J. Am. Chem. Soc. 1988, 110, 3092-3099

Kinetics and Thermochemistry of CH_3, C_2H_5, and *i*-C_3H_7. Study of the Equilibrium R + HBr $\rightleftharpoons$ R–H + Br

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Received October 5, 1987

Abstract: The kinetics of the reactions between CH_3, C_2H_5, and *i*-C_3H_7 with HBr were studied in a tubular reactor coupled to a photoionization mass spectrometer. Rate constants were measured as a function of temperature to determine Arrhenius parameters. The following rate constant expressions were obtained (units of the preexponential factors are cm^3 $molecule^{-1}$ s^{-1} and those of the activation energies are kJ mol^{-1}; the temperature range covered in each study is also indicated): CH_3 + HBr {$8.7 \times 10^{-13} \exp(1.3/RT)$, 296–532 K}; C_2H_5 + HBr {$1.0 \times 10^{-12} \exp(3.4/RT)$, 295–532 K}; *i*-$C_3H_7$ + HBr {$1.1 \times 10^{-12} \exp(4.5/RT)$, 478–532 K}. These results were combined with determinations of the reverse rate constants to obtain equilibrium constants for the reactions R + HBr $\rightleftharpoons$ R–H + Br. Second-law-based analyses yielded heats of formation and entropies of CH_3, C_2H_5, and *i*-C_3H_7 that are in close agreement with recent determinations of heats of formation in prior investigations of dissociation–recombination equilibria and calculations of entropies. The observed negative activation energies for R + HBr reactions (and negative activation energies inferred for R + I_2 reactions from the current results) provide the basis for a detailed explanation for the disparities that currently exist between heats of formation of alkyl radicals that have been obtained from studies of bromination and iodination kinetics and those that are derived from kinetic studies of other reactions. A complex mechanism for R + HBr reactions that is consistent with the observed kinetic behavior of these reactions is discussed.

The iodination and bromination of organic molecules have been extensively studied during the past 30 years.[1–9] Interest in these reactions is due in part to the fact that their rates, measured under controlled conditions, can be used to determine the heats of formation of polyatomic free radicals produced in these systems.[1–10] Today, a significant fraction of our knowledge of the thermochemistry of these intermediates is still based on these experiments.

In these kinetic studies of iodination or bromination processes, the free radical heat of formation is obtained from a determination of the enthalpy change associated with an H-atom or I-atom transfer reaction (e.g., I + R–H $\rightleftharpoons$ R + HI). The enthalpy change is obtained from the difference between the activation energies of the forward and reverse reactions; that for the forward reaction (I + R–H, I + R–I, or Br + R–H) is measured and that for the reverse reaction (R + HI, R + I_2, or R + HBr) is assumed or presumed.[4,5] It has been the practice to assume that the activation energies of all R + I_2 (Br_2) reactions are in a narrow range, 0 ± 4 kJ mol^{-1}.[4–6] Similar narrow ranges for the activation energies of the R + HI (4 ± 4 kJ mol^{-1}) and R + HBr (8 ± 4 kJ mol^{-1}) reactions have been inferred from these assumptions and from knowledge of activation energy differences (e.g., between R + HI and R + I_2 reactions). The evidence supporting these assumptions and inferences has been discussed in detail by Benson and Golden[4] and by O'Neal and Benson.[5]

One of these presumed activation energies was recently found to be inaccurate, that of the *t*-C_4H_9 + HBr reaction. In the preceding study[11] (part 1), the kinetics of the equilibrium

$$t\text{-}C_4H_9 + HBr \rightleftharpoons i\text{-}C_4H_{10} + Br \quad \Delta H° = -35 \text{ kJ mol}^{-1} \qquad (1)$$

was investigated. Rate constants of both the forward and reverse reactions were measured as a function of temperature, and this information was used to determine the heat of formation and entropy of the *t*-C_4H_9 radical. It was discovered that the forward reaction has a significant *negative* activation energy (−5.8 ± 0.9 kJ mol^{-1}).[11]

Currently, unexplained differences exist between the heats of formation of free radicals derived from iodination and bromination studies and those obtained from kinetic studies of other systems.[6,12,13] (also see part 1). The 14 kJ mol^{-1} disparity between the measured and presumed activation energy for the *t*-C_4H_9 + HBr reaction provides a direct explanation for this difference for one case only, but this finding does suggest that the comparable disparities connected with the heats of formation of other free radicals may have similar explanations.

In order to gain more knowledge of the unusual and unexpected temperature dependencies of R + HBr reactions, we have now investigated the kinetics of three additional ones:

$$CH_3 + HBr \rightleftharpoons CH_4 + Br \quad \Delta H° = -74 \text{ kJmol}^{-1} \qquad (2)$$

$$C_2H_5 + HBr \rightleftharpoons C_2H_6 + Br \quad \Delta H° = -57\text{kJ mol}^{-1} \qquad (3)$$

$$i\text{-}C_3H_7 + HBr \rightleftharpoons C_3H_8 + Br \quad \Delta H° = -44 \text{ kJ mol}^{-1} \qquad (4)$$

Rate constants for reactions 2–4 were measured as a function of temperature. The results were used together with determinations of the rate constants of the reverse reactions to obtain the heats of formation and entropies of CH_3, C_2H_5, and *i*-C_3H_7. The results of this investigation are reported here.

While the results of these experiments now provide direct tests of the presumed activation energies for R + HBr reactions (for three alkyl radicals), they also provide knowledge that can be used to reassess the accuracy of the basic assumption underlying the determinations of heats of formation from kinetic studies of iodination processes, that R + I_2 activation energies are 0 ± 4 kJ mol^{-1}. This important assumption was also found to be less accurate than has been presumed.[4,5] With new assessments of R + I_2 activation energies that are developed here, alkyl radical heats of formation were recalculated from the results of prior iodination experiments. The new heats of formation are higher and in good agreement with those that have been obtained from experiments involving other equilibria.

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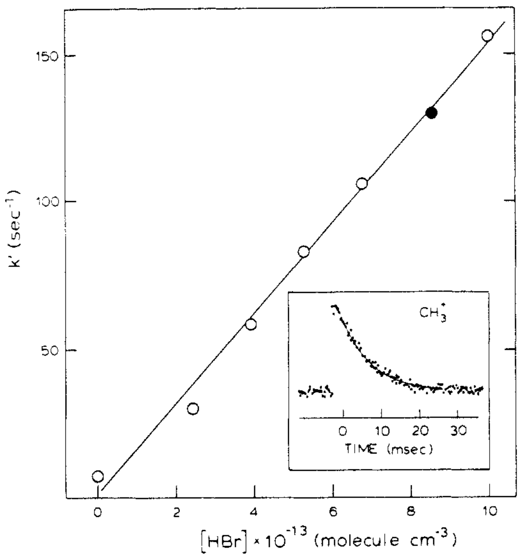

Figure 1. Plot of first-order decay constants (k') for CH_3 vs [HBr] for experiments conducted at 298 K. Insert is CH_3 decay profile recorded during one experiment (shaded point) in this set of experiments ([HBr] = 8.59 × 10^{13} molecule cm^{-3}). The line through the data is an exponential function fitted to the data by a least-squares method (k' = 131 s^{-1}).

In the current investigation, negative activation energies were obtained for all the R + HBr reactions studied. In part 1,[11] this kind of kinetic behavior of the t-C_4H_9 + HBr reaction was interpreted as an indication of a different mechanism for R + HBr reactions from one involving direct H-atom metathesis, which has been presumed to date. The suggested mechanism involves the initial formation of a bound intermediate (R·HBr). The kinetic results obtained for reactions 2–4 are shown to be consistent with this more complex mechanism.

Experimental Section

Studies of the kinetics of reactions 2–4 were conducted by using a heatable, coated {with halocarbon wax or poly(tetrafluoroethylene) (PTFE)} tubular reactor coupled directly to a photoionization mass spectrometer with which it is possible to monitor reactants and products in time-resolved experiments. Details of the facility and its use for the study of the t-C_4H_9 + HBr reaction have been discussed in part 1.[11] Only those features and procedures that were different in the current investigation are described here.

The free-radical precursors used were acetone (for CH_3), acetone-d_6 (for CD_3), diethyl ketone (for C_2H_5), and diisopropyl ketone (for i-C_3H_7).

Rate constants were measured as a function of temperature from 295 to 532 K. The upper temperature limit was determined by the use of the PTFE wall coating in the reactor. Reaction 4 was studied at only two temperatures, 478 and 532 K. Below 450 K, conditions could not be found that yielded a complete independence of radical decay times on the photolysis laser fluence and completely linear relationships between radical decay constants and [HBr] for this reaction. Such behavior is an indication that in the study of this reaction, secondary reactions could not be completely suppressed below 450 K.

In the studies of reactions 2 and 3 (as well as in the study of reaction 1 in part 1[11]), a special effort was directed at searching for a possible dependence of the measured rate constants on gas density and on the identity of the bath gas. Experiments were conducted at 296 K covering a sixfold density range with the principal bath gas (He) and using N_2 in place of helium at at least one density. No dependence of the rate constants of reactions 2 and 3 on these factors was observed (see Table I). It is presumed on the basis of these results and on the similar independence of k_1 on these same variables[11] that the rate constant of reaction 4 is also independent of these variables.

A sample ion signal profile from one set of experiments to measure k_2 and the dependence of this radical decay constant (k') on [HBr] are displayed in Figure 1. The conditions and results of all experiments are presented in Table I, and the measured rate constants are plotted in Figure 2 to display their temperature dependencies.

A single set of experiments was conducted at 296 K to measure the CH_3/CD_3 isotope effect in reaction 2 in order to obtain a rate constant for the CD_3 + HBr reaction that could be compared with the results of a direct study of this reaction. In this group of experiments, both the CH_3 and CD_3 precursors were present, and the two radical decay profiles were recorded at each value of [HBr]. These measurements yielded accurate determinations of both rate constants as well as a very accurate measure of the isotope ratio, $k(CD_3 + HBr)/k(CH_3 + HBr) = 1.2 \pm 0.1$. The conditions of this experiment are also given in Table I.

Table I. Conditions and Results of Experiments To Measure Rate Constants of R + HBr → R–H + Br Reactions[a]

T,[b] K	P, Torr	10^{-13}[HBr], molecule cm^{-3}	k_B,[c] s^{-1}	wall coating material[d]	$10^{12}k$, cm^3 molecule^{-1} s^{-1}
		$CH_3 + HBr \rightarrow CH_4 + Br$ Reaction (k_2)			
296	1.06	3.1–14.4	30.7	HW	1.48[e]
	3.93	3.4–15.8	28.0	HW	1.52
	0.597	2.8–14.2	18.5	HW	1.56
	1.07	2.4–10.1	7.7	PTFE	1.52
	1.09	2.9–10.2	19.8	PTFE	1.39[f]
	3.19	3.0–10.3	25.7	PTFE	1.44[f]
319	1.15	3.2–13.8	23.6	PTFE	1.47
348	1.24	2.9–13.7	20.7	PTFE	1.37
385	1.37	2.8–11.7	10.9	PTFE	1.30
427	1.51	2.9–12.3	7.3	PTFE	1.23
478	1.68	3.4–12.8	7.0	PTFE	1.22
532	1.86	3.5–12.0	7.4	PTFE	1.20
		$CD_3 + HBr \rightarrow CD_3H + Br$ Reaction			
296	1.06	3.1–14.4	29.2	HW	1.81[e]
		$C_2H_5 + HBr \rightarrow C_2H_6 + Br$ Reaction (k_3)			
295	1.06	0.78–2.23	9.3	HW	4.24
	3.93	0.70–2.86	14.8	HW	3.90
	0.60	0.63–2.38	8.1	HW	4.20
	1.07	1.00–3.90	4.8	PFTE	4.34
	1.08	1.35–4.16	7.5	HW	4.22[f]
319	1.14	0.64–2.54	6.9	HW	3.77
348	1.25	0.63–2.94	4.5	HW	3.35
385	1.37	0.79–3.84	0.0	PFTE	3.06
427	1.51	0.82–3.81	0.0	PFTE	2.58
478	1.68	0.86–4.30	0.0	PFTE	2.50
532	1.86	1.08–4.81	0.0	PFTE	2.25
		i-$C_3H_7 + HBr \rightarrow C_3H_8 + Br$ Reaction (k_4)			
478	1.68	0.97–6.41	10.5	PFTE	3.23
532	1.86	0.92–6.68	1.4	PFTE	2.72

[a] Concentration ranges of free-radical precursors used (molecule cm^{-3}): CH_3COCH_3 (CH_3), (5.4–6.4) × 10^{13}; $C_2H_5COC_2H_5$ (C_2H_5), (1.1–3.7) × 10^{13}; $(i\text{-}C_3H_7)_2CO$ (i-C_3H_7), (5.0–5.7) × 10^{13}. [b] Temperature, uncertainty; ±3 K (296–385 K), ±4 K (427–478 K), ±5 K (532–571 K). [c] Heterogeneous wall loss rate constant (measured in the absence of the second reactant). [d] Wall coating materials used: HW (halocarbon wax) and PTFE (poly(tetrafluoroethylene)). [e] Experiment in which CH_3 + HBr and CD_3 + HBr were simultaneously measured. Both CH_3 and CD_3 precursors present. [f] N_2 used as carrier gas (helium used when not otherwise noted). Accuracy of rate constants reduced to ±20% when N_2 is the carrier gas.

Assessment of Accuracy of Kinetic Measurements. The most probable uncertainty in each measured value of k_{2-4} is ±15%. This assessment takes into account the accuracies of the measured gas flow rates and total pressure, the accuracy of each determination of k', and the data analysis procedures used to calculate k_{2-4} from the laboratory measurements.

An additional assessment was made of the temperature dependencies of k_{2-4} (as expressed by an Arrhenius activation energy) because of the importance of this energy in the determination of the free-radical heats of formation. For the activation energies of reactions 2 and 3 it is ±0.9 kJ mol^{-1} at 370 K (near the middle of the temperature range of the study of these reactions). For reaction 4 it is ±1.5 kJ mol^{-1} (see below). This latter assessment takes into account the temperature range of the study, the random error in each rate constant determination, and the realization that most possible systematic erorrs would have little effect on the calculated Arrhenius activation energy.

Gas Sources and Purification Procedures. The gases and liquids used were obtained from Matheson (HBr, >99.8%), Aldrich (diethyl ketone, >96%; diisopropyl ketone, >98%), Mallinckrodt (acetone, >99.5%), MSISOTOPES (acetone-d_6, >99.96%), and Linde (He, >99.995%; N_2, >99.998%). The carrier gases, He and N_2, were used as provided. All other gases and liquids (with the exception of HBr) were purified and degassed by using freeze–pump–thaw cycles. The HBr was not purified but was analyzed and found to be free of Br_2.

Photoionization Energies Used To Detect Reactants. Three photoionization energies were used in this investigation. An argon resonance lamp (11.62, 11.83 eV) was used to detect HBr, a hydrogen lamp (10.2

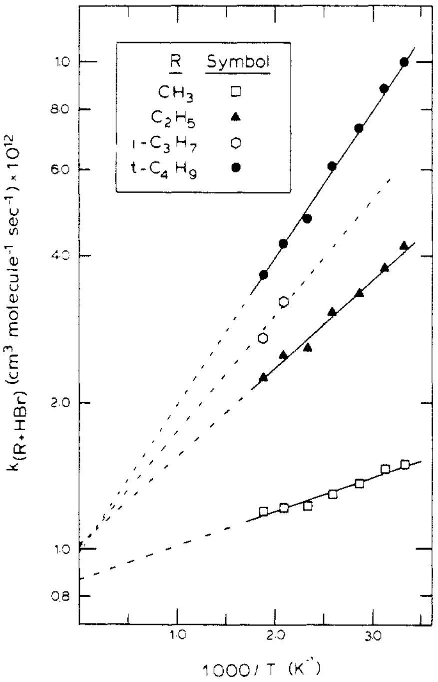

Figure 2. Plot of R + HBr rate constants measured in the current study and in part 1 (t-C_4H_9 + HBr)[11] vs $1000/T$. Solid lines are calculated Arrhenius expressions for reactions 1–3. Extrapolations are indicated by dashed lines. The Arrhenius expression for k_4 was obtained from the two measured rate constants and a presumed intercept at $1000/T = 0$ between that of the C_2H_5 + HBr and t-C_4H_9 + HBr reactions (see text).

eV) to detect CH_3 and CD_3, and a chlorine lamp (8.9–9.1 eV) to detect C_2H_5 and i-C_3H_7.

Calculation of Enthalpies of Formation and Entropies

Second-law determinations of the heats of formation and entropies of CH_3, C_2H_5, and i-C_3H_7 were obtained by using the measurements of k_2 to k_4 from the current investigation and determinations of the rate constants for the reverse reactions, k_{-2} to k_{-4}. The single largest source of possible error in these determinations (or in third-law calculations of these heats of formation using known entropies of reactants and products) is the significant uncertainty associated with the Arrhenius A factors of the rate constant ratios used to calculate the expressions for k_{-2} to k_{-4} (see below). For this reason, third-law calculations of these heats of formation (while still in substantial agreement with the second-law values) are less accurate and are not reported here.

The procedure used to obtain thermodynamic properties of the three alkyl radicals was as follows (units of rate constants are always cm^3 $molecule^{-1}$ s^{-1}):

1. Arrhenius expressions for reactions 2–4 were obtained from the measured rate constants in Table I:

$$k_2 = 8.7\ (\pm 0.8) \times 10^{-13} \exp\{1.3\ (\pm 0.9)\ \text{kJ mol}^{-1}/RT\}$$

$$k_3 = 1.0\ (\pm 0.1) \times 10^{-12} \exp\{3.4\ (\pm 0.9)\ \text{kJ mol}^{-1}/RT\}$$

$$k_4 = 1.1\ (\pm 0.2) \times 10^{-12} \exp\{4.5\ (\pm 1.5)\ \text{kJ mol}^{-1}/RT\}$$

The Arrhenius parameters for reactions 2 and 3 were obtained directly from the measured rate constants. Those for reaction 4 were obtained by using the measured rate constants at the two temperatures at which this reaction was studied and knowledge of the Arrhenius A factors of reactions 1–3. It was observed that the Arrhenius A factors for reactions 1–3 are very similar (see Figure 2). The A factor for reaction 4 was presumed to be in accord with the other three, and it was assigned a value that is essentially the same as that for the C_2H_5 + HBr and t-C_4H_9 + HBr reactions. The uncertainty in this assigned value of A_4 is larger than that of those associated with A_2 and A_3, and the activation energy, E_4, has a correspondingly higher uncertainty than does E_2 and E_3, ±1.5 kJ mol^{-1}.

2. Arrhenius expressions for reactions −2 to −4 were calculated by using the measurements of k_{-1}(Br + i-C_4H_{10}) made between 298 and 478 K reported in part 1[11] combined with relative rate constant determinations of Br + hydrocarbon (Hc) reactions reported in the literature.

$$k_{-2} = 5\ (\pm 6) \times 10^{-10} \exp\{-73.9\ (\pm 2.5)\ \text{kJ mol}^{-1}/RT\}$$

$$k_{-3} = 7\ (\pm 7) \times 10^{-10} \exp\{-53.4\ (\pm 2.3)\ \text{kJ mol}^{-1}/RT\}$$

$$k_{-4} = 4.7\ (\pm 2.2) \times 10^{-10} \exp\{-39.8\ (\pm 1.7)\ \text{kJ mol}^{-1}/RT\}$$

The investigation of Fettis, Knox, and Trotman-Dickenson[2,14] as well as that of Coomber and Whittle[15] was used as the source of the temperature-dependent ratios of Br + Hc reaction rate constants. In the study of Fettis et al.,[14] it was also reported that the product of reaction −4 is that indicated up to 446 K, the highest temperature of their investigation of this reaction. Thus it has been confirmed that k_{-4} applies to the reaction as written, i.e., to the exclusive removal of the secondary hydrogen atom by Br.

The expression for k_{-2} was obtained by combining the k_{-1} measurements reported in part 1[11] with the following ratios: k(Br + C_3H_8)/k(Br + i-C_4H_{10}),[2] k(Br + C_2H_6)/k(Br + C_3H_8),[2] k(Br + CH_3CHF_2)/k(Br + C_2H_6),[15] and k(Br + CH_4)/k(Br + CH_3CHF_2).[15] To obtain the expression for k_{-3}, the k_{-1} measurements were combined with the ratios for k(Br + C_3H_8)/k(Br + i-C_4H_{10}) and k(Br + C_2H_6)/k(Br + C_3H_8).[2] The Arrhenius parameters for k_{-4} were determined by using the same measurements of k_{-1} but by using only the single ratio k(Br + C_3H_8)/k(Br + i-C_4H_{10}).[2]

The indicated error limits of the Arrhenius parameters for k_{-2} to k_{-4} incorporate those of the measured values of k_{-1} and those reported for each ratio used in these calculations. The uncertainty limits reported by Fettis and Knox[2] represent actual assessments of the accuracy of the reported Arrhenius parameters of their rate constant ratios.[14] However, the error limits reported by Coomber and Whittle[15] are standard deviations of fits of Arrhenius expressions to the measured rate constant ratios, and therefore are not genuine uncertainty limits. The ratios from this source were required only in the determination of the thermodynamic properties of CH_3. The resulting uncertainty limits associated with the calculated thermodynamic properties of C_2H_5 and i-C_3H_7 are considered accurate while those associated with the entropy of CH_3 are regarded as lower limits. However, it is likely that the activation energy error limits for reaction 2 are also accurate. It has been pointed out that the determination of activation energies of rate constant ratios is essentially unaffected by possible systematic experimental errors such as those associated with the calibration of detectors used to measure product yields. Such errors appear directly as systematic errors in the Arrhenius A factors of the rate constant ratios.[9c] Therefore, the Coomber and Whittle error limits for activation energies of rate constant ratios are likely to also be assessments of overall accuracy while those associated with the A factors are not.

There has been a single absolute determination of one of these Br + hydrocarbon rate constants. King, Golden, and Benson measured the thermal rate of bromination of ethane and obtained values of k_{-3} between 519 and 617 K which they fit to an Arrhenius expression, $k_{-3} = 6.6\ (\pm 1.3) \times 10^{-10} \exp\{-58.5\ (\pm 1)\ \text{kJ mol}^{-1}/RT\}$.[16] (The error limits are those of the fit of the Arrhenius function to the data.) This Arrhenius expression for k_{-3} was not used because it was obtained from experiments conducted at higher temperatures than those of k_3. Because of the need to obtain an accurate measure of E_{-3} at 370 K (see below), the method used to obtain it was considered more accurate than one that required presuming that this activation energy has the same value at 370 and 550 K.

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Table II. Thermodynamic Properties of Reactions 1–4 and Their Alkyl Radicals Determined in the Current Study[a]

reaction/ radical	reaction thermochemistry[a]			radical thermochemistry[a]	
	$-\Delta G°(370)/-\Delta G°(298)$	$-\Delta H°(370)/-\Delta H°(298)$	$-\Delta S°(370)/-\Delta S°(298)$	$\Delta H°_f(298)$	$S°(298)$
2/CH_3	55.6/59.4 (±2.5)	75.3/74.5 (±2.9)	53/51 (±15)	148 (±3)	213 (±15)
3/C_2H_5	36.6/40.5 (±1.8)	56.8/56.7 (±2.7)	54/54 (±12)	120 (±3)	260 (±12)
4/*i*-C_3H_7	25.6/29.1 (±2.1)	44.3/43.7 (±2.5)	51/49 (±13)	88.0 (±2.5)	294 (±13)
1[b]/*t*-C_4H_9	18.4/21.6 (±0.4)	34.5/35.2 (±1.7)	43/46 (±7)	48.6 (±1.7)	316 (±7)

[a] Units used for energy are kJ mol^{-1} and for entropy are J mol^{-1} K^{-1}. [b] Entries for reaction 1 taken from ref 11.

Steps 3–6 are similar to those used by others[9c] and in part 1[11] (where they are discussed in more detail). The thermodynamic properties of CH_3, C_2H_5, and *i*-C_3H_7 determined by the procedure described below are given in Table II.

3. The Arrhenius activation energies are associated with the actual activation energies for these reactions near the middle of the temperature range of the investigation of reactions 2–4 (370 K). (This same temperature is also in the range of all the measured rate constant ratios used to determine k_{-2} to k_{-4}.) $\Delta H°(370)$ for reactions 2–4 was obtained from the differences in activation energies for the forward and reverse reactions.

4. $\Delta G°(370)$ for each reaction studied was calculated from the equilibrium constant at this temperature by using the appropriate Arrhenius expressions for the forward and reverse reactions; e.g., $K_2(370) = k_2(370)/k_{-2}(370)$. The entropy changes at 370 K were also calculated by using the appropriate values of $\Delta H°(370)$ and $\Delta G°(370)$.

5. Tabulated heat capacity functions were used to calculate $\Delta G°(298)$, $\Delta H°(298)$, and $\Delta S°(298)$ for reactions 2–4 from the values of these variables at 370 K.[17,18]

6. Known heats of formation and entropies of Br, HBr, and RH (CH_4, C_2H_6, and C_3H_8) were used to determine the enthalpy of formation and entropies of CH_3, C_2H_5, and *i*-C_3H_7.[17]

Discussion

I. Comparison of Measured Rate Constants with Values Obtained in Prior Studies. Prior determinations of R + HBr rate constants are few. Those that have been made are based almost entirely on determinations of rate constant ratios. In these cases, the rate constant of the reference reaction (typically R + I_2) is itself not known. Data compilations that have listed R + HBr rate constants derived from these kinds of investigations have had to rely on a calculated value of the CH_3 + I_2 rate constant based on simple collision theory determinations of the Arrhenius *A* factor and an assumed activation energy.[20] No detailed comparisons with these determinations will be made here.

There have been two studies that have reported absolute determinations of k_2. One yielded a value a factor of ≈2 lower than was obtained in the current study and one a factor of ≈2 higher. Gac, Golden, and Benson studied the CH_3 + DBr reaction between 608 and 1000 K using a very low pressure pyrolysis reactor.[21] The measured rate constants in this temperature range were found to be essentially temperature independent (3.2×10^{-13}). With the authors' suggested primary isotope effect for the reaction, $k(CH_3 + HBr)/k(CH_3 + DBr) = 1.5$, a value of 4.8×10^{-13} for k_2 is obtained. This value of k_2 is about half that indicated by the temperature dependence of k_2 determined in the current study. Were the actual isotope effect larger (the value of 1.5 is an estimate by the authors), agreement would be better.

Donaldson and Leone[22] have determined the CD_3 + HBr rate constant at 300 K from time-resolved measurements of the chemiluminescence emitted by the vibrationally excited CD_3H produced by this reaction. The measured value ($(4.7 \pm 0.4) \times 10^{-12}$), when converted to a CH_3 + HBr rate constant using the secondary isotope effect ratio of 1.2 (determined by Donaldson and Leone[22] as well as in the current study), yields a value of $(3.8 \pm 0.4) \times 10^{-12}$ for k_2. The separation between this value and that determined in the current investigation ($(1.5 \pm 0.2) \times 10^{-12}$) at this temperature is larger than can be accounted for by the respective rate constant error limits.

A possible cause of this latter difference in measured values of k_2 is not apparent. In chemiluminescence experiments of this kind involving detection of emission from several vibrational states, as was used in the study of Donaldson and Leone,[22] data analysis must rely on the assumption that there is no cascading of the vibrationally excited product, i.e., that deactivation by collisions is "strong". In a recent study of the Cl + HBr reaction, Dolson and Leone avoided this potential problem by monitoring selected emission from the highest of the populated states of HCl (v = 2 alone).[23] The true rate constant for this reaction was slightly *higher* (20–30%) than the apparent one obtained when the total emission (from v = 1 and 2) was monitored. Interference from cascading cannot be invoked as a possible cause of disagreement in measured values of k_2 unless this interference can be more severe and unless it can also result in raising the apparent rate constant instead of lowering it.

II. Heats of Formation Derived from Bromination Experiments. Studies of thermal and photochemical bromination processes have been used for over 40 years (since the first investigation of this sort by Kistiakowsky and Van-Artsdalen[24]) to obtain information on the kinetics of reaction A, which could be used to determine

$$R + HBr \rightleftharpoons R\text{-}H + Br \qquad (A)$$

the heat of formation of the free radical R.[1,5,9,11,25] In all studies prior to the current one (and part 1), presumed values of the R + HBr activation energies have been used to determine the enthalpy change of reaction A and the heat of formation of R. These presumed values, which have been obtained from measured activation energy differences between R + HBr and R + Br_2 reactions (and more recently from activation energy differences between R + HBr and R + I_2 reactions[5]) have all been positive numbers. Currently these activation energies are believed to all be in the range 8 ± 4 kJ mol^{-1}.[5]

It is now apparent from the measured R + HBr activation energies that lower heats of formation of the alkyl radicals (C_2H_5 to *t*-C_4H_9) were obtained in prior studies of reaction A because the presumed R + HBr activation energies used to determine them were 10–15 kJ mol^{-1} too high. The new direct determinations of heats of formation and entropies of the alkyl radicals from studies of reaction A yield values that are in complete accord with others obtained from kinetic studies of dissociation–recombination equilibria.[12,13] (or with knowledge of the free-radical structures and internal motions in the case of the entropies). (See below and Table III.)

Below, the values obtained for the heats of formation and entropies of CH_3, C_2H_5, and *i*-C_3H_7 are compared with those obtained or derivable from other studies. The numbers in par-

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(17) Thermodynamic functions "$S°(T)$, $\Delta H°_f(T)$, and $C°_p(T)$" for Br, HBr, CH_4, C_2H_6, and C_3H_8 were taken from ref 19.

(18) For the free radicals CH_3, C_2H_5, and *i*-C_3H_7, the thermodynamic functions $C°_p(T)$ were taken from ref 19.

(19) Burcat, A. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984; Chapter 8.

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(25) Benson, S. W.; Kondo, O.; Marshall, R. M. *Int. J. Chem. Kinet.* **1987**, *19*, 829.

Table III. Comparison of Measured Heats of Formation of Alkyl Radicals with Other Determinations and Assessments

	heats of formation, kJ mol^{-1}			
radical	current study	Tsang assessment[a]	from iodination kinetics[b] (recalculated)	other recent determinations or evaluations
CH_3	148 (±3)		148	147[c] 149[d]
C_2H_5	120 (±3)	119.5 (±2.5)	(118–123)	119,[e] 117[f] 117[g]
i-C_3H_7	88 (±3)	93.3 (±2.5)	(88–93)	
t-C_4H_9	48.6 (±1.7)	51.7 (±2.2)	(44–49)	47.3 ± 4[h] 40 ± 2 (48 ± 2)[i]

[a] C_2H_5 entries from ref 12; others from ref 13. [b] Redeterminations of heats of formation from kinetic studies of iodination processes (original values in ref 4) using reassessments of $R + I_2$ activation energies (see text). Numbers do not include error limits of original studies. Ranges indicate only stated uncertainties for $R + I_2$ activation energies. [c] Reference 26. [d] Reference 27. [e] Reference 29. [f] Reference 31. [g] Reference 30. [h] Reference 56. [i] Reference 25. Study of reaction 1. Number in parentheses is recalculation using measured activation energy of t-C_4H_9 + HBr reaction (ref 11).

entheses for heats of formation all have units of kJ mol^{-1} and those of entropy all have units of J mol^{-1} K^{-1}.

CH_3 Heat of Formation. The study of the thermochemistry of CH_3 provides a stringent test of the accuracy of the Arrhenius parameters of rate constant ratios that were used to determine the Br + Hc rate constants and subsequently the thermodynamic properties of CH_3, C_2H_5, and i-C_3H_7. Both the heat of formation and entropy of CH_3 are accurately known, making very quantitative comparisons of thermodynamic functions possible. Four rate constant ratios from two sources were used to determine ΔH°_f and S° for CH_3 (only two were required, both from the same source, to obtain the C_2H_5 thermodynamic variables, and only one ratio was needed to determine the i-C_3H_7 enthalpy of formation and entropy).

The measured heat of formation of CH_3 (148 ± 3) is in very close agreement with the currently most directly measured value (147 ± 0.4) reported by Heneghan, Knoot, and Benson from a study of the equilibrium $Cl + CH_4 \rightleftharpoons CH_3 + HCl$.[26] A slightly higher value (149 ± 0.4) has been obtained by Chupka in a study of the photoionization of methane.[27]

The measured entropy for CH_3 (213 ± 15) is not in agreement with the accurately known calculated value (194).[28] The correct value lies just below the lower limit of the measured one. As was discussed above, two of the rate constant ratios required for the calculation of the heat of formation and entropy of CH_3 had reported error limits that were not assessments of accuracy and should more properly be regarded as lower limits of uncertainty. Thus this disagreement in entropies was not unexpected. (This ambiguity regarding the interpretation and use of error limits does not arise in the studies involving the other two free radicals for the reason discussed above.)

The very good agreement between the heat of formation of CH_3 determined here and the most direct prior determinations is confirmation that measurements of relative rate constants in systems that are free of kinetic complications do yield very accurate determinations of activation energy differences.[9c] These results obtained for CH_3, taken together with the fact that more favorable and direct calculations were possible to obtain the thermodynamic variables of C_2H_5 and i-C_3H_7, provide support for the stated accuracies of the heats of formation and entropies of these two free radicals.

C_2H_5 Heat of Formation. The C_2H_5 heat of formation obtained in this investigation (120 ± 3) is in very close agreement with the most direct determination to date, the study of reaction 2 by Brouard et al., who obtained a similar value (118.6 ± 1.7).[29]

Recent reviews and reassessments of the results of prior kinetic studies connected with equilibria involving C_2H_5, equilibria not involving halogenation processes, have all concluded that the heat of formation of this radical must be in a narrow range (117–121) to reconcile the results obtained for rate constants of the forward and reverse processes.[12,30–32]

The measured entropy obtained for C_2H_5 (260 ± 15) is also in accord with the calculated value (247).[29] The largest contribution to the error limits associated with the measured entropy is from the combined uncertainties in the *A* factors of the rate constant ratios required to determine this entropy.

i-C_3H_7 Heat of Formation. Tsang has calculated heats of formation for i-C_3H_7 from the results of eight kinetic studies that (when combined with related kinetic data for the reverse reactions) were used to obtain equilibrium constants for two processes: either (I) $(i\text{-}C_3H_7\text{–})_2 \rightleftharpoons 2i\text{-}C_3H_7$ or (II) $i\text{-}C_3H_7 \rightleftharpoons C_3H_6 + H$.[13] The results of these analyses yielded values for the i-C_3H_7 heat of formation in two narrow adjacent ranges (89.0–92.5) from studies of equilibrium I and (92.3–94.8) from investigations related to equilibrium II. A nonweighted average of these eight determinations was the basis for the recommended heat of formation of i-C_3H_7 (93.3 ± 3.8). The value obtained in the current investigation (88.0 ± 2.5) is in agreement with Tsang's reassessment (but see below).

The measured entropy for i-C_3H_7 (294 ± 13) is close to a calculated value obtained by using current knowledge of the structure and internal motions of this radical.[28,33] Tsang has calculated a value (290) that is based on current spectroscopic evidence.[13] This value may be a slight overestimate since it involves assuming a free rotation for the two methyl groups. A small energy barrier (≈0.5) for this rotation is considered likely.[34] Such a barrier would lower the entropy only slightly (289) and would not change the very good agreement between measured and calculated entropies for this radical.

Since Tsang's calculations were all third-law determinations of the i-C_3H_7 heat of formation, they depend on the entropy chosen for this radical. It is thus more appropriate to compare free energies of formation for i-C_3H_7 which Tsang could determine using only the kinetic data he considered. Such a comparison yields a difference in free energies of formation for i-C_3H_7 (6.6) that is still just within the stated uncertainties of these two studies.

The fact that studies of the two equilibria considered by Tsang yielded essentially adjacent narrow ranges for the heat of formation of i-C_3H_7 could be an indication that one of these groups of experiments leads to a slightly more accurate determination of the i-C_3H_7 heat of formation than the other. The free energy of formation of i-C_3H_7 obtained in the current investigation is in very good agreement with all the values derived by Tsang from equilibrium I but not with those obtained from equilibrium II. Although the disagreement in the latter case is small, less than 6 kJ mol^{-1} for the i-C_3H_7 heat of formation, it is outside the

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(27) Chupka, W. A. *J. Chem. Phys.* **1968**, *48*, 2337.

(28) Calculated entropies were obtained from ref 19 (CH_3), ref 29 (C_2H_6), and ref 13 (i-C_3H_7).

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(34) Pacansky, J. IBM Research Laboratory, San Jose, personal communication.

uncertainty limits of the current investigation. It is therefore necessary to conclude that the calculations required to obtain the free energy of formation of i-C_3H_7 from studies related to equilibrium II involve approximations or assumptions that lead to slightly less accurate determinations of this heat of formation than do those calculations related to equilibrium I.

III. Heats of Formation Derived from Iodination Experiments. The activation energies of the four R + HBr reactions studied provide new knowledge that can be used to reassess the fundamental assumption underlying the determinations of free-radical heats of formation from studies of iodination kinetics. In this section, the assumption will be broken down into two parts and discussed separately: (1) the activation energy of the $CH_3 + I_2$ reaction is zero, and (2) all $R + I_2$ activation energies are the same (implying that they are also zero).

Assumption 1. The $CH_3 + I_2$ Activation Energy. The rate constant of the $CH_3 + I_2$ reaction has never been directly measured. It is, of course, known that the reaction is extremely fast,[35] and there have been numerous estimates of its obviously low activation energy during the past 50 years, most of which are in the range 0–4 kJ mol^{-1}.[4–6,35–39]

There is evidence from numerous sources that the activation energy for the $CH_3 + I_2$ reaction is lower than that of the CH_3 + HBr reaction, from 4 to 6 kJ mol^{-1} less, the most likely value being 4 kJ mol^{-1} lower.[36,38,40] Using either the slightly *negative* CH_3 + HBr activation energy measured in the current study or the *positive* CH_3 + HCl activation energy recently determined by Heneghan, Knoot, and Benson,[26] coupled with determinations of the activation energy differences between R + HX (X = Cl, Br) and $R + I_2$ reactions measured by Williams and Ogg,[40] one calculates the same activation energy of −5.4 kJ mol^{-1} for the $CH_3 + I_2$ reaction, a value just below the lower limit of assumption 1. (Use of activation energy differences measured by others such as Andersen and Kistiakowsky[38] or Fettis and Trotman-Dickenson[36] yields a comparable negative value for this activation energy.)

An observation that has been used to support assumption 1 is that there is evidence that another free-radical reaction with I_2 ($CF_3 + I_2$) has no activation energy.[4,5] In recent years, evidence has accumulated that the activation energies of CF_3 + halogen reactions are higher than those of the corresponding CH_3 + halogen reactions.[41,42] Therefore this observation can no longer be regarded as supporting this assumption.

Assumption 2. The $R + I_2$ Activation Energies. There is an indication that the $R + I_2$ activation energies decrease significantly between $CH_3 + I_2$ and $C_2H_5 + I_2$, a change that is analogous to that observed in the R + HBr activation energies in the current study. Fettis and Trotman-Dickinson report that the $C_2H_5 + I_2$ activation energy is 9–10 kJ mol^{-1} less than that of the C_2H_5 + HBr reaction.[36] This would indicate a −13 kJ mol^{-1} activation energy for the $C_2H_5 + I_2$ reaction. (In the current study, the range −10 to −15 kJ mol^{-1} is suggested as the likely limits for this activation energy.) There is no additional direct evidence pertaining to the value of the $C_2H_5 + I_2$ activation energy. However, there is an indication that the results of Fettis and Trotman-Dickenson are accurate. In the same study, they also measured the difference in activation energies between the $CH_3 + I_2$ and CH_3 + HBr reactions. The value obtained is in good agreement with that obtained by Williams and Ogg.[40]

There have been no prior experiments that provide a measure of the activation energies of the i-$C_3H_7 + I_2$ and t-$C_4H_9 + I_2$ reactions. The R + HBr activation energies decrease significantly between CH_3 + HBr and C_2H_5 + HBr and then more gradually to the t-C_4H_9 + HBr reaction. Using this trend as a guide, we suggest that the corresponding two reactions in the $R + I_2$ series have activation energies in the −12 to −17 kJ mol^{-1} range. Direct measurement of these activation energies would be desirable not only to establish their values but also to explore the cause of these unusual temperature dependencies (see section IV).

Two observations have been offered as evidence that assumption 2 is correct. The first is that there is good agreement between values of the heats of formation for radicals other than CH_3 (e.g., C_2H_5) that were obtained from iodination and bromination experiments where, in each case, assumption 2 was made (the activation energy of the $C_2H_5 + I_2$ reaction is zero).[5,6] This argument does not provide significant support for the assumption because such bromination and iodination experiments use presumed values of R + HBr and R + HI activation energies determined from the same basic assumption. An error in assumptions 1 and 2 results in identical errors in the heats of formation obtained from the two kinds of experiments.

The second observation that has been used to support assumption 2 is that there is agreement between the allyl and benzyl radical heats of formation derived from iodination experiments (in which assumption 2 was made) and those values obtained from studies of dissociation–recombination equilibria.[5,6] A recent study has shown that the activation energies of atom-transfer reactions involving resonance-stabilized hydrocarbon radicals are higher than those of comparable reactions involving alkyl radicals.[42] Thus, the assumption that these two $R + I_2$ reaction activation energies are zero may indeed be true but still not be valid for the alkyl radicals.

Recalculation of Heats of Formation from Studies of Iodination Kinetics. Values of the CH_3 and C_2H_5 heats of formation were recalculated from the results of iodination kinetic studies[4,43,44] using the new indicated values for the $CH_3 + I_2$ and $C_2H_5 + I_2$ activation energies (values that were derived from the results of the current and prior experiments). In addition, new heats of formation for i-C_3H_7 and t-C_4H_9 were also recalculated from the results of other iodination experiments[4,45,46] using the plausible range for the i-$C_3H_7 + I_2$ and t-$C_4H_9 + I_2$ activation energies suggested above. (In these recalculations, the observed 4 kJ mol^{-1} difference between R + HI and $R + I_2$ reactions[4,5] was preserved.) These revised determinations are presented in Table III together with other measured values.

Agreement between the recalculated heats of formation of the alkyl radicals and those determined in the current investigation (as well as those reported in recent prior determinations) is excellent. (*All* the original iodination-based heats of formation are outside the stated range of uncertainty of the more current higher values.) This agreement suggests that most of the other disagreements between determinations of free-radical heats of formation from iodination studies and studies of other equilibria are largely associated with the poor accuracy of the assumed activation energies of $R + I_2$ and R + HI reactions. Once these activation energies are measured, the large body of kinetic studies of iodination processes can be used again to obtain significantly more accurate heats of formation of many polyatomic free radicals.

IV. Mechanisms of the R + HBr and $R + I_2$ Reactions. In part 1,[11] an alternate mechanism was proposed to account for the observed kinetic behavior of the t-C_4H_9 + HBr reaction, which involves an indirect H-atom transfer process, a mechanism that includes the formation of a bound intermediate that is capable of dissociating to re-form the original reactants or rearranging to form the rate-determining transition state that leads to the formation of the observed products, i-C_4H_{10} + Br. The rate constant parameters of the other three R + HBr reactions studied are in accord with what is expected from such a mechanism. The absence of a detectable pressure dependence in the measured R + HBr rate constants continues to indicate that the binding energy of the complexes is low enough to result in intrinsic lifetimes for

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these adducts that are short compared to collision frequencies below atmospheric pressure.

It is now well recognized that negative activation energies of the magnitude observed in the current study can result from apparent bimolecular reactions proceeding by such a mechanism.[47,48] Recently such behavior has been modeled for a reaction between a free radical and a stable molecule, OH + HNO_3.[49]

The results of the current study provide new support for such a mechanism for all the R + HBr reactions studied. The activation energies *decrease* as the reaction becomes less exothermic. It is apparent from this trend alone that there are strong attractive forces between the reactants, forces that increase in magnitude with the size of the alkyl radical and that are capable of reducing the potential energy along the reaction coordinate to such a degree that the expected opposite trend in activation energies associated with the reaction thermochemistry is not only suppressed but completely reversed.

The Arrhenius parameters for the four R + HBr reactions reveal that this increase in reactivity proceeding from CH_3 to $t\text{-}C_4H_9$ + HBr is associated essentially entirely with a lowering of the activation energy. If the R + HBr reactions, which have no energy barriers along the reaction coordinate, proceeded via an *irreversible* mechanism (such as a conventional H-atom metathesis), this increase in reactivity would be associated with another factor, a major increase in the rate constant for the formation of the bound intermediate (e.g., as is the case for R + O_2 reactions[50] below the ceiling temperature and also R + O_3 reactions[51]). These rate constant increases are directly associated with the increase in the range of the dispersion forces between reactants in such a homologous series and are manifested in the values of the Arrhenius *A* factors (the activation energies are all essentially zero). In the proposed R + HBr mechanism, the preequilibrium between the reactants and the adduct makes the overall reaction rate constant insensitive to the rate constant for the formation of the adduct.

As was discussed in part 1,[11] there is ample evidence that reactions involving both atoms and free radicals with halogen-containing diatomic molecules proceed via the formation of a bound intermediate. In the case of the R + I_2 reactions, such bound intermediates now also seem indicated by the apparent temperature dependencies of their rate constants. Evidence for such bound species has been reported ($H\cdot I_2$[52] and $O\cdot I_2$[53]) or suspected (e.g., as the cause of the low CH_3 + I_2 activation energy[4]). In a detailed investigation of dynamics of the CH_3 + I_2 reaction, Hoffmann et al. found no evidence of a $CH_3\cdot I_2$ bound intermediate (one that lived longer than one rotational period under the conditions of the study) in their molecular beam investigation of this reaction.[54] The relative translational energy for the reactants was ≈30 kJ mol^{-1}. It is possible that a weakly bound $CH_3\cdot I_2$ adduct, one adequate to explain the apparent kinetic behavior of the CH_3 + I_2 reaction under thermal conditions (relative kinetic energies of the reactants <3 kJ mol^{-1}), was simply not detectable in these experiments.

Summary

In the current study of the kinetics of R + HBr reactions (including part 1[11]), negative activation energies were obtained for the four reactions investigated (R = CH_3, C_2H_5, $i\text{-}C_3H_7$, and $t\text{-}C_4H_9$) which decrease from -1.3 ± 0.9 kJ mol^{-1} for the CH_3 + HBr reaction to -5.8 ± 0.9 kJ mol^{-1} for the $t\text{-}C_4H_9$ + HBr reaction. The measured rate constants for these reactions and determinations of the reverse rate constants from prior kinetic measurements were used to calculate the heats of formation and entropies of all four free radicals. The determinations of the $i\text{-}C_3H_7$ heat of formation and entropy are the most direct to date. These second-law determintions of thermodynamic properties of the alkyl radicals are in very good agreement with current assessments of heats of formation based on kinetic studies of other types of equilibria and entropies derived from current knowledge of the structures and internal motions of these free radicals.

The results of these studies have directly provided an explanation for the disparities that heretofore had existed between heats of formation derived from bromination studies and those based on investigations connected with equilibria not involving the halogens. The presumed activation energies (≈8 kJ mol^{-1}) for R + HBr reactions that had been used to determine heats of formation from the kinetic measurements were 10–14 kJ mol^{-1} too high.

A comparable explanation with supporting evidence was also presented to account for the origin of the disparities that still exist between the heats of formation of the alkyl radicals obtained from measurements of the rates of iodination processes and those derived from studies of the kinetics of other systems. The indicated source is again the assumption required to obtain heats of formation from these kinetic measurements, the assumption that all R + I_2 reactions have activation energies in the range 0 ± 4 kJ. There is now evidence from kinetic studies that the CH_3 + I_2 reaction has an activation energy very close to -5 kJ mol^{-1} and that of the C_2H_5 + I_2 reaction is within the range -10 to -15 kJ mol^{-1}. It is suggested on the basis of the trends in the R + HBr rate constants that the $i\text{-}C_3H_7$ + I_2 and the $t\text{-}C_4H_9$ + I_2 activation energies are slightly more negative still, in the range -12 to -17 kJ mol^{-1}. When these assessments of the R + I_2 activation energies are used to recalculate the heats of formation of the four alkyl radicals from the results of the iodination experiments, higher values are obtained that are in very good agreement with values derived from studies of other chemical equilibria (ones not involving halogenation processes).

To account for these negative activation energies, the kinetic results have been interpreted in terms of a more complex mechanism, one involving the reversible formation of a bound intermediate. There has been a reluctance to accept the existence of significant negative activation energies for these and other apparent direct atom transfer reactions based on the large amount of evidence from both experimental and theoretical studies that such reactions do not have significant negative activation energies even if they proceed along a purely attractive potential. The current study now provides an example of one group of reactions (R + HBr → R–H + Br) that has the proper stoichiometry of an atom-transfer process but whose reactions not only have negative activation energies but also display a trend in the magnitudes of their activation energies that is entirely counter to that expected for direct atom transfer processes.[55] The explanation used to account for this unusual kinetic behavior involves a more complex mechanism, one that does not propose exceptions to what is known about the kinetics of direct atom transfer processes.

Additional studies of the kinetics and dynamics of R + I_2 reactions and others involving hydrocarbon free radicals and halogen-containing diatomic molecules are needed to provide a more quantitative and complete picture of the mechanisms of these interesting reactions.

It is probable that these sets of reactions have ranges of activation energies that span the values that have been assumed to date. This could account for the agreements between heats of formation from iodination studies and those from other kinds of investigations in some cases (e.g., allyl, benzyl, CF_3, HCO, and phenyl) and the disagreements in others (e.g., the alkyl radicals).

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Acknowledgment. The research was supported by the National Science Foundation under Grant CHE-8318481. J.A.S. thanks the Natural Science Research Council of the Academy of Finland and The Alfred Kordelin Foundation for fellowships. We appreciate useful discussions of this research with W. Tsang, D. Golden, S. W. Benson, and J. Pacansky. We also thank Dr. I. R. Slagle for her advice, help, and support.

Registry No. H_2, 1333-74-0; $CH_3^{\bullet}$, 2229-07-4; $C_2H_5^{\bullet}$, 2025-56-1; *i*-$C_3H_7^{\bullet}$, 2025-55-0; HBr, 10035-10-6; D_2, 7782-39-0; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; Br, 10097-32-2; I_2, 7553-56-2; *t*-$C_4H_9^{\bullet}$, 1605-73-8; acetone, 67-64-1; acetone-d_6, 666-52-4; diethyl ketone, 96-22-0; diisopropyl ketone, 565-80-0.

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2 + 1 REMPI Spectra of Cyclic Ketones in a Cold Molecular Beam. 2. The n → 3s Rydberg Transition of Methyl-Substituted Cyclohexanones and Cyclopentanones

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Abstract: The two-photon excitation of the n → 3s Rydberg transition in monomethyl and dimethyl isomers of cyclohexanone and cyclopentanone has been studied by resonance enhanced multiphoton ionization (2 + 1 REMPI). This transition has been found to be highly sensitive to both the orientation and position of methyl substituents on the cyclic ketone ring. Cis and trans configurations of dimethyl isomers show characteristic 3s transition energy shifts which are additive in nature and can be used to predict the transition energy of other structures. The spectroscopic energies of configurational isomers appear to reflect relative ground-state stabilities. This correlation has been supported by thermodynamic data and molecular mechanics calculations of ground-state energies. Laser polarization effects are found to be useful in determining the degree of chromophore asymmetry in chiral molecules.

I. Introduction

Recent advances in laser and molecular beam technology have enabled the high resolution examination of ultraviolet transitions in large molecules. In the past, solution phase electronic absorption has been of limited value for structural analysis due mainly to broad absorption bands and complicated spectral congestion. However, numerous recent studies of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of aromatics and heterocycles in cold molecular beams have shown the electronic spectrum to be highly sensitive to structure and location of alkyl substituents at various ring positions.[1,2a] The present study shows that the n → 3s transition of saturated cyclic ketones is particularly sensitive to molecular configuration. In fact, the relative shifts of the 3s transition energies in methyl-substituted cyclic ketones can be correlated with the ^{13}C NMR chemical shifts of the carbonyl carbons in the same series of isomers. This relationship will be discussed in a future publication.[3]

Since hot ro-vibrational transitions are greatly reduced in cold molecular beam spectroscopy, the severe spectral congestion normally observed in electronic spectra is dramatically simplified. If the transitions are chosen so that little nuclear reorientation occurs in the excited state (such as in the promotion of a nonbonding electron to nonbonding orbitals), the resulting vibrational spectrum is rather uncomplicated compared to the ground-state IR spectrum since only those frequencies which change upon excitation are observed. Once identified, these vibrational modes aid in determing both ground- and excited-state molecular structure.

The electronic levels observed in resonance enhanced multiphoton ionization (REMPI) are predominantly long-lived Rydberg orbitals. These states, located in the far and vacuum UV spectral regions, are often obscured by overlapping valence transitions in conventional one-photon absorption. Since the REMPI signal is dependent upon long lifetimes of the intermediate state, valence levels are normally suppressed in the MPI spectrum[4] due to the dissociative nature of antibonding orbitals. The atomic-like Rydberg states have received less attention than the lower energy valence shell orbitals so that little is known about their sensitivity to molecular structure compared to the shifts observed in chromophores absorbing in the near UV and visible spectral regions.

We have investigated the REMPI spectrum of cyclic ketones through the intermediate 3s Rydberg state for the purpose of studying the transition's sensitivity to stereochemistry. The Rydberg spectrum is generated by scanning a dye laser across an easily accessible wavelength region (380–420 nm) producing the desired resonance ionization through a two-photon absorption to the 3s state. In a previous study,[5] this transition was examined in unsubstituted cyclic ketones of various ring sizes. The samples were seeded in a cold molecular beam and ionized by using a 2 + 1 REMPI scheme. Briefly, the results included the following points. The promotion of the nonbonding electron to the 3s Rydberg state was found to have a significant effect on the carbonyl geometry. The C=O stretching frequency was reduced from about 1730 cm^{-1} in the ground state to approximately 1250 cm^{-1} in the 3s state, a decrease that is consistent with an increased C=O bond length in the excited state. In addition, the electronic transition is accompanied by the excitation of low-frequency ring bending and torsional modes which appear to be a consequence of sp^2 hybridization relaxation in the excited state and subsequent reorientation to a less strained geometry. The shift in the 3s transition origin was found to correlate with the C–CO–C bond angle, reflecting the release of angle strain. Laser polarization effects characteristic of two-photon transitions were used to aid in the identification of some excited state vibrational modes. In this study, we have examined the n → 3s transition of methyl-substituted isomers of cyclohexanone and cyclopentanone. The array of spectroscopic parameters studied includes the shift in the

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