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# Kinetics and Thermochemistry of the Reactions of Alkyl Radicals ($CH_3$, $C_2H_5$, *i*-$C_3H_7$, *s*-$C_4H_9$, and *t*-$C_4H_9$) with HI: A Reconciliation of the Alkyl Radical Heats of Formation

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**Abstract:** The kinetics of the reactions of $CH_3$, $C_2H_5$, *i*-$C_3H_7$, *s*-$C_4H_9$, and *t*-$C_4H_9$ with HI were studied in a tubular reactor coupled to a photoionization mass spectrometer. Rate constants were measured as a function of temperature (typically between 295 and 648 K) to determine Arrhenius parameters. These results were combined with determinations of the rate constants of the reverse reactions (I + hydrocarbon) determined previously by others to obtain equilibrium constants for the following reaction: R + HI ⇔ R-H + I. Second and Third Law based analyses using these equilibrium constants yielded heats of formation for the five alkyl radicals whose R + HI reactions were studied. The Third Law heats of formation (obtained using calculated entropies) are extremely accurate, within ±2 kJ $mol^{-1}$ of the current best values. (The Second Law heats of formation are less accurate, within ±8 kJ $mol^{-1}$ of the current best values.) Each of the R + HI reaction rate constants has a negative activation energy, decreasing from −1 kJ $mol^{-1}$ for the $CH_3$ + HI reaction to −6 kJ $mol^{-1}$ for the *t*-$C_4H_9$ + HI reaction. The cause of the long-standing disparity that has existed between the heats of formation of the alkyl radicals derived from studies of R + HI ⇔ R-H + I equilibria and those obtained from investigation of dissociation-recombination equilibria has been identified. It is the difference between the assumed generic activation energy of R + HI rate constants (4 kJ $mol^{-1}$) that had been used in all prior thermochemical calculations and the actual values of these activation energies. A complex mechanism for R + HI reactions that is consistent with the observed kinetic behavior of these reactions is discussed.

Equilibria involving the reactions of polyatomic free radicals (R) with the hydrogen halides (HX: X = Cl, Br, I) have been studied for over 45 years to obtain information on the thermochemistry of the radicals involved.[1-7] In particular, the kinetics of the reactions

$$R + HI \Leftrightarrow RH + I \qquad (1)$$

have been investigated extensively to obtain the heats of formation of a large number of labile intermediates, particularly hydrocarbon free radicals. These studies have all involved determinations of the enthalpy change of reaction 1 from the difference in the activation energies of the forward and reverse reactions.

To date, in virtually each investigation of this kind, $\Delta H°$ for reaction 1 was obtained by combining a measured activation energy of the I + RH reaction with an *assumed* activation energy for the reverse process, the R + HI reaction.[4,5,7] From knowledge that R + HI reactions are generally quite rapid and from the presumption that H-atom transfer reactions cannot have negative activation energies, it has generally been assumed that all R + HI reactions must have activation energies very near zero, more specifically, within the narrow range 4 ± 4 kJ $mol^{-1}$.[4,5,7]

There is now reason to believe that this assumed generic activation energy for R + HI reactions can be significantly in error, by perhaps up to 10 kJ $mol^{-1}$ in selected cases. Such an error translates directly into an analogous error in the heat of formation of R. We have recently investigated the kinetics of four R + HBr reactions involving alkyl radicals and discovered that, in each case, the reaction rate constant has a negative activation energy,[8,9] as low as −6 kJ $mol^{-1}$ in the case of the *t*-$C_4H_9$ + HBr reaction.[8] Since R + HI reactions are still more rapid than R + HBr reactions,[10] the likelihood exists that the former reactions also have significant negative activation energies.[6,11,12]

A well-known disparity exists among the heats of formation of polyatomic free radicals (particularly the alkyl radicals) that have been determined in investigations involving different equilibria. Investigators who have used reaction 1[4-6] generally obtained values that are 4–12 kJ $mol^{-1}$ lower than those who obtained their results from studies of dissociation-recombination equilibria:[11,12]

$$R\text{-}R' \Leftrightarrow R + R' \qquad (2)$$

$$R \Leftrightarrow \text{olefin} + H \text{ (or } CH_3) \qquad (3)$$

In our recent investigations of the kinetics of R + HBr reactions,[8,9] we demonstrated that this disparity (when X = Br) originates entirely from the difference between the measured R + HBr activation energies and the generally assumed value for all R + HBr reactions[5] (8±4 kJ $mol^{-1}$) used in prior investigations to determine free radical heats of formation.

We have now begun to investigate the kinetics of R + HI reactions, in part to determine more accurately the heats of formation of many free radicals for which there already exists accurate kinetic information on the reverse reactions. In addition, we hope to obtain some understanding of the dynamics of these reactions from their kinetic behavior. The significant negative activation energies may be an indication that these reactions are proceeding by a mechanism that is more complex than direct H-atom metathesis, a suggestion also made in our study of the kinetics of R + HBr reactions.[8,9]

We have now investigated the kinetics of five R + HI reactions.

$$CH_3 + HI \rightarrow CH_4 + I$$
$$\Delta H° = -140 \text{ kJ mol}^{-1} \qquad (4)$$

$$C_2H_5 + HI \rightarrow C_2H_6 + I$$
$$\Delta H° = -122 \text{ kJ mol}^{-1} \qquad (5)$$

$$i\text{-}C_3H_7 + HI \rightarrow C_3H_8 + I$$
$$\Delta H° = -113 \text{ kJ mol}^{-1} \qquad (6)$$

$$s\text{-}C_4H_9 + HI \rightarrow n\text{-}C_4H_{10} + I$$
$$\Delta H° = -116 \text{ kJ mol}^{-1} \qquad (7)$$

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$$t\text{-C}_4\text{H}_9 + \text{HI} \rightarrow i\text{-C}_4\text{H}_{10} + \text{I}$$
$$\Delta H^\circ = -103 \text{ kJ mol}^{-1} \qquad (8)$$

Rate constants were measured as a function of temperature using a heatable tubular reactor coupled to a photoionization mass spectrometer. The results of this investigation are reported here together with an analysis of the thermochemistry of these reactions derived from the measured rate constants and those obtained previously by others for the reverse reactions.

There have been surprisingly few prior investigations of the kinetics of these or any other R + HI reactions, particularly studies that have been able to isolate the reaction of interest for direct investigation. Older studies, ones that have yielded ratios or functions of rate constants involving those of particular R + HI reactions, have been reviewed.[3-5,10,13] In the most direct investigation to date, Donaldson and Leone have obtained the rate constant of the $CD_3$ + HI reaction at room temperature from experiments in which $CD_3$ was produced by the pulsed photolysis of $CD_3I$ and the production of the vibrationally excited product, $CD_3H^*$, was monitored by detecting its infrared emission in time-resolved experiments.[10]

Using a very-low-pressure well-stirred reactor, Rossi and Golden,[14-16] as well as Müller-Markgraf et al.,[17] have investigated the kinetics of three R + HI reactions: R = allyl, benzyl, and $t$-$C_4H_9$. The study by Müller-Markgraf et al. obtained the $t$-$C_4H_9$ + DI as well as the $t$-$C_4H_9$ + DBr rate constants at two temperatures. While the measured rate constants at a single temperature varied widely (as much as a factor of 3), the authors found adequate indications to conclude that both rate constants have activation energies, presumably ones within the range of the assumed values. There are major disagreements between the $t$-$C_4H_9$ + DBr (and DI) rate constants obtained by Müller-Markgraf et al. (properly corrected for isotope effects) and those we obtained in our investigations of the same reaction,[8] as large as a factor of 25! This disagreement is addressed in this paper.

## Experimental Section

Rate constants for reactions 4–8 were measured as a function of temperature. The experimental facility[19] as well as its use for kinetic studies of this type[8,9] has been described in detail elsewhere. Only a summary will be presented here. Pulsed unfocused 193- or 248-nm radiation from a Lambda Physik EMG 101E exciplex laser was collimated and then directed along the axis of a heatable 1.05 cm i.d. coated Pyrex tubular reactor. Gas flowing through the tube at 5 m $s^{-1}$ was completely replaced between laser pulses. The flowing gas contained the free radical precursor in very low concentration (typically 0.001%), HI in varying amounts, and the carrier gas, He or $N_2$, in large excess (>98%). Gas was sampled through a 0.4-mm-diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and then mass selected. Temporal ion signal profiles were recorded from a short time before each laser pulse to as long as 26 ms following the pulse with a multichannel scalar. Data from 2000–30000 repetitions of the experiment were accumulated before the data were analyzed.

Experiments were conducted under conditions where only two significant reactions consumed the labile reactant R.

$$\text{R} + \text{HI} \rightarrow \text{RH} + \text{I} \qquad (9)$$

$$\text{R} \rightarrow \text{heterogeneous loss} \qquad (10)$$

In all sets of experiments conducted to determine a reaction rate constant, tests were also conducted to ensure that radical–radical or radical–atom reactions had negligible rates compared to either reaction 9 or 10. Initial concentrations of R were reduced until the measured atom or radical decay constants in the presence or absence of the stable reactant no longer depended on the initial radical precursor concentration or on the laser fluence. Typically, the initial concentration of R was in the range 1–10 × $10^{10}$ molecule $cm^{-3}$.

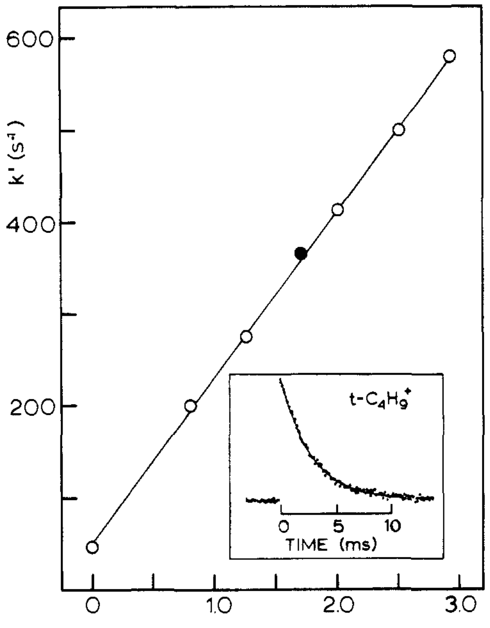

**Figure 1.** Plot of first-order decay constants $k'$ vs [HI] for one set of experiments conducted to measure $k_8$, the $t$-$C_4H_9$ + HI rate constant at 480 K. (For additional information, see Table I.) The insert is the actual ion signal profile of $t$-$C_4H_9^+$ recorded during one of the plotted experiments ([HI] = 2.1 × $10^{13}$ molecule $cm^{-3}$). The line through the data is an exponential function fitted by a nonlinear least-squares procedure. The first-order decay constant ($k'$) for $t$-$C_4H_9$ in the displayed ion signal profile is 350 $s^{-1}$.

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

The stable reactant, HI, was always in great excess over the initial concentration of R. Rate constants for reactions 4–8 were obtained from slopes of plots of the exponential radical decay constant ($k'$, from $[R] = [R]_0 \exp(-k't)$) vs [HI]. A representative ion signal decay profile and decay constant plot from one set of experiments to measure $k_8$ are shown in Figure 1.

One set of experiments was conducted in which the $CH_3$ + HI and $CD_3$ + HI rate constants were simultaneously determined in order to obtain the ratio of their rate constants as accurately as possible. This information was needed to compare our $CH_3$ + HI rate constants with the $CD_3$ + HI rate constants obtained by Donaldson and Leone.[10] The experiment involved flowing both the $CH_3$ and $CD_3$ precursors (acetone and acetone-$d_6$) through the system at the same time and monitoring alternately the $CH_3$ and $CD_3$ decays at each HI concentration.

The results obtained from all experiments are given in Table I. The rate constants obtained for reactions 4–8 are also displayed on an Arrhenius plot in Figure 2.

For each reaction studied, conditions that were not expected to influence the determination of thermal R + HI rate constants were varied to test for possible interferences in these experiments. UV photolysis produces the radicals of interest with an excess of internal energy. From what is known about vibrational deactivation of alkyl radicals,[20] there is reason to believe that, under all our experimental conditions, this relaxation occurs rapidly (<0.5 ms) compared to the observed reaction time (11–26 ms). To vary the degree of internal energy of R or the vibrational relaxation time, experiments were conducted (on a selective basis) with different free radical precursors, different photolysis wavelengths, different bath gases (e.g., $N_2$ instead of He), and different total gas densities (in which the bath gas pressure was altered without changing the pressure of the reactants). While not all of these parameters were varied in the study of each R + HI reaction, it was always found that, when these

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**Table I** Conditions and Results of Experiments to Measure Rate Constants of R + HI Reactions, $k_4$–$k_8$

| $T$,[a] K | $10^{-16}$[M], molecule cm$^{-3}$ | $10^{-13}$[HI], molecule cm$^{-3}$ | $k_w$, s$^{-1}$ | wall coating material[b] | $10^{12}k_{4-8}$, cm$^3$ molecule$^{-1}$ s$^{-1}$ | $T$,[a] K | $10^{-16}$[M], molecule cm$^{-3}$ | $10^{-13}$[HI], molecule cm$^{-3}$ | $k_w$, s$^{-1}$ | wall coating material[b] | $10^{12}k_{4-8}$, cm$^3$ molecule$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ + HI Reaction ($k_4$) | | | | | | | | | | | |
| 292 | 5.79 | 0.6–2.98 | 20 | HW | 7.32 | 383 | 5.90 | 0.88–3.78 | 26 | FHW | 6.16 |
| | 5.81 | 1.13–3.44 | 7.1 | HW | 7.13 | 419 | 5.91 | 1.50–5.51 | 11 | T | 6.11 |
| 293 | 2.80 | 1.05–3.04 | 19 | HW | 7.71 | 427 | 5.81 | 1.83–4.52 | 13 | N | 5.94 |
| | 5.77 | 0.91–3.72 | 22 | HW | 7.17[c] | 474 | 5.90 | 0.97–5.78 | 4.2 | T | 6.03 |
| 294 | 20.1 | 1.15–3.39 | 26 | HW | 7.25 | 483 | 5.79 | 1.21–4.88 | 13 | N | 5.80 |
| | 19.9 | 0.71–3.15 | 15 | HW | 6.99[d] | 541 | 5.90 | 1.85–6.10 | 11 | T | 5.95 |
| | 5.82 | 1.57–4.19 | 5.4 | T | 7.44 | 554 | 5.76 | 1.24–5.03 | 14 | N | 5.69 |
| 319 | 5.81 | 1.00–3.49 | 26 | HW | 7.02 | | 5.76 | 1.19–5.10 | 10 | N | 5.75 |
| | 5.83 | 0.88–3.64 | 17 | HW | 7.10 | 648 | 5.73 | 0.97–5.01 | 12 | N | 6.00 |
| 344 | 5.91 | 0.83–3.25 | 11 | T | 6.61 | | | | | | |
| 348 | 5.86 | 1.04–3.17 | 29 | HW | 6.55 | | | | | | |
| | 5.84 | 1.10–3.54 | 18 | FHW | 6.50 | | | | | | |
| $k_4 = (4.5 \pm 0.8) \times 10^{-12} \exp((1.2 \pm 0.6)\ \text{kJ mol}^{-1}/RT)$ | | | | | | | | | | | |
| $CD_3$ + HI Reaction | | | | | | | | | | | |
| 293 | 5.77 | 0.91–3.72 | 21 | HW | 7.25[c] | | | | | | |
| $C_2H_5$ + HI Reaction ($k_5$) | | | | | | | | | | | |
| 294 | 5.76 | 0.51–2.91 | 15 | HW | 16.6 | | 5.81 | 0.95–3.35 | 17 | FHW | 14.1 |
| 295 | 19.9 | 0.57–2.88 | 19 | HW | 16.6 | 383 | 5.85 | 0.82–3.45 | 12 | FHW | 12.4 |
| | 2.37 | 0.52–2.14 | 9.2 | HW | 17.7 | 419 | 5.93 | 1.14–4.16 | 11 | T | 11.2 |
| | 19.5 | 0.58–2.75 | 29 | HW | 16.1[d] | 474 | 5.90 | 0.77–4.67 | 6.3 | T | 10.4 |
| 319 | 5.80 | 0.54–2.96 | 12 | HW | 15.3 | 541 | 5.92 | 1.08–4.70 | 7.0 | T | 9.08 |
| 344 | 5.90 | 0.65–2.68 | 13 | T | 14.1 | 554 | 5.81 | 0.96–4.94 | 12 | N | 9.45 |
| 348 | 5.79 | 0.57–2.96 | 8.8 | HW | 14.4 | 648 | 5.73 | 1.09–5.38 | 13 | N | 8.07 |
| $k_5 = (4.5 \pm 0.9) \times 10^{-12} \exp((3.2 \pm 0.6)\ \text{kJ mol}^{-1}/RT)$ | | | | | | | | | | | |
| $i$-$C_3H_7$ + HI Reaction ($k_6$) | | | | | | | | | | | |
| 295 | 5.81 | 0.41–1.48 | 59 | HW | 29.1[e] | 349 | 5.83 | 0.53–1.82 | 51 | T | 22.9 |
| | 19.8 | 0.37–1.28 | 88 | HW | 29.8[e] | 383 | 5.85 | 0.64–1.88 | 43 | FHW | 18.9 |
| 296 | 5.78 | 0.45–1.39 | 66 | HW | 29.7 | 426 | 5.84 | 0.76–3.25 | 26 | T | 16.5 |
| 297 | 2.59 | 0.31–1.15 | 52 | HW | 31.4[e] | 480 | 5.86 | 1.09–3.65 | 19 | T | 13.6 |
| 319 | 5.80 | 0.53–1.75 | 55 | HW | 25.9[e] | 552 | 5.80 | 1.09–4.31 | 11 | T | 11.2 |
| | 5.82 | 0.55–1.75 | 53 | T | 25.4 | 554 | 5.81 | 0.88–3.94 | 41 | N | 11.9 |
| 348 | 5.85 | 0.83–1.96 | 50 | FHW | 22.5 | 648 | 5.73 | 0.84–4.95 | 38 | N | 9.68 |
| | 5.84 | 0.48–2.24 | 53 | HW | 21.3[e] | | | | | | |
| $k_6 = (3.9 \pm 0.8) \times 10^{-12} \exp((5.1 \pm 0.7)\ \text{kJ mol}^{-1}/RT)$ | | | | | | | | | | | |
| $s$-$C_4H_9$ + HI Reaction ($k_7$) | | | | | | | | | | | |
| 297 | 22.8 | 0.61–1.25 | 139 | HW | 34.2 | 348 | 5.82 | 0.62–1.66 | 98 | HW | 24.9 |
| 298 | 5.82 | 0.55–1.12 | 133 | HW | 36.6 | 383 | 5.82 | 0.49–1.85 | 63 | T | 21.2 |
| 319 | 5.82 | 0.61–1.41 | 116 | HW | 28.4 | 426 | 5.83 | 0.61–2.83 | 58 | T | 17.0 |
| | 5.83 | 0.41–1.38 | 113 | FHW | 28.3 | 480 | 5.84 | 0.73–3.08 | 56 | T | 13.7 |
| $k_7 = (3.2 \pm 0.6) \times 10^{-12} \exp((5.9 \pm 0.9)\ \text{kJ mol}^{-1}/RT)$ | | | | | | | | | | | |
| $t$-$C_4H_9$ + HI Reaction ($k_8$) | | | | | | | | | | | |
| 294 | 5.86 | 0.69–1.36 | 104 | HW | 41.5 | 348 | 5.82 | 0.63–1.79 | 65 | HW | 26.9[f] |
| 297 | 2.74 | 0.59–1.12 | 100 | HW | 40.0 | 349 | 5.81 | 0.60–1.74 | 70 | T | 27.7 |
| 299 | 19.9 | 0.66–1.15 | 133 | HW | 38.9 | 383 | 5.90 | 0.84–2.02 | 71 | FHW | 22.6 |
| | 5.79 | 0.53–1.13 | 126 | T | 38.1 | 426 | 5.83 | 0.65–2.75 | 51 | T | 17.7 |
| 319 | 5.83 | 0.51–1.27 | 104 | HW | 35.2 | | 5.83 | 0.80–2.94 | 48 | T | 18.0 |
| | 5.84 | 0.58–1.23 | 101 | FHW | 34.0 | 480 | 5.82 | 0.77–3.01 | 34 | T | 15.3 |
| | 5.82 | 0.59–1.49 | 97 | T | 33.4 | 552 | 5.80 | 0.98–2.93 | 18 | T | 12.7 |
| $k_8 = (3.1 \pm 0.6) \times 10^{-12} \exp((6.3 \pm 0.8)\ \text{kJ mol}^{-1}/RT)$ | | | | | | | | | | | |

[a] Temperature uncertainty: ±1 K (292–383 K), ±3 K (419–474 K), and ±7 K (480–648 K). [b] Wall coating materials used: HW (halocarbon wax), FHW fluorinated halocarbon wax (FHW), T (Teflon), and N (none). [c] Experiment in which $CH_3$ + HI and $CD_3$ + HI rate constants were measured simultaneously. [d] $N_2$ used as carrier gas. (Helium used in all other experiments.) [e] Radical produced by 248-nm photolysis (Photolysis at 193 nm used in all other experiments). [f] 4.4-Dimethyl-1-pentene was used as the $t$-$C_4H_9$ precursor. In all other experiments done to measure $k_8$, 2,2,4,4-tetramethyl-3-pentanone was used.

changes were made, they had no effect on the value of the R + HI rate constant.

There is always a possibility of heterogeneous *bimolecular* reactions occurring during these experiments. (The heterogeneous unimolecular reaction is taken into account in the data analysis.) In the case of the $t$-$C_4H_9$ + DI reaction, Müller-Markgraf et al.[17] report evidence that such bimolecular processes were important in their investigation. In our experiments, such processes, if important and unrecognized, would appear as part of the homogeneous bimolecular R + HI rate constant. To test for the presence and importance of such heterogeneous reactions, different wall coatings were used. They included Halocarbon Wax,[21] fluorinated Halocarbon Wax,[22] and poly(tetrafluoroethylene).[23] In the study of reactions 4–6, an uncoated reactor was also used. While coatings did reduce the unimolecular heterogeneous loss of R (i.e., reduced the value of $k_{10}$), they did not affect the value of the R + HI rate constant. From these observations, we conclude that bimolecular heterogeneous R + HI reactions are not significant under our experimental conditions. All of the materials and conditions used in these tests and in the rate constant experiments are presented in Table I.

The most probable error in each measured value of $k_4$–$k_8$ is ±20%. This assessment takes into account the accuracies of the measured gas flow rates and total pressure, the accuracy of each determination of the radical decay constant, and the data analysis procedures used to calculate $k_4$–$k_8$.

The Arrhenius expressions for $k_4$–$k_8$ were determined from the measured rate constants. They are given in Table I. An additional assess-

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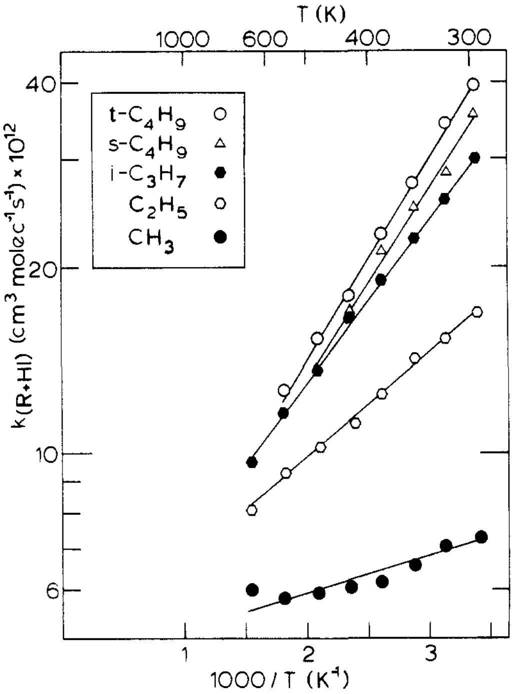

**Figure 2.** Arrhenius plot of R + HI rate constants. Arrhenius parameters are presented in Table I.

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

**Reagent Sources and Purification Procedures.** The gases and liquids used were obtained from Aldrich (acetone, >99.5%; diethyl ketone, >96%; 2,2,4,4-tetramethyl-3-pentanone, 99%), Eastman Kodak (2-bromopropane, 99%; 2-bromobutane, 99.7%), Fluka (4,4-dimethyl-1-pentene, 99%), Matheson (HI, 98%), MSD Isotopes (acetone-$d_6$, >99.96%), and Linde (He, 99.995%; $N_2$, >99.998%).

The free radical precursors were degassed with freeze-pump-thaw cycles. HI was passed over red phosphorus to remove $I_2$ and repeatedly distilled to remove water as well as residual $I_2$. The HI was stored in a dark Pyrex bulb. Frequent checks were made for the decomposition products ($H_2$ + $I_2$). Distillations were repeated when these products were observed. The carrier gases (He and $N_2$) were used as provided.

**Photoionization Energies Used To Detect Reactants.** Two photoionization energies were used to detect the free radical reactants. A hydrogen resonance lamp (10.2 eV) was used to detect $CH_3$ and $CD_3$ and a chlorine lamp (8.9–9.1 eV) to detect $C_2H_5$, $i$-$C_3H_7$, $s$-$C_4H_9$, and $t$-$C_4H_9$. HI was ionized with an argon lamp (11.6, 11.8 eV).

## Discussion

**Comparison of R + HI Rate Constants with Prior Determinations.** There is excellent agreement between the direct determination of the $CD_3$ + HI reaction rate constant reported by Donaldson and Leone[10] at room temperature, 7.7 × $10^{-12}$, and the value that we obtained at this temperature for the $CH_3$ + HI rate constant, 7.3 × $10^{-12}$. (All bimolecular rate constants in this discussion have units of cm$^3$ molecule$^{-1}$ s$^{-1}$.) Direct comparison is possible because there is no secondary isotope effect in this reaction.

In our simultaneous study of the $CH_3$ + HI and $CD_3$ + HI reactions, we obtained the following result: $R = k(CD_3 + HI)/k(CH_3 + HI) = 1.01 \pm 0.05$. Donaldson and Leone made one determination of the $CH_3$ + HI rate constant from which they determined that $R = 1.3$.[10] While they report no error limits for their value of $R$, from their discussion of the greater difficulty of measuring $k_4$, we conclude that their value of $R$ has a significant uncertainty, and therefore our two values of this ratio are in basic agreement.

The much older indirectly determined values of the $CH_3$ + HI rate constants that can be derived from measurements of the rates of iodination processes at higher temperatures, when extrapolated to room temperature, typically yield values that are over a factor of 10 below the directly obtained values. The results obtained in the older investigations of reaction 4 have been discussed by Donaldson and Leone.[10]

**Table II.** Materials and Conditions Used in Experiments To Measure R + HI Reaction Rate Constants

| R | free radical precursor | photolysis wavelengths, nm | reactor wall coatings used[a] | bath gas |
|---|---|---|---|---|
| $CH_3$ | acetone | 193 | HW, FHW, T, N | He, $N_2$ |
| $C_2H_5$ | diethyl ketone | 193 | HW, FHW, T, N | He, $N_2$ |
| $i$-$C_3H_7$ | 2-bromopropane | 193, 248 | HW, FHW, T, N | He |
| $s$-$C_4H_9$ | 2-bromobutane | 193 | HW, FHW, T | He |
| $t$-$C_4H_9$ | 2,2,4,4-tetramethyl-3-pentanone<br>4,4-dimethyl-1-pentene | 193 | HW, FHW, T | He |

[a] Halocarbon wax (HW), fluorinated Halocarbon Wax (FHW), poly(tetrafluoroethylene) (T), and none (N).

There is serious disagreement between our $t$-$C_4H_9$ + HI rate constants and those of Müller-Markgraf et al.[17] (and the previous values from the same laboratory reported by Rossi and Golden[15,16]). Correcting for the likely primary isotope effect,[24] our value at 298 K is a factor of 25 higher than that of Müller-Markgraf. In addition, their report of a small but distinct increase in the $t$-$C_4H_9$ + DI rate constant with increasing temperature is opposite to what we observed, a rate constant that decreases significantly with increasing temperature. The origin of the major disagreement with the results of Müller-Markgraf et al. regarding the magnitude and temperature dependence of $k_8$ described above has not been identified. However, there is new evidence that our values of $k_8$ are accurate.

Richards et al.[18] have now directly determined the rate constants of the reactions of $t$-$C_4H_9$ with HI, HBr, and DBr using conditions that preclude "wall effects", the single most likely cause of the major disagreement between our results and those of Müller-Markgraf et al. Richards et al. monitored the growth of $i$-$C_4H_{10}$ (or $i$-$C_4H_9D$) produced by these reactions in time-resolved experiments. Conditions used were such that radical diffusion to the reactor wall did not occur during the observation time of the experiments. The values of $k_8$ that they obtained are in good agreement with ours, both in magnitude and temperature dependence. For example, their determination of $k_8$ at room temperature (2.4 ± 0.5 × $10^{-11}$) is 40% below our value (4.0 ± 0.8 × $10^{-11}$). The difference of the two determinations at this temperature is virtually within the range defined by the two uncertainty limits.

In the case of the $t$-$C_4H_9$ + HBr reaction, agreement with Richards et al.[18] is perfect. Their room temperature value of the rate constant of this reaction (1.0 ± 0.5 × $10^{-11}$) is the same as ours (1.0 ± 0.2 × $10^{-11}$).[8] The negative activation energies for the $t$-$C_4H_9$ + HBr and $t$-$C_4H_9$ + HI reactions that were obtained by Richards et al. also agree closely with our values, within 0.4 kJ mol$^{-1}$.

The $t$-$C_4H_9$ + HBr rate constant that can be obtained from the $t$-$C_4H_9$ + DBr rate constant reported by Müller-Markgraf et al. at room temperature[17] and the isotope effect for the reaction $t$-$C_4H_9$ + HBr determined by Richards et al.[24] is 6 × $10^{-13}$. This is a factor of 16 below our value and a factor of 26 below that obtained by Richards et al.

In summary, our determinations of R + HI rate constants for reactions 4 and 8 are in excellent agreement with the two prior investigations of these reactions in isolation, and, in particular, under conditions that are free from possible interfering heterogeneous processes.

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[24] In ref 18 it was reported that $k(t\text{-}C_4H_9 + HBr)/k(t\text{-}C_4H_9 + DBr) = 4$. The same isotope effect was assumed in the $t$-$C_4H_9$ + HI(DI) reaction to estimate a $t$-$C_4H_9$ + HI rate constant from the $t$-$C_4H_9$ + DI reaction reported in ref 17.

**Table III.** Determinations of Alkyl Radical Heats of Formation from Kinetics of R + HI ⇔ RH + I Equilibria[a]

| | | second law determination | | third law determination | | other $\Delta H°_{f,298}$ | |
|---|---|---|---|---|---|---|---|
| R | $k$(I + RH) | $\Delta H°_{f,298}$ | $S°_{298}$ | $\Delta H°_{f,298}$ | $S°_{298}$[b] | Tsang's evaluation[c] | "best value"[d] |
| CH3 | Goy, Pritchard (1965)[e] | 150 | 204 | 145 | 194 ± 0.4[f] | | 146 ± 1[f,g] |
| $C_2H_5$ | Knox, Musgrave (1967)[h] | 110 | 236 | 117 | 247 ± 1[i] | 119 ± 2 | 118.5 ± 1.7[i] |
| $i$-$C_3H_7$ | Nangia, Benson (1964)[j] | 87 | 283 | 91 | 289 ± 8[k] | 90.0 ± 2.5 | 89 ± 3[l] |
| | Knox, Musgrave (1967)[h] | 82 | 278 | 88 | 289 ± 8[k] | | |
| $s$-$C_4H_9$ | Chekhov et al. (1968)[m] | 67 | 324 | 76 | 337 ± 8[k] | 71.0 ± 1.6 | 71 ± 1.6[k] |
| $t$-$C_4H_9$ | Bracey, Walsh (1988)[n] | 55 | 322 | 50 | 313 ± 10[o] | 50.0 ± 2.2[p] | 48.6 ± 1.7[q] |
| | Teranishi, Benzon (1963)[r] | 45 | 309 | 47 | 313 ± 10[o] | | |
| | Knox, Musgrave (1967)[h] | 50 | 317 | 48 | 313 ± 10[o] | | |

[a] Units of $\Delta H°_f$ are kJ mol$^{-1}$ and those of $S°$ are JK$^{-1}$ mol$^{-1}$. [b] Calculated entropies. Error limits are our assessments of most probable uncertainties.[12] [c] From ref 12 except for $C_2H_5$ which is from ref 11. The heat of formation of $i$-$C_3H_7$ in Table III from ref 12 includes an unpublished correction (W. Tsang, private communication). [d] Current "best values" of alkyl radical heats of formation from most direct investigations to date or from data assessment. [e] Reference 27. [f] Reference 28. [g] Reference 29. [h] Reference 30. [i] Reference 31. [j] Reference 32. [k] Tsang's assessment, ref 12. [l] Mean of Tsang's assessment (ref 12) and the value from the study of the $i$-$C_3H_7$ + HBr ⇌ $C_3H_8$ + Br equilibrium (ref 9). [m] Reference 33. [n] Reference 34. [o] Reference 8. [p] From Tsang's assessment (ref 12) using measured and theoretical $t$-$C_4H_9$ entropy in ref 8. [q] Reference 8. [r] Reference 35.

**Thermochemistry of Alkyl Radicals.** We have calculated the heat of formation of the five alkyl radicals involved in reactions 4–8 using both a Second Law and Third Law method. The former, which begins by taking the difference between the activation energies of the forward and reverse reactions to obtain $\Delta H°$ for the reaction at a particular temperature, is the most direct, but it is very sensitive to the accuracy of the activation energies.[1-7]

Because the entropies of the reactants and products in reactions 4–8 can be calculated with considerable certainty, we have also determined the alkyl radical heats of formation using the entropy changes for the reactions combined with values of the forward and reverse rate constants at a particular temperature. This Third Law method[11,12] is relatively insensitive to the experimental activation energies but, of course, relies on the accuracy of the calculated entropies.

In two cases, there has been more than one kinetic study performed on the I + hydrocarbon reaction. Where this was the case, calculations were done by using the results of each study separately. This was done to obtain indications of the precision and accuracy of these data.

The Second and Third Law procedures used to obtain the alkyl radical heats of formation were essentially the same as those described previously in our investigation of the kinetics and thermochemistry of R + HBr reactions.[8,9] In each calculation, the temperature in the middle of the range used to study the I + hydrocarbon reaction was used as the initial temperature of the thermochemical calculation. The R + HI rate constant and activation energy at this temperature were obtained from the Arrhenius expression. In the cases of reactions 7 and 8, the temperature ranges of the studies of the forward and reverse reactions did not overlap. So for these two systems, extrapolations of the kinetic behavior of the R + HI reactions to slightly higher temperatures were required. This resulted in little additional uncertainty in the final calculated thermochemical properties of R because of the relatively small activation energies of the R + HI reactions, and because these extrapolations were over relatively short temperature ranges. The extrapolation required for reaction 8 is illustrated in Figure 3.

**1. Second Law Determination of Alkyl Radical Heats of Formation.** The difference between the activation energies for the forward (R + HI) and reverse (R–H + I) reactions was taken as the enthalpy change of the reaction at the midtemperature of the investigation of the R–H + I reaction. This enthalpy change was corrected to obtain its value at 298 K by using tabulated heat capacities of reactants and products.[25,26] Finally, the radical heat of formation was obtained by using the well-known values of the heats of formation of the other reactant and the products in the reaction of interest.[25]

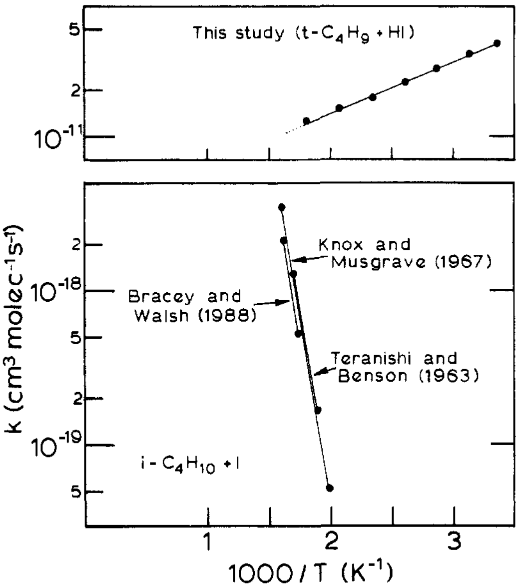

Figure 3. Arrhenius plot of measured $t$-$C_4H_9$ + HI and I + $i$-$C_4H_{10}$ rate constants. Solid lines indicate temperature ranges and display Arrhenius expressions reported in individual investigations. The dotted extension of the line through the $t$-$C_4H_9$ + HI rate constants was used to obtain $t$-$C_4H_9$ + HI rate constants at the mid-temperatures of each of the three I + $i$-$C_4H_{10}$ studies.

The free radical entropies were also determined from the data as described previously.[8,9] The results obtained are presented in Table III.

**2. Third Law Determination of Alkyl Radical Heats of Formation.** For each reaction, the standard free energy at the designated overlapping temperature was obtained from the ratio of forward and reverse rate constants at this temperature. This free energy change, $\Delta G°(T)$, was also corrected to obtain its value at 298 K, again using knowledge of the reactant and product heat capacities and their temperature dependencies.[25,26] $\Delta S°(298)$ was obtained from the known entropies of reactants and products.[25,26]

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Finally $\Delta H^\circ(298)$ was calculated by using the relationship $\Delta G^\circ(298) = \Delta H^\circ(298) - 298\Delta S^\circ(298)$.

The free radical heats of formation were obtained from $\Delta H^\circ(298)$ values as described above. Their values are also given in Table III as are the radical entropies that were used in these calculations.

**3. Analysis of Free Radical Heats of Formation.** In the following analysis, comparisons will be made with the heats of formation of the alkyl radicals determined in studies of dissociation–recombination equilibria, reactions 2 and 3. Tsang has conducted a comprehensive evaluation of all kinetic studies of reactions 2 and 3 involving the C2–C4 radicals of interest here.[11,12] He has recommended heats of formation for these free radicals based on this evaluation. These values, which are also listed in Table III, are used in these comparisons. (More recent determinations based on the same equilibria are in essential agreement.)

Several conclusions can be drawn from the results presented in Table III about the determination of the alkyl radical heats of formation from investigations of the kinetics involved in R + HI $\Leftrightarrow$ RH + I equilibria.

(1) A comparison of heats of formation *for the same radical* (R = $i$-$C_3H_7$ or $t$-$C_4H_9$) obtained by using the results of different kinetic studies of the I + R–H reaction reveals that the Third Law heats of formation have a significantly higher precision than do the Second Law determinations. This is particularly apparent in the case of the $t$-$C_4H_9$ radical where the three Third Law heats of formation (using I + RH rate constants from three different investigations) yield heats of formation that differ by a very small amount (3 kJ $mol^{-1}$) while the Second Law values span a much wider range (10 kJ $mol^{-1}$).

Because the entropies of the alkyl radicals are known with considerable certainty, we conclude that the Third Law heats of formation are not only more precise but also more accurate.

(2) The Third Law alkyl radical heats of formation obtained in the current investigation are in excellent agreement with Tsang's values, ones that are based on studies of reactions 2 and 3. *There is no systematic deviation between the heats of formation derived from studies of iodination equilibria and those obtained from studies of reactions 2 or 3 when the measured R + HI rate constants are used to calculate radical heats of formation.*

It is apparent that the disparity that has existed between these determinations in the past is associated entirely with the prior use of a generic R + HI activation energy that was less accurate than had been presumed. The R + HI activation energies are all negative decreasing from −1.2 kJ $mol^{-1}$ for the $CH_3$ + HI reaction to −6.3 kJ $mol^{-1}$ for the $t$-$C_4H_9$ + HI reaction. They are between 5.2 and 10.3 kJ $mol^{-1}$ below the measured common value.

(3) The Third Law alkyl radical heats of formation obtained here from studies of the kinetics of *both* the forward and reverse reactions, R + H $\Leftrightarrow$ RH + I, are highly accurate. They are within ±2 kJ $mol^{-1}$ of the current best values (see Table III). The one exception is the value for $s$-$C_4H_9$ derived from these experiments. The poorer agreement in this case is most likely due to the reported much larger uncertainty in the I + hydrocarbon rate constants.[33]

The apparent accuracy of the Second Law heats of formation is poorer, ±10 kJ $mol^{-1}$. The larger uncertainty is associated with what appears from these results to be a ±6–8 kJ $mol^{-1}$ experimental uncertainty in the I + hydrocarbon reaction activation energies.

These observations and conclusions provide new confidence that studies of reaction 1 (in particular ones free of assumptions regarding the kinetic behavior of R + HI reactions) yield highly accurate free radical heats of formation. This is supported by the better than "chemical accuracy" (±4 kJ $mol^{-1}$) of the alkyl–radical heats of formation obtained here.

**Comments on the $t$-$C_4H_9$ Heat of Formation.** The results reported here and those in our prior investigation of four R + HBr $\Leftrightarrow$ R–H + Br reactions[8,9] now provide what we believe to be a complete reconciliation of formerly disparate values of the common alkyl radical heats of formation. However, one new study, that of Müller-Markgraf et al.,[17] casts doubt on this claim. As discussed above, their reported rate constants for the $t$-$C_4H_9$ + HBr and $t$-$C_4H_9$ + HI reactions are in serious disagreement with our own both in magnitude and apparent temperature dependence. From their results, they obtained a $t$-$C_4H_9$ heat of formation, 38.5 ± 2 kJ $mol^{-1}$, that is still in agreement with the older "low" value that results from using assumed R + HBr and R + HI activation energies.

While the source of this serious disagreement between our two studies is most likely associated with heterogeneous processes that have not been properly taken into account, something both Müller-Markgraf et al.[17] and we[8] have commented on before, its exact origin has yet to be identified. The fact that there is now confirmation from the study of Richards et al.[18] that our R + HBr and R + HI rate constants are as accurate as stated both in magnitude and temperature dependence[8,9] strongly indicates that our experiments were not affected by unrecognized heterogeneous effects.

It is our opinion that there is now overwhelming and convincing evidence that the $t$-$C_4H_9$ radical heat of formation at 298 K is 48.6 ± 1.7 kJ $mol^{-1}$ (which indicates a tertiary bond energy DH($t$-$C_4H_9$–H) = 401.2 ± 1.7 kJ $mol^{-1}$). This is the value we obtained in our study of the equilibrium

$$t\text{-}C_4H_9 + HBr \Leftrightarrow i\text{-}C_4H_{10} + Br \qquad (11)$$

In this investigation, both the forward and reverse reaction rate constants were measured as a function of temperature in the same range. Subsequently, the accuracy of both of these rate constant determinations has been confirmed in independent investigations by others ($k_{11}$ by Richards et al.[18] and $k_{-11}$ by Seakins et al.[36]). There has not been a more direct nor more accurate determination of this free radical heat of formation. The value resulting from the current investigation of reaction 8 is essentially identical, 48.2 ± 6 kJ $mol^{-1}$, but has a larger uncertainty.

## Mechanisms of R + HI Reactions

A significant apparent negative activation energy, particularly when associated with a low Arrhenius $A$ factor, is frequently an indication that the reaction of interest involves the reversible formation of a stable or quasistable complex,[37–40] which can also form the ultimate products in an irreversible unimolecular step. The negative activation energy results from cases where the potential energy barrier for the unimolecular step is below the potential energy of the reactants.[41]

To date, theoretical studies of simple H-atom transfer reactions, even ones occurring on an attractive surface, have never found significant negative activation energies (usually no lower than −0.8 kJ $mol^{-1}$) in the calculated thermal rate constants.[42,43] These theoretical results have tended to reinforce the belief that a significant negative activation energy is an indication of a more complex mechanism.

In the case of the R + HI reactions, a reasonable model for a complex reaction mechanism would involve the alkyl radical initially being attracted to the iodine end of HI to form a quasistable complex. Rotation of the hydrogen in the complex completes the reaction. (An analogous mechanism was proposed in our studies of the kinetics of R + HBr reactions.[8,9])

In our investigations of R + HBr and R + HI no pressure dependence (typically in the range 1–6 Torr) was found. Richards et al.[18] also report no pressure dependence in the $t$-$C_4H_9$ + HI rate constant in the range 5–70 Torr. This would indicate that a collision complex, if formed, has a short lifetime ($<10^{-9}$ s in the

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case of the $t$-$C_4H_9$·HI complex) compared to the collision frequency.

There is ample evidence from molecular beam studies by Lee and co-workers[44,45] as well as Grice and co-workers[44,47] of such bound complexes being formed during reactions between atoms (or radicals) with diatomic molecules containing iodine. The reactions include the following: $CH_3$ + IF,[44] $CH_3$ + ICl,[46] O + ICl,[47] O + IBr,[47] O + $I_2$,[47] and H + $I_2$.[45] Mei and Moore[48] have observed unusual temperature dependencies in rate constants of the Cl + HI and Br + HI reactions and have interpreted the results using an analogous mechanism.

The temperature dependence of the $CH_3$ + HI rate constant that we observed is atypical. There is an indication of a reversal in temperature dependence of the reaction rate constant at the highest temperatures used to study this reaction (see Figure 2). This apparent change, from a negative to a positive activation energy, could indicate the emerging importance of a direct H-atom abstraction route that proceeds over a small potential energy barrier. This more direct process should become the dominant mechanism for reaction 4 (as well as reactions 5–8) at a suitably high temperature. The onset of this changing behavior would be observable first in the $CH_3$ + HI reaction because the low-temperature route has the lowest rate constant of all the R + HI reactions studied.

## Summary

Rate constants of five R + HI reactions have been determined as a function of temperature. The results have been used to recalculate alkyl radical heats of formation and to begin to obtain an understanding of the reaction mechanisms. Use of measured rate constants of these reactions in thermochemical calculations to obtain the radical heats of formation has yielded heats of formation that are in complete accord with values obtained from other kinds of studies, particularly from investigations of dissociation–recombination equilibria. The negative activation energies found for these reactions are interpreted as an indication that these apparently simple H-atom transfer reactions are in fact complex processes proceeding via the formation of a complex intermediate.

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**Registry No.** $CH_3$, 2229-07-4; $C_2H_5$, 2025-56-1; $i$-$C_3H_7$, 2025-55-0; $s$-$C_4H_9$, 2348-55-2; $t$-$C_4H_9$, 1605-73-8; HI, 10034-85-2.

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# Solvent Structural Effects on Proton Dissociation

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**Abstract:** Lifetime and quantum yield measurements are performed on the excited states of 1-naphthol-2-sulfonic acid potassium salt and its associated anion in aqueous solutions. In comparison to 1-naphthol, the intramolecular hydrogen bonding in the sulfonate derivative sterically reduces the extramolecular proton dissociation $k_{dis}$ and recombination $k_{rec}$ rates. Despite the large differences between excited state rates in 1-naphthol-2-sulfonic acid and those in 1- and 2-naphthol, proton dissociation in all these molecules is controlled by reorientational motions of the adjacent water and requires a common $(H_2O)_{4\pm1}$ cluster as the proton acceptor. It is indeed found that $k_{dis}^{-1}$ and $k_{rec}^{-1}$ at different temperatures are scaled to the Debye orientation time $\tau_D$. These findings further support the Robinson–Lee–Moore hydration model for endothermically produced protons in aqueous environments.

The increase in acidity of naphthol derivatives upon photoexcitation was first demonstrated by Förster in 1949.[1] A rate scheme incorporating proton dissociation and recombination was later formulated by Weller.[2] Since that time a considerable research effort has been focused on understanding the variation of $k_{dis}$ and $k_{rec}$ effected by the local solvent environment.[3-8]

Proton dissociation from 1- and 2-naphthol (1- and 2-ROH) was found to depend on a specific water structure.[4,5,8] Lee et al. correlated such a specific structure to a cluster composed of a minimum of four water molecules.[7-10] Robinson et al. further suggested that formation of such a water cluster in these weak acid systems is determined by reorientational motions of the neighboring solvent. These in turn are related to the Debye relaxation time ($\tau_D$) of water.[7,8] Since then, molecular aspects of weak acid dissociation in aqueous solutions have been experimentally and theoretically developed. It is not clear, however, whether the model is applicable to more complicated weak acids, where intramolecular hydrogen bonding, which interferes with proton dissociation,[11,12] occurs. For example, contradictory $k_{dis}$ and an unexpectedly large proton induced quenching rate $k_q$ are still debatable for 1-naphthol-2-sulfonic acid (1-ROH-2-S).[11,12] In this paper it will be of interest to reevaluate systematically $k_{dis}$,

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