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Kinetic Isotope Effects in H and D Abstraction Reactions from Alcohols by D Atoms in Aqueous Solution

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Electron paramagnetic resonance free induction decay attenuation measurements were performed in the range of liquid D_2O for the reactions of D atoms with undeuterated and deuterated alcohols. Excellent Arrhenius behavior represented by $\log(k/\text{M}^{-1}\ \text{s}^{-1}) = (10.97 \pm 0.14) - [(24.7 \pm 0.8)\ \text{kJ mol}^{-1}/2.303RT)]$ for CH_3OD, $\log(k/\text{M}^{-1}\ \text{s}^{-1}) = (11.09 \pm 0.12) - [(20.8 \pm 0.6)\ \text{kJ mol}^{-1}/2.303RT)]$ for CH_3CH_2OD, $\log(k/\text{M}^{-1}\ \text{s}^{-1}) = (11.45 \pm 0.10) - [(28.4 \pm 0.6)\ \text{kJ mol}^{-1}/2.303RT)]$ for CD_3CD_2OD, $\log(k/\text{M}^{-1}\ \text{s}^{-1}) = (11.32 \pm 0.15) - [(21.3 \pm 0.8)\ \text{kJ mol}^{-1}/2.303RT)]$ for $CH_3CH_2CH_2OD$, $\log(k/\text{M}^{-1}\ \text{s}^{-1}) = (11.60 \pm 0.06) - [(21.2 \pm 0.3)\ \text{kJ mol}^{-1}/2.303RT)]$ for$(CH_3)_2C(H)OD$, $\log(k/\text{M}^{-1}\ \text{s}^{-1}) = (11.48 \pm 0.12) - [(24.7 \pm 0.7)\ \text{kJ mol}^{-1}/2.303RT)]$ for$(CD_3)_2C(D)OD$, was found in all cases. Compared with the gas phase, the reactions exhibit slightly higher activation energies, in agreement with expectation for solvation based on a predicted decrease of the dipole moment from the reactant alcohol to the transition state. A pronounced increase in Arrhenius preexponential factors is attributed mostly to equilibrium solvation of the D atom, but a significant difference between H_2O and D_2O suggests contributions of a dynamic solvent effect.

Introduction

Deuterium oxide serves as an efficient moderator for fast neutrons created in nuclear fission reactions inside nuclear reactors. Both light and heavy water are commonly used as coolants in reactors fueled with natural uranium.[1] Deuterium and hydrogen atoms are primary products of water radiolysis. To model radiolytical reactions in primary heat transport systems of nuclear power reactors at 523−573 K, an excellent knowledge of reaction rates and mechanisms with inorganic and organic compounds over a wide temperature range is of great interest.[2]

A number of previous papers have dealt with H atom reactions in light water, but only few results have been published for experiments in heavy water, and they were mostly performed at room temperature. The scarcity of data for D atom reactions in the condensed phase stimulated our present study of temperature-dependent rate constants. This paper reports an extension of an earlier publication[3] of direct measurements of rate constants and activation energies for the hydrogen and deuterium abstraction reactions by H atoms from simple alcohols and their deuterated derivatives in aqueous solution.

Direct EPR detection of the decay of D atoms following pulse radiolysis was the monitoring method of choice. The pulsed EPR-based free induction decay (FID) attenuation technique is convenient because of the simple pseudo-first-order scavenging kinetics, and it seems to be the most precise method to date.

The data are also of interest from a theoretical point of view. The activation energies (E_a) are related to bond dissociation energies (BDE) of the abstracted atom and to associated zero point energies (ZPE) in the reactants and in the transition state (TS). Comparison of rate constants and Arrhenius parameters for abstraction reactions in the liquid with those in the gas phase reveals the importance of equilibrium and nonequilibrium solvation effects. Previously, a pronounced enhancement of the rate constant for H addition to benzene in aqueous solution was ascribed to equilibrium solvation of the H atom, whereas in the case of the lighter hydrogen isotope muonium also nonequilibrium solvation was found to play a role.[4] Tunneling appeared to be quenched in aqueous solution.[5]

Analysis of kinetic isotope effects (KIE) is based on transition state theory which allows a quantitative prediction of Arrhenius preexponential factors. The study is supported by ab initio calculations of reaction barriers and zero point energies.

Experimental Details and Data Analysis

Experimental technique and data treatment have been described in detail in previous publications.[3,4,6−9] In short, they are as follows.

D atoms were generated in D_2O solution in analogy to H atoms in H_2O[10] within an EPR cavity containing a flat glass cell, using a 3 MeV Van de Graaff accelerator. Electron pulses of 12, 25, and 55 ns width correspond to radiation doses of roughly 15, 30, and 70 Gy, respectively. The radiolysis of water is based predominantly on ionization which occurs within a picosecond and yields D_2O^+ and electrons, and a simultaneous homolytic dissociation of the excited D_2O leading to OD and D radicals. Secondary electrons loose their energy to surrounding water molecules, causing further ionization and excitation before they become solvated. Via D abstraction from the solvent, D_2O^+ forms D_3O^+ ions and OD radicals. Furthermore,

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in acid solution, solvated electrons recombine with D^+ to generate additional D atoms. Shortly after the formation of the D atoms, a $\pi/2$ (35 ns) microwave pulse was applied and the resulting free induction decay of the D atom (high field line, $m_I = -1$) with a magnetic field offset of about 3 G from the center of the EPR resonance was displayed and recorded on a digital oscilloscope. In general, we used a repetition frequency of 120 Hz which was lowered to 60 Hz for all experiments with 1-propanol because of the small concentrations which were necessary at high temperatures. To improve the signal-to-noise ratio 1000−10000 shots were averaged.

Stock solutions were prepared using at least triply distilled D_2O (97−99%) and 0.01 M $HClO_4$ (Mallinckrodt, AR grade, 69.05%) to adjust for pD ≈ 2.0. The concentrations of the acid were checked against 1.029 N HCl (Aldrich, volumetric standard). In preparation of the experiments, the solutions were deoxygenated by bubbling with argon and sealed off in a glass reservoir with a volume of 175 ± 2 mL. To avoid vaporization of the alcohols, no gaseous headspace could be tolerated. 2-Propanol-d_8 solutions were buffered ($(4-10) \times 10^{-3}$ M KH_2PO_4, Baker Analyzed) and bubbled with N_2O, which also scavenges hydrated electrons. The total concentrations of methanol (Mallinckrodt, AR grade, 99.9%; Aldrich, 99.5%, 4−250 mM), ethanol (MidWest Grain Products Co., USP, 99.5%, 1−38 mM), ethanol-d_6 (Aldrich, 99+ atom %D, 7−175 mM), 1-propanol (Sigma-Aldrich, 99.5%, HPLC grade, 1−30 mM), 2-propanol (Aldrich, HPLC grade, 99.5%, 1−12 mM), and 2-propanol-d_8 (Aldrich, 99+ atom %D, 2−80 mM) are considered to be better than 2%. For a set of experiments the concentrations were slowly raised by successive injections into the continuous flow in Teflon tubing. The high flow rate of the aqueous solution guaranteed a lower limit of the irradiated volume of about 0.1 mL per pulse, and the solution was totally replaced before the next pulse approached the cell. The accuracy of the temperature determination by a thermocouple sitting directly in the flow was ±1 K. During experiments, the temperature was constant to ±0.3 K or better.

The FID was well described by a damped cosine characterized by the exponential damping rate

$$\frac{1}{T_2(\mathrm{eff})} = \frac{1}{T_2{}^0} + k_s[S] + \sum_i k_{ex}^i[R_i] \qquad (1)$$

where $T_2{}^0$ is the relaxation time in the absence of scavenger, and $k_s[S]$ stands for the D atom scavenging rate in the presence of a solute of concentration [S]. As in previous measurements of H and D atoms with organic compounds, a slight dose dependence was observed. This is due to the spin−dephasing contribution of second-order spin exchange between D atoms and other free radicals over the experimental time scale of 5 μs, and it is represented by the last term of eq 1, $\sum_i k_{ex}^i[R_i]$. For that reason the data were corrected in a relative dose vs relative rate constant plot and extrapolated by a weighted fit (1σ error bar) to zero dose to yield the absolute rate constant at each temperature.[3,7,11] The error bars shown in the Arrhenius plot (Figure 1) are estimated from the dose dependence, and the fit to the Arrhenius law is weighted by these reciprocal errors.

All ab initio calculations using a Gaussian 6.31G** basis set were carried out using the SPARTAN molecular modeling program of Wavefunction, Inc.[12] Thermodynamic properties relate to 298.15 K and 1 atm pressure.

Results

Methanol. In analogy to previous measurements for H atoms,[13] rate constants were determined as a function of temperature for the reaction of deuterium with methanol

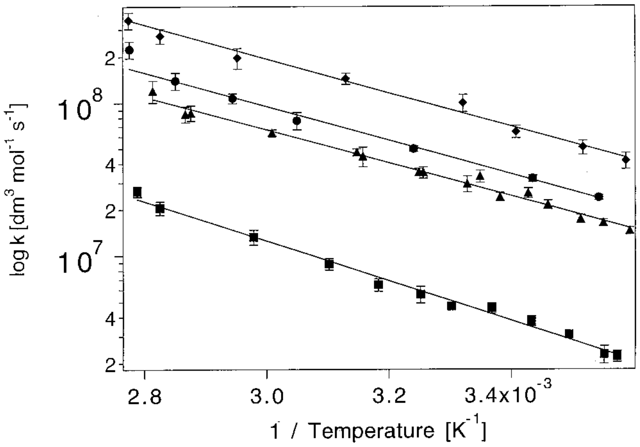

Figure 1. Arrhenius plot for the reactions of D atoms with methanol (■), ethanol (▲), 1-propanol (●), and 2-propanol (◆). Solid lines are fitted values represented by the Arrhenius parameters in Table 1.

$$CH_3OD + \dot{D} \rightarrow \dot{C}H_2OD + HD \qquad (2)$$

Here and below we generally assume that in acidic heavy water the hydroxylic proton exchanges for D. At 298 K and pD = 2.1, a rate constant of $(4.4 \pm 0.3) \times 10^6$ M^{-1} s^{-1} was obtained. Over a temperature range of 279.8−358.7 K, experiments lead to an Arrhenius plot of good linearity, as shown in Figure 1. The rate constants and Arrhenius parameters are collated and compared with those of other alcohols and with the results of ab initio calculations in Table 1.

Smaller et al.[14] published a rate constant of 3.6×10^6 M^{-1} s^{-1} at room temperature, which is in good agreement with our work. Gas-phase measurements by Meagher[15] et al. using a flow discharge method gave a value of 4.33×10^6 M^{-1} s^{-1} (298 K) and an activation energy of about 21.7 kJ mol^{-1}, which is lower than our aqueous phase value by 3 kJ mol^{-1}. For the reactions of H with CH_3OD and CD_3OD, Anbar et al.[16] determined a KIE k_H/k_D of 20.0 ± 1. Our present experimental technique was not suited to determine accurate rate constants lower than 10^5 M^{-1} s^{-1}. Further studies with fully deuterated methanol using competition kinetics are in progress.

Ethanol and Ethanol-d_6. As with methanol, deuterium atoms react with ethanol primarily by abstraction of the secondary hydrogen atom

$$CH_3CH_2OD + \dot{D} \rightarrow CH_3\dot{C}HOD + HD \qquad (3)$$

Over a temperature range of 278.2−355.4 K, the curve for ethanol lies above that of methanol (Figure 1). We determined a rate constant of $(2.79 \pm 0.14) \times 10^7$ M^{-1} s^{-1} (pD ≈ 2.0, 298 K), which is about 1 order of magnitude higher than that for methanol. Smaller et al.[13] obtained 2.4×10^7 M^{-1} s^{-1} using a direct EPR technique in water. Competition experiments carried out by Lifshitz et al.[17] gave 2.6×10^7 M^{-1} s^{-1} using H_2SO_4 to adjust for pD = 1. Both results are consistent with ours.

The reaction of ethanol-d_6

$$CD_3CD_2OD + \dot{D} \rightarrow CD_3\dot{C}DOD + D_2 \qquad (4)$$

was studied over the temperature range 283.6−360.0 K. A rate constant of $(3.0 \pm 0.4) \times 10^6$ M^{-1} s^{-1} was obtained at 298 K. Thus, deuterated ethanol reacts by 1 order of magnitude more slowly with D atoms than CH_3CH_2OD, and the activation energy is higher by 7.6 kJ mol^{-1}. To avoid extensive overlap of points, these data are displayed separately in Figure 2.

TABLE 1: Rate Constants at 298 K and Arrhenius Parameters of the Reaction of Alcohols with H and D Atoms in Aqueous Solution in Comparison with Literature Values and ab Initio Calculations

		$k[10^6\ M^{-1}\ s^{-1}]$			$\log (A/M^{-1}\ s^{-1})$		E_a [kJ mol^{-1}]	ΔH (vib.) [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J mol^{-1} K^{-1}]	BDE[25] [kJ mol^{-1}]
reaction		exptl	lit.		exptl	ab initio	exptl	ab initio	ab initio	
$CH_3OH + H$	ref 3	3.10 ± 0.17	2.5	ref 13	11.64 ± 0.17	9.99	29.4 ± 0.8	−9.71	−96.86	410 ± 6
$CH_3OD + D$		4.4 ± 0.3	3.6	ref 13	10.97 ± 0.14	9.82	24.7 ± 0.8	−12.44	−100.15	
$CH_3CH_2OH + H$	ref 3	20.4 ± 0.6	17	ref 31	11.53 ± 0.09	10.02	24.1 ± 0.5	−9.64	−96.36	389 ± 4
$CH_3CH_2OD + D$		27.9 ± 1.4	24	ref 13	11.09 ± 0.12	9.85	20.8 ± 0.6	−12.32	−99.66	389 ± 4
$CD_3CD_2OH + H$	ref 3	2.77 ± 0.26	6.0	ref 16	12.03 ± 0.21	10.03	31.9 ± 1.2	−4.21	−96.19	
$CD_3CD_2OD + D$		3.0 ± 0.4			11.45 ± 0.10	9.85	28.4 ± 0.6	−6.86	−99.64	
$CH_3CH_2CH_2OD + D$		39 ± 2			11.32 ± 0.15		21.3 ± 0.8			
$(CH_3)_2C(H)OH + H$	ref 3	101 ± 7	74	ref 31	11.86 ± 0.05	10.04	22.0 ± 0.3	−9.34	−95.94	381 ± 4
			82 ± 1	ref 17						
$(CH_3)_2C(H)OD + D$		77 ± 4[a]	49	ref 13	11.60 ± 0.06	9.87	21.2 ± 0.3[a]	−11.98	−99.24	381 ± 4
			63 ± 1	ref 17						
$(CD_3)_2C(D)OH + H$	ref 3	15.6 ± 0.7	11	ref 19	12.00 ± 0.07	10.06	27.4 ± 0.3	−3.95	−95.54	
			10 ± 1	ref 17						
$(CD_3)_2C(D)\ OD + D$		14.2 ± 0.8	12 ± 1	ref 17	11.48 ± 0.12	9.88	24.7 ± 0.7	−6.56	−98.97	

[a] May be slightly in error; see text.

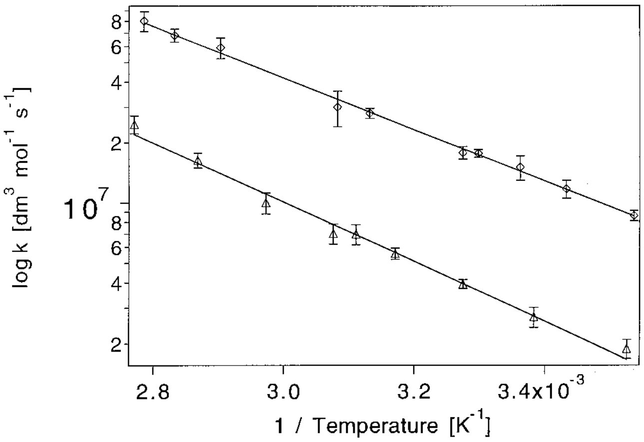

Figure 2. Arrhenius plots for the reactions of ethanol-d_6 (△) and 2-propanol-d_8 (◇) with D-atoms. Solid lines correspond to fitted values from Table 1.

No kinetic data are available in the literature for these reactions in gas phase.

1-Propanol. The reaction of 1-propanol

$$CH_3CH_2CH_2OD + \dot{D} \rightarrow CH_3CH_2\dot{C}HOD + HD \qquad (5)$$

is thought to occur primarily by abstraction from the α-carbon. Over the temperature range 282.2−360 K, the results are similar to those for methanol and ethanol (Figure 1). At 298 K, the rate constant was found to be (3.9 ± 0.2) × 10^7 M^{-1} s^{-1}, and the activation energy of 21.3 kJ mol^{-1} is close to that for H abstractions from ethanol in D_2O. No other kinetic measurements were reported for abstraction of H by D atoms, independent of the method and the phase.

2-Propanol and 2-Propanol-d_8. 2-Propanol has been used for many years to study kinetic behavior in competition experiments. The measurements for H abstraction reactions

$$(CH_3)_2C(H)OD + \dot{D} \rightarrow (CH_3)_2\dot{C}OD + HD \qquad (6)$$

yielded a rate constant of (7.7 ± 0.4) × 10^7 M^{-1} s^{-1} at 298 K and pD ≈ 2.0. This is about 18 times higher than for the corresponding reaction with methanol. Smaller et al.[13] reported a slightly lower value of 4.9 × 10^7 M^{-1} s^{-1} at room temperature. An investigation at pD = 1 by Geimer et al.[17] gave (6.3 ± 0.1) × 10^7 M^{-1} s^{-1} at room temperature, which corresponds to our value at 291 K and could thus be slightly lower.

Measurements with deuterated 2-propanol in deuterium oxide (282.7 − 359 K)

$$(CD_3)_2C(D)OD + \dot{D} \rightarrow (CD_3)_2\dot{C}OD + D_2 \qquad (7)$$

gave a rate constant of (1.42 ± 0.08) × 10^7 M^{-1} s^{-1} at 298 K, which is about 5.4 times lower than that for H abstraction by D atoms. For previous measurements with 2-propanol in light water, Mezyk and Bartels[3] used at higher temperatures a buffered solution at pH ≈ 5 to avoid the build-up of propene due to an acid- or metal-catalyzed H_2O elimination which occurs at lower pH. Here, rate constants in acidic and buffered D_2O solution were found to be in good agreement up to 303 K. Above this critical temperature, an acceleration of the reaction was observed at pD ≈ 2.0, so that the data from the buffered solution were used.

Figure 2 exhibits a slightly lower slope for the reaction of 2-propanol-d_8 compared to the deuterated ethanol with D atoms, which corresponds to a smaller activation energy by about 3.7 kJ mol^{-1}, correlated with a slightly lower preexponential factor. Geimer et al.[17] determined a rate constant of (1.2 ± 0.1) × 10^7 M^{-1} s^{-1} at room temperature and pD = 1, which is in good agreement with our result (Table 2). Vacek et al.[18] found a value of (10.0 ± 0.3) for k_H/k_D at 299 K, and a difference in activation energies of (5.6 ± 0.6) kJ mol^{-1} between 2-propanol and 2-propanol-d_7 in their reactions with H atoms. They discussed also a contribution of about 11.6% of H abstraction from the hydroxyl group, which was later investigated also by Dainton et al.,[19] giving a preexponential factor of (2.5 ± 0.6) × 10^{10} M^{-1} s^{-1} and a corresponding E_a of 22 ± 3 kJ mol^{-1}.

In contrast to the well-studied situation in solution, no reliable rate constants are known for the reaction of 2-propanol-d_8 in the gas phase.

Discussion

The empirical Arrhenius relation provides conventional preexponential factors and activation energies from experimental data within a limited temperature range, but transition state theory appears more useful for theoretical analysis since it predicts absolute rate constants and their temperature dependence and gives a deeper insight on a molecular level. We first have to briefly recapitulate some of the formulas of TS theory as a basis for the discussion of activation energy, preexponential factors, contributions of tunneling, and solvation effects. We

TABLE 2: Kinetic Isotope Effects and Comparison of Arrhenius Parameters for the Reactions of Alcohols with H and D Atoms in H_2O and D_2O

isotope is abstracted atom, attacking atom is i	$k_i(H)/k_i(D)$ at 298 K	$\log A_i(H) - \log A_i(D)$		$E_{a\ i}(H) - E_{a\ i}(D)$ [kJ mol^{-1}]	
		exptl	calcd	exptl	calcd
$CH_3CH_2OH + H$ ref 3 $CD_3CD_2OH + H$ ref 3	7.36 ± 0.10	−0.50 ± 0.23	−0.01	−7.8 ± 1.2	−5.4
$CH_3CH_2OD + D$ $CD_3CD_2OD + D$	9.33 ± 0.12	−0.36 ± 0.16	0.00	−7.6 ± 0.8	−5.4
$(CH_3)_2C(H)OH + H$ ref 3 $(CD_3)_2C(D)OH + H$ ref 3	6.38 ± 0.04 8.20 ± 0.14 ref 17	−0.13 ± 0.08	−0.02	−5.5 ± 0.4	−5.4
$(CH_3)_2C(H)OD + D$ $(CD_3)_2C(D)OD + D$	5.42 ± 0.07 5.25 ± 0.14 ref 17	−0.12 ± 0.10	−0.01	−3.5 ± 0.7	−5.4

isotope is attacking atom, abstracted atom is i	$k_H(i)/k_D(i)$ at 298 K	$\log A_H(i) - \log A_D(i)$		$E_{a\ H}(i) - E_{a\ D}(i)$ [kJ mol^{-1}]	
		exptl	calcd	exptl	calcd
$CH_3OH + H$ ref 3 $CH_3OD + D$	0.71 ± 0.08	0.67 ± 0.22	0.17	4.7 ± 1.1	2.7
$CH_3CH_2OH + H$ ref 3 $CH_3CH_2OD + D$	0.73 ± 0.05	0.44 ± 0.15	0.17	3.3 ± 0.8	2.7
$CD_3CD_2OH + H$ ref 3 $CD_3CD_2OD + D$	0.92 ± 0.15	0.58 ± 0.22	0.18	3.5 ± 1.3	2.7
$(CH_3)_2C(H)OH + H$ ref 3 $(CH_3)_2C(H)OD + D$	1.32 ± 0.05 1.30 ± 0.14 ref 17	0.26 ± 0.08	0.17	0.9 ± 0.4	2.6
$(CD_3)_2C(D)OH + H$ ref 3 $(CD_3)_2C(D)OD + D$	1.12 ± 0.07 0.83 ± 0.14 ref 17	0.52 ± 0.13	0.18	2.8 ± 0.7	2.6

also introduce the following nomenclature:

$$R{-}H + H \rightarrow [R\cdots H\cdots H]^{\ddagger} \rightarrow R + H_2\ [k_H(H)] \qquad (8)$$

$$R{-}H + D \rightarrow [R\cdots H\cdots D]^{\ddagger} \rightarrow R + HD\ [k_D(H)] \qquad (9)$$

$$R{-}D + H \rightarrow [R\cdots D\cdots H]^{\ddagger} \rightarrow R + DH\ [k_H(D)] \qquad (10)$$

$$R{-}D + D \rightarrow [R\cdots D\cdots D]^{\ddagger} \rightarrow R + D_2\ [k_D(D)] \qquad (11)$$

where the index of k_i represents the attacking atom, and the abstracted atom is in parentheses. Since in all reactions the bond to the isotope is either broken or formed in the rate-determining step, the isotope effects are all primary.[20] However, since the entire alcohol molecules are deuterated we also have secondary isotope effects superimposed on the primary ones.

This discussion relies particularly also on the work by Mezyk and Bartels[3] for the analogous reactions of the H isotope which was based on the identical experimental technique and is therefore ideally suited for comparison.

Transition State Theory. The rate constant for bimolecular reactions is given by

$$k_c = \frac{k_B T}{h c_0}\Gamma \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right) \qquad (12)$$

where k_B stands for the Boltzmann constant, h is the Planck constant, Γ is a tunneling correction factor, and

$$\frac{1}{c_0} = \frac{V}{n} = \frac{RT}{p} = 24.45\ \frac{\mathrm{dm}^3}{\mathrm{mol}} \text{ at 298 K} \qquad (13)$$

converts between standard states for concentrations and accounts for the fact that $\Delta S^{\ddagger}$ is evaluated on the basis of the gas-phase standard (1 atm) but the rate constant is given in liquid-phase standard units (1 mol per dm^3). This factor is often missed out in elementary textbooks so that the intrinsic preexponential factor is erroneously suggested to be the same for unimolecular and for bimolecular reactions, although they obviously must have different dimensions.

Due to the proportionality of the rate to T/c_0, a shallow down concave curvature is expected in the Arrhenius plot. However, observation of this deviation from linear Arrhenius behavior requires very precise measurements over a wide temperature range; it could also be masked by other effects (see below).

The Arrhenius activation energy is related to the activation enthalpy in eq 12 via[21,22]

$$E_a = \Delta H^{\ddagger} + 2RT \qquad (14)$$

and for $\Gamma = 1$ the preexponential factor is related to the activation entropy via[21,22]

$$\log A = \log\left(\frac{e^2 k_B T}{h c_0}\right) + \left(\frac{\Delta S^{\ddagger}}{2.303R}\right) = 15.05 + \left(\frac{\Delta S^{\ddagger}}{2.303R}\right) \text{ at 298 K} \qquad (15)$$

Ab Initio Calculations. Ab initio calculations at the Hartree−Fock level predict a range of 65−87 kJ mol^{-1} for the activation energies of the reactions. These values are too high by a factor of 3 since electron correlation is neglected at this level. They are thus not used any further in this work, while transition state geometries and vibrational frequencies (omitting the reaction coordinate) are believed to be far more reliable.

In all cases the TS $R\cdots H(D)\cdots H(D)$ was predicted to be linear. The $R\cdots H$ bond lengths in the transition state were calculated to be ca. 0.134 nm, the $H\cdots H$ bond lengths 0.096 nm, almost independent of the type of alcohol. It is well-known that the calculated vibrational frequencies are too high by ca. 10%.[23] Consequently, calculations of kinetic isotope effects are expected to be fairly accurate since the inaccurate electronic barrier and uncertainties in the structure of the TS or due to solvent shifts cancel. In particular, predictions of differences between activation energies involving abstraction from the same alcohol molecule should be too high by only ca. 10%, which certainly provides a stringent test on experimental numbers. Since calculations were done also for the fully deuterated molecules, they take care of the secondary isotope effects.

The dipole moments were predicted to decrease from the reactant to the transition state, specifically from 1.87 to 1.62 D for methanol, from 1.82 to 1.45 D for ethanol, and from 1.75 to 1.59 D for 2-propanol.

Systematic Experimental Errors. Figures 1 and 2 show excellent linear Arrhenius behavior for all systems investigated here. The individual error bars are quite small and do not leave much room for statistical errors. This, however, does not exclude the possibility of systematic errors.

Even though the heavy water has a purity of only 97−99%, this does not introduce any systematic errors in the rate constants of D reactions since the disappearance of D is observed directly. The isotopic purity of the alcohols is more important. Assuming $k_H(H) \approx 10k_H(D)$ [or $k_D(H) \approx 10k_D(D)$], a 1% impurity can increase the observed absolute value of $k_H(D)$ or $k_D(D)$ by as much as 10%, and assuming it enters solely into the preexponential factor it increases log *A* by 0.04. This is still within experimental error.

The rate constants of parallel reactions enter additively into the pseudo-first-order rate constant for the disappearance of the D atoms. This is of relevance in particular for the higher alcohols where abstraction from positions other than the α-carbon occurs. A contribution of abstraction from the hydroxyl group (11.6% at 299 K and 18.8% at 232 K) was claimed by Dainton et al.[19] in the case of 2-propanol. Considering that the BDE of O−H is higher by 62 kJ mol^{-1} [24,25] than for the tertiary C−H bond, such a significant contribution is hard to accept. Rather than abstraction from O−H, the effect may have to be attributed to incompletely deuterated 2-propanol (stated to be 99% D).

Lifshitz[16] investigated CH_3CD_2OH and found also H abstraction from the methyl group, even though the bond dissociation energy (BDE) is higher by 41.4 kJ mol^{-1}.[24,25] Still, abstraction from the methylene group was found to be more important by a factor of 12.6. We thus have to assume that abstraction from the methyl groups will interfere in general. The effect is illustrated by an arbitrary example where the rate constant $k_H(H)$ for ethanol (assuming it represents abstraction from the methylene group) is added to $k_H(H)$ for methanol (abstraction from the methyl group), which is an order of magnitude lower and has nearly the same preexponential factor but a higher activation energy by 5.3 kJ mol^{-1}. The sum has a higher preexponential factor by 0.16 in log *A* and an increased activation energy by 0.5 kJ mol^{-1} compared with the individual ethanol number. These deviations are of the order of the experimental errors and are thus suited to slightly distort the data. The interference of abstraction from the methyl group should be less serious for 2-propanol since the two BDEs are further apart. Anbar and Meyerstein[15] concluded that it is suppressed by a factor of 110 over the abstraction of the α-H.

For 2-propanol, more likely than for 1-propanol or ethanol, H_2O elimination under formation of the olefin may occur at elevated temperatures. The olefin would be expected to react at a considerably higher rate, leading to an increase of the observed rate constant. For this reason, the reaction of D with 2-propanol-d_8 was examined at pD 4.8. This case illustrates that the absence of any highly reactive impurities in the solutions is essential. As we shall see below, H_2O elimination may have slightly affected the rate constant for the reaction of D with undeuterated 2-propanol, even though test experiments at a higher pD gave similar results.

Many of the systematic errors are reduced or canceled when the ratio between rate constants of isotopic molecules is taken, which allows for a much more compelling discussion. It is this strategy which will be followed below.

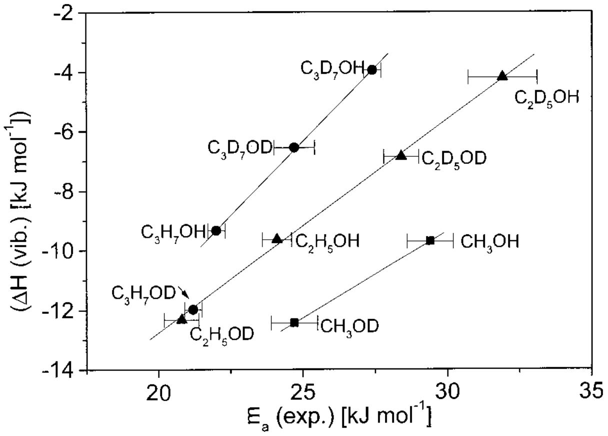

Figure 3. Correlation of the calculated vibrational contributions to the activation enthalpies with the experimental activation energies for the reactions of the isotopomers of methanol (■), ethanol (▲), and 2-propanol (●) with D (alcohols: ROD) and H (alcohols: ROH) atoms.

Kinetic Isotope Effects. KIE of the type $k_H(H)/k_H(D)$ and $k_D(H)/k_D(D)$ where the abstracted atom is the isotope are given in the upper half of Table 2. Values of about 6−9 as found in the present work are quite typical for abstraction of H vs D near room temperature.[20] They are clearly larger for the reactions of ethanol than those of 2-propanol. This is plausible, since for the lower BDE of the abstracted atom the reaction is more exothermic, and therefore the transition state is earlier and resembles more the reactants. For $k_H(H)/k_H(D)$ of 2-propanol we find a value of 6.38 ± 0.04, which coincides with the values of 6.8 ± 0.4 by Dainton et al.[19] and of 7.5 ± 1.0 reported by Anbar and Meyerstein.[15]

KIE of the type $k_H(H)/k_D(H)$ and $k_H(D)/k_D(D)$ where the attacking atom is the isotope are found in the lower half of Table 2. Since they arise from a competition of the effects of the translational partition function of the attacking isotope which favor the reactions of H over those of D by a factor of $2^{3/2} = 2.8$, and of the counteracting energy differences in the TS they are expected to be small. Indeed they are found to be close to unity, and actually <1 for methanol and ethanol where the TS is relatively late and therefore dominating the KIE, and >1 for 2-propanol where the TS is earlier.

Activation Energies. Experimental activation energies range between ca. 20 and 32 kJ mol^{-1}. They represent a sum of at least three contributions, namely, (i) the electronic barrier, (ii) 2*RT* (eq 14), and (iii) the differences of the enthalpies in internal degrees of freedom between transition state and reactants, which is mostly zero-point energy. Since the latter is expected to be accurate to within ca. 10% in the ab initio calculations and far more reliable than electronic barriers, we have plotted the calculated vibrational enthalpy differences, ΔH(vib.), against the experimental activation energies in Figure 3. In this plot we ideally expect the points to lie on separate straight lines (one for all isotopic variants of each alcohol reaction) with a slope of unity and an intercept at $\Delta H(\text{vib.}) = 0$ which corresponds to the "experimental" electronic barrier incremented by 2*RT*. This is well obeyed for 2-propanol, except for the point for C_3H_7OD which lies on the ethanol line. Extrapolation leads to an electronic barrier of 26 kJ mol^{-1} for abstraction from 2-propanol. The points for ethanol make a perfect straight line from which we obtain an electronic barrier of 32 kJ mol^{-1} although the slope is slightly below unity. From the two points for methanol we obtain a barrier of about 38 kJ mol^{-1}. The straight-line behavior suggests that the mass-dependence of the vibrational energies is predicted consistently. The deviations of these slopes from unity are also reflected as deviations between experimental and calculated differential activation energies in the last column of Table 2, and they are discussed in that context.

The electronic barriers are strongly related to the variation in bond strength, reflected by the BDE of the reacting molecules. The BDEs[25] (Table 1) are defined as enthalpy changes involved in breaking 1 mol of R−X bond and refer to gas-phase standard conditions. They follow the trend of the experimental E_a in the liquid. BDEs are higher for the primary C−H bond of the methyl group (methanol) than for the secondary hydrogen in the methylene group (ethanol, 1-propanol) due to inductive electronic effects. The lowest energy is needed to break the C−H bond of 2-propanol.

In the gas phase, E_a decreases from ca. 22.9 kJ mol^{-1} [14,26] for the reaction of H atoms with methanol to 19.2 kJ mol^{-1} [27] for ethanol. Inconsistent with the trend of the BDEs, the gas-phase activation energy for 2-propanol was reported to be 26.77 kJ mol^{-1},[28] which is about 7.5 kJ mol^{-1} *higher* than for ethanol and also 4.77 kJ mol^{-1} higher than in the liquid; it may therefore be in error.

The calculated differences of ΔH(vib.) between undeuterated and deuterated alcohols are the same for all alcohols (−5.4 kJ mol^{-1}, Table 2, upper half, fourth column) while the experimental numbers show a trend to more negative values, but the entry of −3.5 kJ mol^{-1} for 2-propanol deviates in the opposite direction, which relates directly to the stray point in Figure 3.

The influence on the transition state is seen by comparison of cases where the attacking atom is the isotope, and abstraction is from the same molecule (Table 2, lower part). The relevant bond dissociation energy is then the same, but the activation energy for the reaction of H is found to be higher than that for D by between 3 and 5 kJ mol^{-1}, while the difference between ab initio values is nearly constant at 2.7 kJ mol^{-1}. The experimental entry of 0.9 kJ mol^{-1} for 2-propanol appears too low and looks out of range.

Different solvation of reactant and transition state contributes to the activation energy and should justify deviations from gas-phase values. The Kirkwood formula for solvation of a dipole in a dielectric continuum is[29]

$$\Delta G_{\mathrm{solv}} = -\frac{\mu^2(\epsilon - 1)}{4\pi\epsilon_0 b^3(2\epsilon + 1)}$$

where μ is the dipole moment, b is the molecular radius, and ϵ is the dielectric constant. Since the calculations predict a smaller dipole moment for the transition state, this leads to an increase in the free energy of activation in going from the gas phase to aqueous solution which amounts to ca. 1.5 kJ mol^{-1} [3,14,26] for methanol. While this is a free energy and not an enthalpy, we note that it is the order of magnitude of the observed increase (E_a of ca. 3 kJ mol^{-1} for the reaction of D and 6.5 kJ mol^{-1} for H with methanol). For the reaction of H with ethanol the increase was reported to amount to ca. +5 kJ mol^{-1}.[3,27] Measurements with 2-propanol, however, yielded a difference of −4.77 kJ mol^{-1}.[28] Since it is difficult to rationalize this change of sign, we expect the gas-phase value to be in error. A further contribution comes from the enthalpy of solvation of the hydrogen atom which is expected to be very similar[4] to that of the H_2 molecule and amounts to only ca. 0.6 kJ mol^{-1} at an intermediate temperature of 323 K, leading to an additional increase of the activation energy in aqueous environment. Recent quantum calculations[30] predict only a small solvation energy difference between H and D, so that both particles can be treated classically.

Preexponential Factors. There are several points which have to be discussed in relation to the Arrhenius preexponential factors. Ab initio values are calculated based on eq 15, using the $\Delta S^{\ddagger}$ values given in Table 1. In the gas, the full loss of translational entropy of the hydrogen atom as it approaches the transition state amounts to −108.8 J mol^{-1} K^{-1} for H and 117.4 J mol^{-1} K^{-1} for D. The calculated values in Table 1 are somewhat smaller, showing still that most of the decrease of log A from the entropy-neutral value of 15.05 (at 298 K) comes from this loss of translational entropy of the hydrogen atom, but that a small fraction is compensated by a gain of vibrational entropy in the new, floppy vibrational degrees of freedom. The calculation works well, which is seen by comparison of the experimental gas-phase value for the reaction of H with methanol [log A = 9.81(5)[14]], ethanol [log A = 9.62(4)[27]], and 2-propanol [log A = 10.39(6)[28]], with the corresponding ab initio values (log A = 9.9, log A = 10.02, and log A = 10.04, respectively). Two independent studies of the reaction of methanol with D atoms in the gas phase[14,26] gave an average for log A of 10.3, which is also in good agreement with the ab initio value of 9.82.

Experimental aqueous phase values of log A are higher than ab initio predictions by 1.56 on the average. Much of this is related to the large negative solvation entropy of H in pure water, $\Delta S_{\mathrm{solv}} = -37$ J mol^{-1} K^{-1} at 323 K.[4] This translates into a predicted shift of 1.9 in log A, which compares well with the experimental results for H reacting with methanol (shift of 1.83 in log A) and ethanol (1.91). For the H atom reaction with 2-propanol, the shift in log A corresponds to 1.47, indicating a smaller impact on the preexponential factor from solvation. The corresponding literature values for the reaction of D atoms with methanol show a shift in log A of 0.86[26] and 0.52,[14] much smaller than predicted.

Rather than only the concentration of reactant molecules it is the concentration of R−H(R−D) bonds to which the number of successful encounters and thus the rate constant is proportional. The number of equivalent H atoms which are to be abstracted from the alcohol is therefore a statistical factor that enters directly into the preexponential factor. To account for this, the predicted values of log A in Table 1 have to be incremented by 0.48 when three equivalent atoms are present, as in methanol, and by 0.30 for two equivalent atoms, as in ethanol. The experimental values for methanol are somewhat lower than those for 2-propanol and obviously do not support this expectation. Possibly, the effect is approximately balanced by a change in H(D) atom solvation due to the higher alcohol concentrations which are necessary for the slower reactions (see preceding paragraph).

For the discussion of isotope effects in preexponential factors, we refer to the third column of Table 2 which gives differences of log A values. In the upper half, where the isotope is the abstracted atom, the prediction gives essentially zero isotope effect, whereas the experimental preexponential factor is larger for D than for H. In the lower part, the attacking atom is the isotope. Here, the preexponential factors are predicted to be larger for H than for D, mainly due to the different translational entropy of the isotopes (if there was no compensation in the transition state one would expect a difference of 0.45 instead of 0.17). Clearly, the experimental values differ by significantly more than predicted, so that we obviously have to resort to additional effects to explain the details of our observations.

Contributions of Tunneling. It is well-known that tunneling plays a role in many chemical reactions which involve the making or breaking of bonds to hydrogen since it is particularly pronounced for low-mass particles moving through narrow, not too high barriers of exothermic reactions. It increases the rate constants over their semiclassical values and leads thus to a curved upward deviation in the Arrhenius plot which is particularly pronounced at the low-temperature end. It thus enhances the slight curvature which is predicted already based on the proportionality to T^2 of the TST preexponential factor (eq 12). No indication of curvature is seen in any of our Arrhenius plots in Figures 1 and 2. However, we should not be too quick in taking this as evidence for the absence of significant contributions of tunneling. The temperature range may be too small to reveal curvature. More important, the nonlinear behavior of H atom solvation[4] counteracts and possibly compensates quantitatively for it. In this context it is of interest that a combination of gas-, liquid-, and solid-state rate constants for the reaction of H atoms with CH_3OH does show a curvature, and an estimate gave a value of 6.8 at 295 K for the tunneling correction factor Γ through a one-dimensional barrier.[32]

The experimental preexponential factors are higher than the predicted gas-phase values, but as discussed above, this increase is somewhat less than expected on the basis of H atom solvation. We should nevertheless be careful about the interpretation of the absolute values, it is safer to analyze the isotope effects as given in Table 2. The upper half of the table refers to reactions where the isotope is the abstracted atom. In the incoming channel the moving mass is essentially that of the attacking H isotope, which is the same for the two reactions considered. In the outgoing channel the moving mass is that of the isotopomer of the hydrogen product molecule, which differs for the two reactions. When the abstracted atom is H, one should therefore expect more tunneling and thus lower preexponential factors and activation energies than expected based on semiclassical theory. This is correctly observed for both the preexponential factors and the activation energies, and it suggests that tunneling is involved.

In the lower part of the table, the isotope is the attacking atom. The experimental shifts of the activation energies agree within errors with the predictions, except for the methanol reaction (and for the entry of 0.8 kJ mol^{-1} for the undeuterated 2-propanol which has already been discussed). However, the preexponential factor for the H reaction is higher by *more* than the calculated amount which should represent an upper limit. This is against expectation for a significant contribution of tunneling and perhaps supports recent theoretical work which showed that tunneling should be quenched in solution.[5] Indeed, the opposite behavior is found for H and D attacking methanol in the gas phase where log A is lower by 0.45 for the H atom reaction, suggesting that tunneling interferes and decreases A and also E_a.

Dynamic Solvent Effects. It emerged from the last paragraph that the preexponential factors for the reactions of H are higher than those of D by an inexplicably large amount. In this context we have to note that H reactions were measured in H_2O and D reactions in D_2O. Thus, there is the possibility of a dynamic solvent effect, implying that the reorganization of the solvent shell around the reacting partners is slower in heavy water and that there is thus a higher friction which impedes the reaction of D. Incomplete equilibrium solvation of the transition state could thus be the reason why we see only a shift in log A of 1.8 in H_2O and 1.5 in D_2O instead of the full expected shift of 1.9 in taking the reaction from the gas phase to the aqueous phase. Such effects were recently found experimentally[4] and verified theoretically[5] for the addition of hydrogen isotopes to benzene. It remains to be seen how this affects the activation energies, possibly it is just what is reflected in the lower part of Table 2. Also Geimer et al.[17] conclude that the small changes of KIE between water and heavy water cannot be explained by a solvent-free model.

Conclusions

For the first time, rate constants were determined as a function of temperature for the hydrogen abstraction reactions by D atoms from alcohols (methanol, ethanol, 1-propanol, and 2-propanol) and their deuterated derivatives in aqueous solution. Excellent Arrhenius behavior was found in all cases. Although there was no indication in the experiment or in the Arrhenius plot, the rate constant for the reaction of D with undeuterated 2-propanol may be slightly high ($<10\%$), and Figure 3 and the discussion of Table 2 show that the activation energy may be too low by as much as 2 kJ mol^{-1}. We suggest that water elimination may have interfered and that the reaction should be reinvestigated at a higher pD. Buffered solutions (pD = 4.7) had to be used in the case of 2-propanol-d_8 to avoid side effects. Other results were found to be internally fully consistent and in good agreement with room-temperature data as far as available in the literature.

The Arrhenius preexponential factor is clearly lower for the reactions of D compared with those of H, which confirms the semiclassical treatment and reflects the loss of translational entropy of the atoms when they become bound in the TS.

A rate enhancement reflected by an increase of the preexponential factor relative to that in the gas phase or in the calculations is attributed to the large negative solvation entropy of the hydrophobic H (D) atom, as it had been discovered in a study of H addition to benzene.[4] The amount of the shift and in particular the trend between H and D may reflect an incomplete solvation equilibrium of the transition state and thus a dynamic solvent effect.

Tunneling contributions may be involved in the reactions, but the expected trend in activation energies and in preexponential factors is observed only when the isotope is the abstracted atom. When the isotope is the attacking atom the effect is clearly reduced in the liquid compared with the gas phase, and it may be that dynamic solvent effects are involved, as it was recently suggested for the addition reaction of H to benzene.[4] This perhaps supports recent theoretical work which showed that tunneling should be quenched in solution.[5] An accurate study of the present reactions in the gas phase may help resolve such questions.

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References and Notes

(1) Williams, W. S. C. *Nuclear and Particle Physics*; Clarendon Press: Oxford, 1991.

(2) Elliot, A. J.; McCracken, D. R. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1539.

(3) Mezyk, S. P.; Bartels, D. M. *J. Phys. Chem.* **1997**, *101*, 1329.

(4) Roduner, E.; Bartels, D. M. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1037.

(5) Garrett, B. C.; Schenter, G. K. In *Structure, Energetics and Reactivity in Aqueous Solution*; Cramer, C. J., Truhlar, D. G., Eds.; ACS Symposium Series 568, American Chemical Society: Washington, DC, 1994.

(6) Bartels, D. M.; Mezyk, S. P. *J. Phys. Chem*. **1993**, *97*, 4101.

(7) Han, P.; Bartels, D. M. *J. Phys. Chem*. **1990**, *94*, 7294.

(8) Han, P.; Bartels, D. M. *Chem. Phys. Lett*. **1989**, *159*, 538.

(9) Han, P.; Bartels, D. M. *J. Phys. Chem*. **1992**, *96*, 4899.

(10) Draganic, I.; Draganic, Z. D. *The Radiation Chemistry of Water*; Academic Press: New York, 1971.

(11) Mezyk, S. P.; Lossack, A.; Bartels, D. M. *Can. J. Chem*. **1997**, *75*, 1114.

(12) Hehre, W. J.; Huang, W. W. *Chemistry with Computation: An Introduction to Spartan*, Spartan, Version 5.0; Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

(13) Smaller, B.; Avery, E. C.; Remko, J. R. *J. Phys. Chem*. **1971**, *55*, 2414.

(14) Meagher, J. F.; Kim, P.; Lee, J. H.; Timmons, R. B. *J. Phys. Chem*. **1974**, *78*, 2650.

(15) Anbar, M.; Meyerstein, D. *J. Phys. Chem*. **1964**, *68*, 3184.

(16) Lifshitz, C.; Stein, G. *J. Chem. Soc*. **1962**, 3706.

(17) Geimer, J.; Beckert, D.; Jenichen, A. *Chem. Phys. Lett*. **1997**, *280*, 353.

(18) Vacek, K.; von Sonntag, C. *Chem. Commun.* **1969**, 1256.

(19) Dainton, F. S.; Holt, B. J.; Philipson, N. A.; Pilling, M. J. *J. Chem. Soc., Faraday Trans. 1*, **1976**, *72*, 257.

(20) Melander, L.; Sauders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Robert E. Krieger Publishing Co.: Malabar, FL, 1987.

(21) Benson, W. S. *Thermochemical Kinetics*; Wiley: New York, 1976.

(22) Robinson, P. J. *J. Chem. Educ*. **1978**, *55*, 509.

(23) Pulay, P.; Fogarasi, G. *J. Chem. Phys.* **1981**, *74*, 3999.

(24) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.

(25) *CRC Handbook of Chemistry and Physics*,; 76th Ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995.

(26) Hoyermann, K.; Sievert, R.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem*. **1981**, *85*, 149.

(27) Aders, W.-K.; Wagner, H. G. *Ber. Bunsen-Ges. Phys. Chem*. **1973**, *77*, 712.

(28) Oganesyan, K. T.; Nalbandyan, A. B. *Izv. Akad. Nauk Arm. SSR, Khim. Nauki* **1965**, *18*, 237.

(29) Entelis, S. G.; Tiger, R. P. *Reaction Kinetics in the Liquid Phase*; John Wiley and Sons: New York, 1976.

(30) Gai, H.; Garett B. C. *J. Phys. Chem*. **1994**, *98*, 9642.

(31) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(32) Roduner, E. *Prog. React. Kinet.* **1986**, *14*, 1.