions 5, 6, 8, and 9) are all systematically higher than were obtained previously in our laboratory,^{6,7} nearly a factor of 2 higher in all cases. This is apparent in Figure 1, where both the new and the old rate constants are displayed. Both sets of rate constants were obtained with the same apparatus using the same data reduction procedures. The only significant difference between the former and present studies was the addition of a new facility and procedures to handle, store, and purify hydrogen halide gases. Clearly, this systematic difference is most likely connected with the failure to repurify the HBr used in the original study (as suggested by Nicovich et al.¹⁶). The presence of a significant amount of H₂ in the HBr used in the original study (effectively an unrecognized diluent) would result in erroneous HBr concentration determinations and a systematic lowering of all R + HBr rate constants.

Agreement with the results of other recent determinations of these same rate constants is excellent to good. The excellent agreement is with the rate constants obtained by Nicovich et al.¹⁶ (reactions 5, 7, 8, and 9) and by Seakins and Pilling¹⁵ (reaction 8 studied at ambient temperature), studies in which the reaction of interest was studied directly. Agreement in these two cases is within $\pm 10\%$. Poorer agreement (but still within a factor of 2) is obtained with less directly obtained rate constants, those reported by Seakins and Pilling near 600 K (obtained from observations of the approach to equilibrium),¹⁵ an ambient temperature determination of k_9 reported by Donaldson and Leone³¹ (obtained from monitoring chemiluminescence from the hydrocarbon product), and a measurement of k_8 at 298 by Richards et al.³² (who studied the reaction which was in competition with another elementary reaction involving t-C₄H₉).

B. Kinetics of Br + RH Reactions. There have been few prior investigations of the kinetics of reactions -5 to -8. The most comprehensive was by Fettis et al.,^{26,30} who studied reactions (-5 to -8) using a competitive-rates method. The initial stages of Br₂ + (RH + R'H) reactions were studied as a function of temperature (270–470 K), and from gas chromatographic end product analyses, values of ratios of Br + RH rate constants involving $k_{-5}-k_{-8}$ were extracted. The relative rate constants were put on an absolute basis by Fettis et al. using values of k_{12} for the reaction

$$Br + CH_3Br \rightarrow HBr + CH_2Br$$
(12)

reported by Kistiakowski and Van Artsdalen.³³ The values of k_{-5} - k_{-8} obtained by Fettis et al.^{26,30} are significantly lower than were obtained in the current investigation. Coomber and Whittle³⁴ used end-product analysis/relative rate techniques similar to those of Fettis and Knox to determine Arrhenius parameters for reaction -5.

King et al.,³⁵ using a spectrophotometric analysis of the initial stages of the Br_2/C_2H_6 reaction, measured absolute rate coefficients for reaction -5 that are in relatively good agreement with the present study. King et al. attributed discrepancies between their study and that of Fettis et al. to an inaccurate determination of the reference reaction rate constant, k_{12} .

In our prior study of R + HBr reaction kinetics,⁶ absolute rate constants were also obtained for reaction -8 in the temperature range 298-710 K. The method used to study the $Br + i-C_4H_{10}$ reaction was analogous to that used in the current investigation. The values of k_{-8} obtained by Russell et al.⁶ in this earlier investigation are in excellent agreement with those obtained in the present study.

Two recent studies of reaction -8 have been performed by Benson and co-workers using a very low pressure reactor (VLPR).^{36,37} A microwave discharge was used to generate a steady flow of bromine atoms into the Knudsen cell. Bromine atoms were monitored by mass spectrometry. Initial results³⁶ produced rate coefficients for reaction -8 that were up to 300 times greater than the literature values at that date. Reinvestigation³⁷ of the reaction in the light of possible complexities caused by reactions involving electronically excited bromine atoms yielded an activation energy for reaction -8 that is in good agreement with this work and ref 6. However, the measured A factor they obtained³⁶ is approximately a factor of 4 below that determined in this study.

Arrhenius parameters obtained from different kinetic investigations, each conducted over a limited temperature range (more specifically limited ranges of 1/T), are often widely scattered even

though the absolute determinations of rate constants may be in substantial agreement. For example, the maximum deviation in the absolute rate constants for reaction -5 between those obtained in the present study and those from ref 33 is only 25% over the common temperature range. Yet the fitted Arrhenius A factors from the two studies differ by a factor of 3 and the activation energies differ by 5 kJ mol⁻¹. The standard deviation of the activation energy returned from the Arrhenius fit to reaction -5(as well as to reactions -6 and -8) is approximately 2 kJ mol⁻¹, significantly less than the discrepancy between the two activation energies obtained in the two studies of reaction -5. The range of the 95% confidence interval, approximately 4 kJ mol⁻¹, comes much closer to bridging this gap. Similar 95% confidence intervals $(3-5 \text{ kJ mol}^{-1})$ were returned for reactions -6 to -8. These larger uncertainty limits provide overlap between the activation energies of reactions -6 to -8 obtained in the current study with the activation energies determined for these reactions in refs 6-8.

As discussed above, the uncertainties in the Arrhenius parameters determined in this kinetic study of Br + RH reactions led us to prefer to use only the absolute values of the current rate coefficients in the current thermochemical calculations (i.e., third-law calculations). The second-law calculations (involving the use of activation energies) were typically performed using kinetic data spanning significantly wider ranges of 1/T.

C. Alkyl-Radical Heats of Formation. 1. From the Present Results. The alkyl-radical heats of formation obtained from these studies of reactions 5,-5 to 8,-8 are in very good agreement with those obtained from kinetic studies of other equilibria, including those involving another hydrogen halide (HI) and dissociationrecombination equilibria (see Table VI). Agreement is typically within "chemical accuracy", ± 4 kJ mol⁻¹. The heats of formation obtained from studies of equilibria involving HI have an indeterminable accuracy.¹⁰ The thermochemical calculations still require reliance on previously determined I + RH rate constants which were obtained indirectly from kinetic observations of complex kinetic systems. Thus, not unexpectedly, if there is a remaining disagreement that is greater than ± 4 kJ mol⁻¹, it is usually with the value or values obtained from the studies of the equilibrium involving HI, reaction 2,-2.

The excellent agreement between the second- and third-law determinations of the alkyl-radical heats of formation in the current study for each of the four alkyl radicals (differences which were no greater than 1.3 kJ mol⁻¹) tends to support the stated accuracy of the values. While this close agreement could, in each case, be fortuitous, it is more likely an indication of the accuracy of the thermochemical results since the determinations use somewhat different kinetic information. The second-law calculation uses only the temperature dependence of the rate constants (ratios of rate constants obtained at different temperatures) while disregarding their absolute values. On the other hand, the third-law determination uses only the magnitudes of the rate constants (at a fixed temperature) combined with calculated reaction entropies and ignores the temperature dependencies of the rate constants. Close agreement between second- and third-law heats of formation is assured only if the kinetic results (rate constants and activation energies) and calculated entropies are all accurate.

In our earlier thermochemical study of reactions 5,-5, 6,-6, and 8,-8, the calculated heats of formation were essentially unaffected by the unknown dilution of the hydrogen halide reactant.^{6,7} All heats of formation were derived from reaction activation energies, i.e., second-law determinations. As can be seen in the Arrhenius plots in Figure 1, the new rate constants are essentially displaced uniformly upward from the old values, retaining the original slopes (Arrhenius activation energies). For the three radicals considered in both the prior^{6,7} and current investigations of $R + HBr \Rightarrow RH + Br$ equilibria (C₂H₅, *i*-C₃H₇, and *t*-C₄H₉), the old and new second-law heats of formation differ by only between 1 and 3 kJ mol⁻¹.

2. Recommended Heats of Formation for Alkyl Radicals. In this section, the heat of formation of each radical is discussed and a recommended value reported, one that takes into account the current results and the recent determinations of others.

 C_2H_5 . Virtually all the recent determinations of the C_2H_5 heat of formation cluster in the 118-122 kJ mol⁻¹ range. Earlier reported values have been reviewed.^{4,7,27} The current study provides two values very close to 122 kJ mol⁻¹. Two direct studies of the equilibrium

$$H + C_2 H_4 \rightleftharpoons C_2 H_5 \tag{13}$$

have obtained equilibrium constants of this reaction which were used in thermochemical calculations to obtain the radical heat of formation, 118.5 ± 1.6^{27} and 120.2 ± 0.8^{28} kJ mol⁻¹. (The error limits do not include the uncertainty in the C₂H₅ entropy. If this uncertainty is included, the uncertainty in the heats of formation rises by ≈ 0.9 kJ mol⁻¹.) Tsang's assessment of dissociation-recombination-based equilibrium studies provides a recommended value of 119 ± 2 kJ mol^{-1.5} Other less direct studies obtained comparable results.

A value of 121.0 ± 1.5 kJ mol⁻¹ for the C₂H₅ heat of formation is recommended on the basis of an assessment of these and the other listed results.

i- C_3H_7 . All recent thermochemical studies of equilibria involving *i*- C_3H_7 have yielded heats of formation that are very close, within the error limits of the current second- and third-law determinations, 89.1 ± 1.4 and 90.5 ± 1.9 kJ mol⁻¹. Therefore a value of 90.0 ± 1.7 kJ mol⁻¹ is adopted as the recommended value.

sec-C₄H₉. In the case of the sec-C₄H₉ radical there is excellent agreement between the second- and third-law determinations obtained in the current study, 67.6 ± 3.0 and 67.5 ± 2.3 kJ mol⁻¹, respectively. Disagreement with the value derived from the equilibrium involving HI (75 kJ mol⁻¹) is not unexpected. The I + n-C₄H₁₀ rate constants needed for the thermochemical calculations come from a very indirect study.¹

Disagreement with Tsang's recommended value⁵ (70.6 \pm 1.6 kJ mol⁻¹) is minor but does bear some discussion. Tsang considered kinetic studies related to two equilibria in his third-law thermochemical analyses. The first was

$$sec-C_4H_9 \rightleftharpoons C_3H_6 + CH_3$$
 (14)

Measured rate constants from two studies conducted near 600 K for both the forward and reverse reactions were used. The use of the new entropy of sec-C₄H₉ from Chen et al.'s recent theoretical study of this radical²⁹ yields an average sec-C₄H₉ heat of formation of 70.0 kJ mol⁻¹ for the two studies of reaction 14 considered, which is in very good agreement with the current results. Tsang also considered the equilibrium

$$(sec-C_4H_9)_2 \rightleftharpoons 2(sec-C_4H_9) \tag{15}$$

In this case, rate constants near 1100 K were used in the thermochemical calculations. Here measured values of the forward rate constant were combined with an estimate of the rate constant of the reverse reaction (presumed to be the same as for the $i-C_3H_7$ + i-C₃H₇ reaction). From the second equilibrium, Tsang obtained a sec-C₄H₉ heat of formation of 74.5 kJ mol⁻¹ (again a recalculated value using Chen et al.'s²⁹ sec-C₄H₉ entropy). This latter determination, which is not in very good agreement with the current results, must be regarded as having a significantly higher uncertainty. An error of only a factor of 2 in the estimated recombination rate constant, k_{-15} , at 1100 K would result in a 6.3 kJ mol⁻¹ error in the radical heat of formation. The 7 kJ mol⁻¹ disparity between Tsang's heat of formation derived from his thermochemical analysis of the equilibrium reaction (15,-15) and the values obtained in the current investigation can be accounted for by an expected large uncertainty in the thermochemical analysis.

The current and our prior⁸ determinations of the sec-C₄H₉ radical heat of formation discussed above appear to be the most accurate and hence are the basis of our recommended value, 67.5 \pm 2.2 kJ mol⁻¹.

 $t-C_4H_9$. For this radical alone, both the second- and third-law determinations rely solely on rate constants and activation energies obtained in the current investigation. There is complete agreement

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TABLE VII: Recommended C-H Bond Energies at 298 K (kJ mol⁻¹)

type of C-H bond	McMillen and Golden ³ (1982)	current study (1992)
primary		
C ₂ H ₅	411 ± 4	422.8 ± 1.5
secondary		
C ₃ H ₈	398 ± 4	412.7 ± 1.7
$n-C_4H_{10}$	400 ± 4	411.1 ± 2.2
tertiary		
$i-C_4H_{10}$	390 ± 8	403.5 ± 1.8

TABLE VIII: Heats of Formation, Entropies, and Sources of Heat Capacity Functions Used in Thermochemical Calculations

species	$\frac{\Delta H_{\rm f} \circ_{298}}{(\rm kJ \ mol^{-1})}$	S ^o ₂₉₈ (J mol ⁻¹ K ⁻¹)	$C_P^{\circ}(T)$ functions (ref)
Br	111.8641	17543	43
HBr	-36.3841	198.7 ⁴³	43
C_2H_6	-83.85 ⁴²	249.6 ⁴³	43
C_3H_8	-104.68 ⁴²	270.144	43
$n-C_4H_{10}$	-125.64 ⁴²	310.744	43
<i>i</i> -C ₄ H ₁₀	-134.18 ⁴²	295.344	43
C ₂ H ₅		247 ± 3^{27}	43
i-C ₃ H ₇		288 ± 4^{28}	43
sec-C4H9		334 ± 6 ²⁹	44
t-C₄H,		313 ± 6^{6}	43

^a For radical entropy error assessments, see text.

between the two determinations, 51.3 ± 1.7 and 51.3 ± 1.8 kJ mol⁻¹ for the second- and third-law determinations, respectively. These values in turn agree completely with Tsang's assessment of the results of dissociation-recombination equilibria which provides a value of 50.1 ± 2.0 kJ mol⁻¹.

Seakins and Pilling observed the equilibrium reaction 8,-8 directly, obtaining equilibrium constants at two temperatures, 573 and 641 K.15 Using the reaction free energies obtained from these equilibrium constants in third-law calculations, they obtained values of 44.2 \pm 4 and 48.1 \pm 4 kJ mol⁻¹ for the t-C₄H₉ heat of formation from the data obtained at these two temperatures respectively. The second determination is in very good agreement with the values obtained in the current study. Agreement with the first value is poorer. In perhaps a somewhat more accurate thermochemical calculation, Seakins and Pilling combined their determination of k_8 at 298 K with the value of k_{-8} measured by Russell et al.⁶ at this temperature to obtain a heat of formation of $t-C_4H_9$ of 50.9 kJ mol⁻¹. Nicovich et al., who combined their k_8 determinations with Russell's k_{-8} results using both secondand third-law calculations, report an average value of 50.6 kJ mol⁻¹ for the two $t-C_4H_9$ heats of formation. Both these latter studies provide results that are in extremely close agreement with the current study.

A heat of formation of $t-C_4H_9$ of 51.3 ± 1.8 kJ mol⁻¹ is our recommended value on the basis of the results of all studies discussed here.

3. C-H Bond Energies. The heats of formation of the alkyl radicals recommended here provide a new set of C-H bond energies. The values are listed in Table VII along with recommended primary, secondary, and tertiary C-H bond energies given by McMillen and Golden in 1982,³ values which are in wide use today. The McMillen and Golden C-H bond energies are derived largely from alkyl-radical heats of formation that were obtained in older thermochemical studies of reaction 2, one in which an assumed generic activation energy of all R + HI reactions (4 kJ mol⁻¹) was used in the thermochemical calculations. The typical difference between bond energies, old and new, in each case is about 12 kJ mol⁻¹, the older bond energies in all cases being weaker. In our study of R + HI reactions involving the simple alkyl radicals, activation energies between -1.2 and -6.3 kJ mol⁻¹ were found. It is the error in the assumed R + HI activation energies which accounts for most of the differences in two sets of C-H bond energies listed in Table VII.

The disparity in alkyl-radical heats of formation based on the type of equilibrium that was used to obtain this thermochemical information no longer exists. Hence, there is no longer an uncertainty in the values of the C-H bond energies associated with these former disparities.

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Registry No. CH₃, 2229-07-4; C₂H₅, 2025-56-1; *i*-C₃H₇, 2025-55-0; t-C₄H₉, 1605-73-8; HBr, 10035-10-6; Br, 10097-32-2; C₂H₆, 74-84-0; C₃H₈, 74-98-6; m-C₄H₁₀, 106-97-8; i-C₄H₁₀, 75-28-5; H₂, 1333-74-0; s-C4H9, 2348-55-2.

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Laser Studies of the Reactivity of NH($X^3\Sigma^-$) with the Surface of Silicon Nitride

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The reactivity of $NH(X^3\Sigma^-)$ with the surface of both a silicon nitride film and a depositing hydrogenated silicon nitride film has been measured to be essentially zero with an upper limit of 0.1 for substrate temperatures of 300-700 K. The reactivity was directly determined using spatially resolved laser-induced fluorescence of NH in a plasma-generated molecular beam incident on the surface. The NH adsorbs and then desorbs from the surface with a spatial distribution consistent with a cosine angular distribution. No dependence of reactivity on rotational state of the NH was observed.

I. Introduction

Understanding the interactions of molecules with surfaces is important for the development of many thin-film materials processing technologies, including chemical vapor deposition (CVD), plasma-enhanced CVD, and plasma etching. These processes are often controlled by chemical reactions that occur when gas-phase molecules collide with a substrate. Unfortunately, very little information is available for gas-surface reactions within these plasma environments, particularly those involving radicals.¹ Thus,

direct measurements of radical reactivities are needed to build a database and develop an understanding of such reactions.

The NH radical is present in NH₃ and NH₃/SiH₄ plasmas³ used for plasma deposition and etching in the semiconductor industry. There is considerable interest in the silicon nitride products deposited from these plasmas at low substrate temperatures since silicon nitride films are used as gate dielectrics and barrier coatings in microelectronic devices^{4,5} and for protective coatings.^{6,7} Specifically, plasma-deposited amorphous SiN_x:H