J. Phys. Chem. A **1999,** *103,* 235−242

Self-Recombination Rate Constants for 2-Propanol and *tert*-Butyl alcohol Radicals in Water[†]

Stephen P. Mezyk* and Keith P. Madden

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46656

Received: March 30, 1998; In Final Form: July 20, 1998

The techniques of electron pulse radiolysis and direct detection ESR have been used to determine Arrhenius parameters for the self-recombination of 2-propanol (hydroxymethylethyl) and *tert*-butyl alcohol (2-hydroxy-2,2-dimethyl-propyl) radicals in water. Rate constants of $2k_7 = (1.56 \pm 0.10) \times 10^9$ and $2k_{23} = (1.18 \pm 0.20) \times 10^9$ dm^3 mol^{-1} s^{-1} for these radicals were measured at 26.4 and 26.6 °C, respectively, with corresponding activation energies of 18.8 ± 1.2 (5.3−71.7 °C) and 15.83 ± 0.92 (8.5−69.8 °C) kJ mol^{-1} for these two reactions. These data are compared to available literature rate constants, and also to the results of diffusion-controlled rate constant calculations, which demonstrate that radical reactivity, not diffusion, dominates both recombination processes in water.

Introduction

Hydroxyalkyl radicals are formed in chemical and biochemical systems by the abstraction of methylenic hydrogen atoms from alcohols, glycols, and carbohydrates, yielding carbon-centered radicals with hydroxyl functions in the positions alpha and beta to the formal radical center. The formation of such species in carbohydrates can lead to secondary radicals via dehydration, carbon−carbon bond cleavage, or ring-opening due to rupture of the hemiacetal bond.[1] The increasing use of free radical chemistry in synthesis, and the importance of carbohydrate radical formation in radiation biology and carbohydrate biosynthesis have motivated us to examine in detail the kinetics of the reactions of these radical species in aqueous solution. As models for such carbohydrate species, we begin by examining the free radical chemistry of simple α- and *β*-hydroxyalkyl species.

Small aliphatic alcohols have been used extensively in mechanistic and kinetic studies to simplify the radical chemistry obtained via radiolysis and photolysis. In particular, the use of 2-propanol and *tert*-butyl alcohol as $^•$H atom and $^•$OH radical scavengers to isolate the reactions of the hydrated electron with substrates in water is a well-established technique in electron pulse radiolysis.[2] These abstraction reactions predominantly occur at the α-carbon position,[3] to produce radicals which subsequently disproportionate or dimerize,

$$H_2O \rightsquigarrow {}^•H, {}^•OH, e^-_{(aq)} + \text{other species} \qquad (1)$$

$$R_1R_2CHOH + {}^•H/{}^•OH \rightarrow {}^•COHR_1{-}R_2 + H_2/H_2O \qquad (2)$$

$$2{}^•COHR_1{-}R_2 \rightarrow R_1{-}R_2CO + R_1{-}R_2CHOH \qquad (3a)$$

$$\rightarrow R_1{-}R_2C(OH)C(OH)R_1{-}R_2 \qquad (3b)$$

Carbon-centered radicals such as 2-hydroxy-2-propyl have been demonstrated to be prototypical nucleophilic radicals, whose reactivity is dominated by polar effects.[4,5] The addition of these types of radicals to alkenes is one of the most important processes in polymer chemistry, and consequently, there exists a large body of kinetic data for such reactions.[6] Many of these radicals have both a usable ESR and UV absorption, which allows for their direct monitoring in a variety of solvents. However, there is substantially less rate constant information for carbon-centered radical reactivity in aqueous solution, especially at nonambient temperatures.

As definitive rate constants and mechanisms are required for accurate kinetic modeling of reaction systems, the temperature-dependence of the total self-termination rate constants for 2-propanol and *tert*-butyl alcohol radicals in water were determined in this study. Direct ESR detection of the decay of these radicals was the monitoring method of choice, where these alcohol radicals were rapidly formed by the reaction of electron pulse radiolysis-generated hydroxyl radicals with the appropriate alcohols in N_2O-saturated aqueous solution. Under the experimental time scales employed, the conversion of the hydrated electrons into hydroxyl radicals, and the reactions of the hydroxyl radicals and hydrogen atoms with the alcohols to produce the desired alcohol radicals were very fast,[2] and hence the only process observed was the decay of the 2-propanol and *tert*-butyl alcohol radicals.

Experimental Section

Stock solutions were prepared at room temperature by N_2O-saturating Millipore Milli-Q reagent grade water containing 0.10 mol dm^{-3} of 2-propanol (Fisher, HPLC grade) or *tert*-butyl alcohol (Fisher, Certified) at natural pH. All chemicals were used as received. N_2O was used to convert the hydrated electrons produced in the radiolysis into hydroxyl radicals, according to the reaction[2]

$$e^-_{(aq)} + N_2O\ (+H_2O) \rightarrow {}^•OH + OH^- + N_2 \qquad (4a)$$

in order to increase the initial alcohol radical yield formed by reaction 2. Experiments at nonambient temperatures were performed by flowing the room temperature solutions through a short, temperature-controlled, condenser tube immediately

---

* To whom correspondence should be addressed.

[†] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution NDRL 4046 from the Notre Dame Radiation Laboratory.

10.1021/jp981680j CCC: $18.00

before irradiation. The temperature stability of this method was found to be better than 0.3 °C, as measured by a thermocouple placed directly above the irradiation cell. At elevated temperatures (>40 °C), significant outgassing of the N_2O occurred, creating bubbles in the flowing solution line. This problem was resolved by using two bubble traps, in series, immediately after the heating cell to reduce the N_2O concentration to its natural solubility limit before it reached the irradiation cell.

In-situ radiolysis ESR data were recorded by irradiating flowing aqueous solutions with a 2.8 MeV electron beam from a Van de Graaff accelerator. A pulsed 150 mA beam of 0.5 μs duration and 100 Hz repetition was used for these kinetic experiments. The initial radical concentration for the experiments was varied over the range (60−300) × 10^{-6} mol dm^{-3}, as determined from the decay of the sulfite anion under basic conditions (pH 11),

$$2\ SO_3^{-\bullet} \rightarrow \text{products} \tag{5}$$

whose rate constant, $2k_5 = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1}, has been established by both conductivity and absorption spectroscopy methods.[7] Corroboration of the initial radical concentration has also been obtained by absolute measurement of nitroxide depletion under similar conditions.[8] The solution was pumped using a continuous syringe injection method at a rate of 20.0 cm^3/min, sufficiently fast to ensure the irradiation volume of the ESR flat cell was replenished completely between electron beam pulses.

ESR kinetic curves were recorded at X-band (9.2GHz) using nonsaturating levels of microwave power. Magnetic field measurements were performed via NMR methods,[9] using the ESR spectrometer and procedures of Madden, et al.[10] Time-resolved ESR kinetic traces were recorded for decay periods of 50−200 μs to observe the evolution of the reaction kinetics corresponding to an ESR intensity decrease of several half-lives. The traces decrease in a monotonic fashion, with no Torrey[11] oscillation observed in the kinetic curve. Kinetic traces were recorded with the magnetic field set to the high field component of the central multiplet of the spectrum, so that, to zeroth order, chemically induced dynamic electron polarization (CIDEP) effects are suppressed.

Kinetic traces were fitted using the Levenberg−Marquardt nonlinear least-squares fitting module with the Origin computer program (MicroCal Software, Inc., Northampton, MA) for both simple second-order decays (sulfite) or mixed first- and second-order decays to allow elucidation of rate constants for the individual processes.

Results and Discussion

2-Propanol Recombination. Typical kinetic traces for the decay of the 2-propanol radical signal obtained at 15.8 and 42.5 °C are shown in Figure 1a. None of the alcohol decay curves obtained in this study exhibited pure second order kinetics, and especially at higher temperatures, it was evident that a large component of first-order decay was present. Therefore, all of the measured data were fitted to the mixed order decay equation:[12]

$$[R^\bullet]_t = \frac{[R^\bullet]_o k_8}{k_8 \exp(k_8 t) - 2[R^\bullet]_o k_7 (1 - \exp(k_8 t))} + B \tag{6}$$

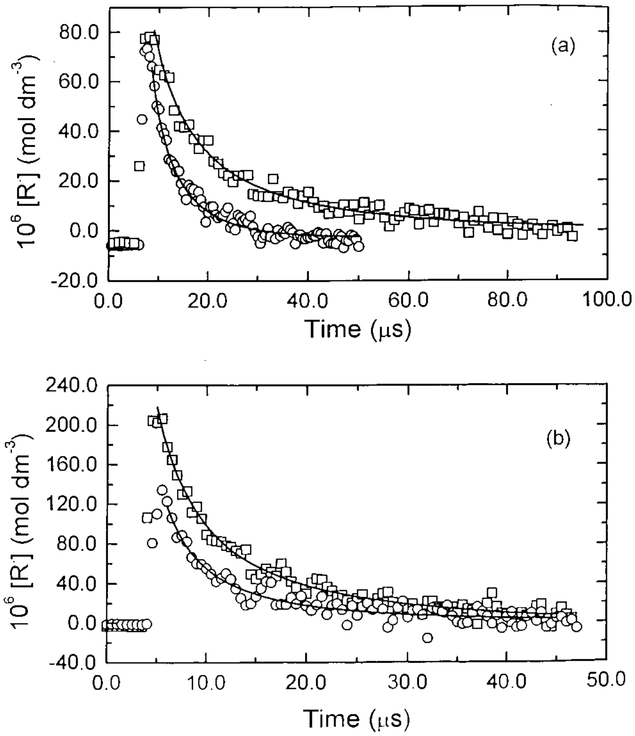

Figure 1. (a) Typical ESR experimental data for 2-propanol radical recombination in aqueous solution at 15.8 °C (□) and 42.5 °C (○). Solid lines correspond to combined first- and second-order fitted decays corresponding to rate constants of $2k_7 = (1.18 \pm 0.33) \times 10^9$ dm^3 mol^{-1} s^{-1}/$k_8 = (2.85 \pm 0.55) \times 10^4$ s^{-1} and $2k_7 = (1.99 \pm 0.38) \times 10^9$ dm^3 mol^{-1} s^{-1}/$k_8 = (1.09 \pm 0.19) \times 10^5$ s^{-1}, respectively. (b) Analogous experimental decays observed for the *tert*-butyl alcohol radical at 18.1 °C (□), $2k_{23} = (8.69 \pm 0.91) \times 10^8$ dm^3 mol^{-1} s^{-1}/$k_{24} = (4.31 \pm 0.62) \times 10^4$ s^{-1} and 50.1 °C (○), $2k_{23} = (1.51 \pm 0.26) \times 10^9$ dm^3 mol^{-1} s^{-1}/$k_{24} = (7.03 \pm 1.27) \times 10^4$ s^{-1}.

to derive the $2k_7$ and k_8 rate constants associated with the reactions

$$2\ (CH_3)_2{}^\bullet COH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \tag{7a}$$

$$\rightarrow CH_2C(CH_3)OH + (CH_3)_2CHOH \tag{7b}$$

$$\rightarrow (CH_3)_2C(OH)C(OH)(CH_3)_2 \tag{7c}$$

and

$$(CH_3)_2{}^\bullet COH \rightarrow \text{products} \tag{8}$$

where $2k_7 = 2k_{7a} + 2k_{7b} + 2k_{7c}$, and B is a fitted base line offset correction. These different pathways have been well-established previously,[13,14] with the rate constant ratio $(2k_{7a} + 2k_{7b})/2k_{7c}$ being determined as 4.4 at 26 °C.[13]

The calculated initial radical concentration ($R^\bullet = (CH_3)_2{}^\bullet COH$) was used to convert the observed signal intensity to absolute concentration. However, the significantly higher 2-propanol concentration (0.1 mol dm^{-3}) as compared to the standard sulfite concentration (5.0 × 10^{-3} mol dm^{-3}) meant that different amounts of intraspur radical scavenging occurred, and this difference also had to be taken into account. This situation is further complicated because both hydrated electrons and hydroxyl radicals were scavenged, by N_2O and sulfite or 2-propanol respectively, thereby increasing the initial yields of both species (having a hydroxyl radical scavenger present which undergoes intraspur scavenging increases the initial yield of hydrated electrons, and vice versa).

TABLE 1: Rate Constants and Calculated Yield Parameters for Initial Radical Yields at Room Temperature

species	concn/mol dm^{-3}	$k_{\bullet OH}$/dm^3 mol^{-1} s^{-1}	k_{e^-}/dm^3 mol^{-1} s^{-1}	$G_{\bullet OH}(s_1,s_2)$	$G_{e^-}(s_1,s_2)$	$2G_C(s_1+s_2)$	$G(R^\bullet)$
N_2O	2.4×10^{-2}		9.1×10^9				
SO_3^{2-}	5.0×10^{-3}	5.1×10^9		3.03	3.36	−0.46	6.44
2-propanol	1.0×10^{-1}	1.9×10^9		3.29	3.36	−0.23	6.92
tert-butanol	1.0×10^{-1}	6.0×10^8		3.11	3.36	−0.37	6.60

Intraspur scavenging in aqueous solution has been the subject of considerable theoretical work,[15−19] from which has been derived empirical equations dealing with these cooperative effects. For the calculation of the initial total alcohol radical yield, G(R$^\bullet$) in the N_2O/2-propanol scavenger system at room temperature, one can use the equation[19]

$$G(R^\bullet) = G_{\bullet OH}(s_1,s_2) + \epsilon_{e^-}^{N_2O} G_{e^-}(s_2,s_1) - 2\epsilon_{e^-}^{N_2O}[G_C(s_1) - G_C(s_1+s_2)] + G_{\bullet H} \quad (9)$$

where the first term is equal to the yield of the hydroxyl radical by sulfite (or alcohol) that would be scavenged if the nitrous oxide did not convert the hydrated electron into $^\bullet$OH, and the second term corresponds to the yield of $^\bullet$OH produced by the scavenging of the hydrated electron by nitrous oxide. The third term represents higher order corrective terms.[20] The $\epsilon_{e^-}^{N_2O}$ factor is the efficiency of the reaction of hydrated electrons with nitrous oxide, and has been assumed to be unity throughout these calculations; as even though the concentration of this gas is decreased at higher temperatures there are no other significant pathways for reaction of the hydrated electron. The last term in this expression is the yield of the product radical produced by hydrogen atom reaction. Unfortunately, no equivalent scavenging equations exist for this radical, and therefore it was assumed that the product radical yield from this pathway was always the experimentally determined value in N_2O-saturated aqueous solution $G_{\bullet H} = 0.51$.[21] It should be noted that there is a slow reaction pathway for hydrogen atoms with N_2O itself,[2]

$$^\bullet H + N_2O \rightarrow {}^\bullet OH + N_2 \qquad k = 2.1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (10)$$

however, the hydroxyl radical produced will also react to give the desired alcohol/sulfite radical and hence there is no loss of yield by this process.

To evaluate the first component term in eq 9 for sulfite one can use the expression:[18]

$$G_{\bullet OH}(s_1,s_2) = G_{\bullet OH}^{esc} + (G_{\bullet OH}^{0} - G_{\bullet OH}^{esc})F[(2.95 \times 0^{-10})s_1] + 1.2(F[(5.5 \times 10^{-10})\{s_1 + s_2\}] - F[(5.5 \times 10^{-10})s_1]) \quad (11)$$

where $G_{\bullet OH}^{esc}$ is the steady-state or escape yield of the hydroxyl radical, $G_{\bullet OH}^{0}$ is its initial radiolysis yield, s_1 is this radicals scavenging efficiency, (defined as the pseudo-first-order rate coefficient equal to the product of the scavenging rate coefficient and the scavenger concentration), s_2 is the equivalent scavenging efficiency for the other radical (hydrated electron), and the function F is defined as[16,17]

$$F(x) = \frac{(x^{1/2} + x/2)}{(1 + x^{1/2} + x/2)} \quad (12)$$

where x is the evaluated product in the square brackets in eq 11. For the N_2O-saturated 5.0×10^{-3} mol dm^{-3} sulfite system, this contribution to the total alcohol radical yield is calculated using the parameters[18]

$$G_{\bullet OH}^{esc} = 2.56$$

$$G_{\bullet OH}^{0} = 5.50$$

$$s_1 = k_{\bullet OH}[\text{sulfite}] = (5.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (5.0 \times 10^{-3} \text{ mol dm}^{-3}) = 2.55 \times 10^7 \text{ s}^{-1}$$

$$s_2 = k_{e^-}[N_2O] = (9.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (2.43 \times 10^{-2} \text{ mol dm}^{-3}) = 2.21 \times 10^8 \text{ s}^{-1}$$

which upon substitution into eq 11 gives $G_{\bullet OH}(s_1,s_2) = 3.03$. An equivalent value for the initial yield of the hydrated electron, based on the same equation with modified parameters

$$G_{e^-}^{esc} = 2.55$$

$$G_{e^-}^{0} = 4.80$$

gives $G_{e^-}(s_1,s_2) = 3.36$.

For the third term in eq 9 the basic parameters are

$$G_{e^-}^{esc} = 1.20$$

$$G_{C}^{0} = 0$$

Substituting these values into eq 11 with the same s_1 and s_2 scavenging capacities, gives $G_C(s_1) = 1.07$, $G_C(s_1 + s_2) = 0.84$ and the correction term $-2[G_C(s_1) - G_C(s_1 + s_2)] = -0.46$. Summing these three values with the initial yield of the hydrogen atom reaction,[21] $G_{\bullet H} = 0.51$, gives $G(R^\bullet) = 6.44$ for 5.0×10^{-3} mol dm^{-3} sulfite.

These calculations were also repeated for the alcohol systems, with all of the relevant parameters and final yields given in Table 1. It is again important to note that these yields are only calculated for "room temperature". The exact extension of these parameters to allow calculation of specific initial yields at higher temperatures was not possible, as not all of the temperature dependent parameters were available. However, for the calculation of the initial alcohol radical concentration only the G-value ratio of the alcohol and sulfite yields is required, therefore it was assumed that this ratio remained constant over the whole temperature range studied. The dose correction required for higher temperature irradiations was included by multiplying the calculated alcohol radical yield by the relative water density change.[22]

On the basis of the calculated alcohol radical yield (116×10^{-6} mol dm^{-3}) for 2-propanol at 15.8 °C, the decay curve shown in Figure 1a could be well fitted by eq 6 to give absolute rate constants of $2k_7 = (1.18 \pm 0.33) \times 10^9$ dm^3 mol^{-1} s^{-1} and $k_8 = (2.85 \pm 0.55) \times 10^4$ s^{-1}. The same fitting to the decay obtained at 42.5 °C gave $2k_7 = (1.99 \pm 0.38) \times 10^9$ dm^3 mol^{-1} s^{-1} and $k_8 = (1.09 \pm 0.19) \times 10^5$ s^{-1}. This procedure was repeated for our measured data over the temperature range 5.3−71.7 °C to give the averaged values listed in Table 2. These

TABLE 2: Summary of Temperature-Dependent Measured and Calculated Parameters for Self-Reaction of 2-Propanol and *tert*-Butanol Radicals in Aqueous Solution

alcohol	temperature/°C	$10^{-9}\ 2k_{\text{obs}}{}^{a}$/ dm^3 mol^{-1} s^{-1}	$10^{-4}\ k_{\text{obs}}{}^{b}$/ dm^3 mol^{-1} s^{-1}	diffusion coefficient/ $10^{-9}\ D_{\cdot\text{R}}$/m^2 s^{-1}	reaction radius/ $10^{-10}\ r_{\cdot\text{R}}$/m	$10^{-9}\ 2k_{\text{diff}}$/ dm^3 mol^{-1} s^{-1}	$10^{-9}\ 2k_{\text{react}}$ dm^3 mol^{-1} s^{-1}
2-propanol	5.3	0.89 ± 0.24	1.71 ± 0.34	0.594	2.75	2.49	1.38 ± 0.58
	15.8	1.15 ± 0.10	3.44 ± 0.52	0.802	2.75	3.34	1.75 ± 0.23
	26.4	1.56 ± 0.10	5.42 ± 1.06	1.06	2.76	4.41	2.41 ± 0.24
	35.7	1.75 ± 0.18	7.08 ± 0.35	1.33	2.76	5.54	2.56 ± 0.38
	42.5	1.98 ± 0.28	10.8 ± 2.7	1.55	2.77	6.50	2.85 ± 0.58
	51.3	3.02 ± 0.45	14.3 ± 2.8	1.88	2.78	7.91	4.88 ± 1.18
	71.7	4.18 ± 0.64	23.0 ± 2.9	2.84	2.80	12.0	6.41 ± 1.51
tert-butanol	8.5	0.73 ± 0.09	2.67 ± 0.41	0.530	2.98	2.39	1.05 ± 0.19
	18.1	0.87 ± 0.16	4.71 ± 0.67	0.733	2.98	3.30	1.18 ± 0.29
	26.6	1.18 ± 0.20	4.32 ± 0.82	0.942	2.98	4.25	1.63 ± 0.38
	39.3	1.39 ± 0.36	5.92 ± 1.02	1.31	2.99	5.91	1.82 ± 0.62
	50.1	1.53 ± 0.42	7.93 ± 1.10	1.67	3.00	7.57	1.92 ± 0.66
	69.8	2.49 ± 0.44	9.73 ± 1.56	2.44	3.02	11.1	3.21 ± 0.73

[a] $2k_{\text{obs}} = 2k_7$ (2-propanol) or $2k_{23}$ (*tert*-butanol). [b] $k_{\text{obs}} = k_8$ (2-propanol) or k_{24} (*tert*-butanol).

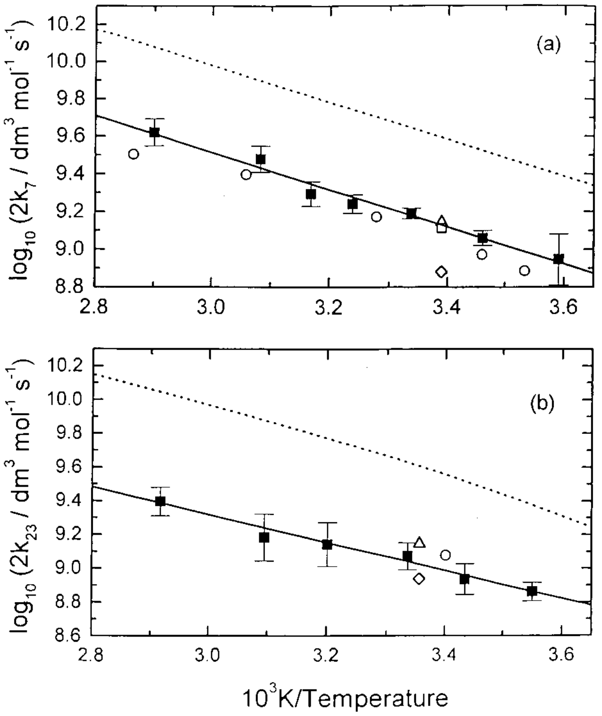

Figure 2. (a) Arrhenius plot for second-order component of 2-propanol radical recombination in aqueous solution. Error bars correspond to one standard deviation as obtained from averaging several decay curve fitted values. Solid line corresponds to theoretical values using eq 13 in text. Also shown are previous literature data for this process; ref 23 (○), ref 24 (◇), ref 25 (□), and ref 26 (△); and the diffusion-controlled limit for this reaction, as calculated from the Smoluchowski equation (dashed line). (b) Analogous Arrhenius plot for *tert*-butyl alcohol radical recombination in aqueous solution with solid line corresponding to eq 25 in text. Also shown are room-temperature literature data of ref 25 (△), ref 37 (◇), and ref 38 (○) and calculated Smoluchowski diffusion-controlled rate constants (dashed line).

second-order rate constants are also depicted in the Arrhenius plot shown in Figure 2a and are seen to be well described by the equation:

$$\log 2k_7 = [(12.46 \pm 0.21) - (18800 \pm 1200)/2.303RT] \qquad (13)$$

Also shown in this plot are the previous measurements of this rate constant available in the literature,[23−26] overall very good agreement was found. The values of this study are in excellent agreement with the previous temperature-dependent data of Lehni and Fischer,[23] who determined recombination kinetics of 2-propanol radicals in water for the temperature range 10−76 °C. Although their data gives a slightly curved Arrhenius plot, their fitted (linear) activation energy of 18.1 ± 1.2 kJ mol^{-1} is essentially identical to our value of 18.8 ± 1.2 kJ mol^{-1}. Similar good agreement was observed for the preexponential factors. For the other three room temperature rate constants, only the value of Shastri et al.[24] ($2k_7 = 7.6 \times 10^8$ dm^3 mol^{-1} s^{-1}) is slightly lower than the data of this study. Based on the measured rate constants and the ratio of 2-propanol radical disproportionation to combination (4.4 at 26 °C)[13] specific rate constants of $(2k_{7a} + 2k_{7b}) = (1.13 \pm 0.12) \times 10^9$ and $2k_{7c} = (2.57 \pm 0.28) \times 10^8$ dm^3 mol^{-1} s^{-1} at this temperature are readily derived.

In the previous temperature-dependent study of this system,[23] where the radicals were produced by flash photolysis of acetone and 2-propanol the measured recombination rate constants were asserted to be equal to the calculated diffusion-controlled values. However, our determined room-temperature rate constant of $2k_7 = (1.36 \pm 0.16) \times 10^9$ dm^3 mol^{-1} s^{-1} ($T = 22$ °C) seemed lower than would be anticipated for diffusion-controlled, uncharged radical recombination in water. To further investigate this, the 2-propanol radical encounter rate in aqueous solution was calculated, using the Smoluchowski equation[27]

$$2k_{\text{diff}} = \sigma 4(1000)\pi(D_{\cdot\text{R}} + D_{\cdot\text{R}})(R_{\cdot\text{R}} + R_{\cdot\text{R}})N \qquad (14)$$

where N is Avogadro's number, $D_{\cdot\text{R}}$ is the diffusion coefficient of the 2-propanol radical in water, $R_{\cdot\text{R}}$ is its effective reaction radius, and σ is the spin statistical factor (=0.25).

To determine the temperature-dependent diffusion coefficients and reaction radii required for calculation of the $2k_{\text{diff}}$ rate constants, the 2-propanol radical was approximated by the parent alcohol. A survey of the literature revealed several experimental measurements of 2-propanol diffusion coefficients in water,[23,28,29] and these are shown in Figure 3a. The values of Lehni and Fischer[23] are seen to be significantly lower than the other measurements,[28,29] especially at lower temperatures, and this difference is attributed to the much higher solute concentrations used in this study (the 2-propanol self-diffusion coefficients are lower by ≥30% over the entire temperature range of study).[23] Under the experimental conditions of this study the necessary diffusion coefficients were therefore determined from the other two datasets, with specific values calculated from the fitted linear expression

$$\log D_{\cdot\text{R}} = -5.669 - (9.906 \times 10^{-3}/T) \qquad (15)$$

where T is the absolute temperature.

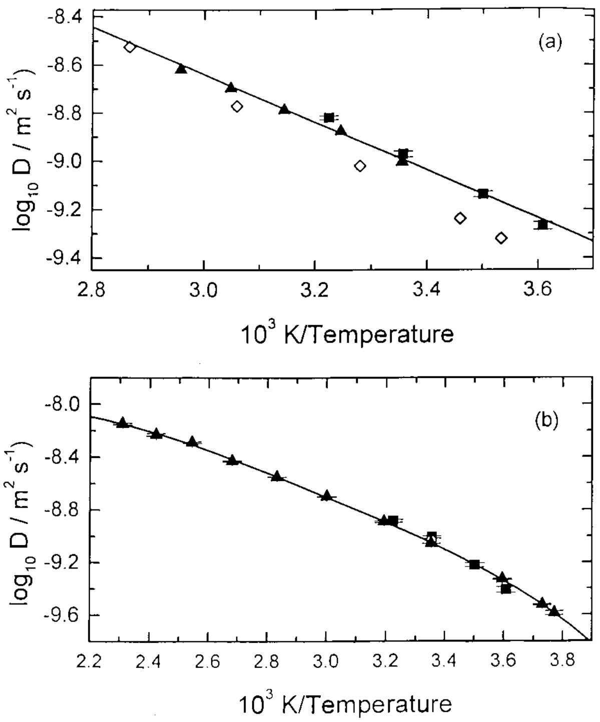

Figure 3. (a) Literature temperature-dependent diffusion coefficients for 2-propanol in water; ref 23 (△), ref 28 (■), and ref 29 (▲). Fitted line based on eq 15 in text. (b) Diffusion coefficients for *tert*-butyl alcohol in aqueous solution; ref 28 (■), ref 40 (○), and ref 41 (▲); and fitted curve given by eq 26 in text.

The calculation of the reaction radius is typically performed using the Stokes−Einstein equation,[27]

$$D_{\bullet\mathrm{R}} = \frac{kT}{6\pi\eta r_{\bullet\mathrm{R}}} \tag{16}$$

however, it has been demonstrated that this equation is inadequate for small reactive species such as the 2-propanol radical.[23,30,31] To determine this parameter for the Smoluchowski equation calculation, the following semiempirical methodology was used.

The molal volume ϕ of 2-propanol in aqueous solution is related to the experimental solution density by the equation[32]

$$\phi = \frac{M}{\rho} - \frac{1000(\rho - \rho_{\mathrm{H_2O}})}{m\rho\rho_{\mathrm{H_2O}}} \tag{17}$$

where m is the molality of the alcohol solute of molecular weight M, and ρ and $\rho_{\mathrm{H_2O}}$ are the densities of the solution and pure water, respectively. The molar volume V_X can be simply calculated from the molal volume, and the reaction radius then determined using the formula[31]

$$r_{\bullet\mathrm{R}} = \left(\frac{3V_X X}{4\pi N}\right)^{1/3} \tag{18}$$

where X is the space filling factor for close packed spheres (=0.74). The 2-propanol solution densities have been experimentally measured over the temperature range 1−50 °C,[33] and by extrapolation of these values, specific reaction radii were determined for each of the temperatures used in this study. These radii are listed in Table 2, and are seen to be significantly larger than the value calculation from eq 16, which gives $r_{\cdot\mathrm{R}} \sim 2.33 \times 10^{-10}$ m.

On the basis of these calculated parameters, the $2k_{\mathrm{diff}}$ rate constants were determined using eq 14, and these values are also given in Table 2. These rate constants are much larger than the $2k_{\mathrm{obs}}$ experimental values determined in this study, indicating that this radical recombination is at best only partially diffusion controlled in water, confirming our intial hypothesis concerning this reaction.

The previous rate constant data found for 2-propanol radical recombination in solution (0.60 mol dm^{-3} acetone, 1.3 mol dm^{-3} 2-propanol) being below the Smoluchowski limit was attributed to the radical forming aggregates.[23] Corroboration of this is also given by the lower diffusion coefficients obtained in this previous work, as compared to the values obtained in only water[28,29] (see Figure 3a). However, radical aggregation is mostly expected to occur with the parent alcohol, or similar compounds (such as acetone), and in our study, the much lower 2-propanol concentration would minimize this process. While we cannot completely discount this effect, we do not believe that it would be sufficient to explain the large difference between the measured and theoretical rate constants, for this recombination process under our conditions.

Furthermore, reactions which are influenced by both diffusion and chemical processes have been shown to be well described by the equation[34,35]

$$\frac{1}{2k_{\mathrm{obs}}} = \frac{1}{2k_{\mathrm{diff}}} + \frac{1}{2k_{\mathrm{react}}} \tag{19}$$

where $2k_{\mathrm{obs}}$ is the measured recombination rate constant, $2k_{\mathrm{diff}}$ is the reaction encounter rate constant (Smoluchowski value), and $2k_{\mathrm{react}}$ is the rate constant that would be measured if diffusion of the species were not rate influencing. From the rate constants listed in Table 2, $2k_{\mathrm{react}}$ values can be readily determined over the temperature range of this study, and these difference values give the very good Arrhenius plot shown in Figure 4a. These data is well fitted by the equation

$$\log 2k_7^{\mathrm{react}} = [(12.55 \pm 0.38) - (18300 \pm 2200)/2.303RT] \tag{20}$$

corresponding to an activation energy for this process of 18.3 ± 2.2 kJ mol^{-1}. The closeness of this value to the overall fitted activation energy of 18.8 ± 1.2 kJ mol^{-1} (Figure 2a) suggests that under the conditions of this study, reactivity, not diffusion, is the dominant process in the self-recombination of 2-propanol radicals.

The additional first-order rate constants derived from the combined fitting procedure are also listed in Table 2, and these values are seen to consistently become larger with increasing temperature. The presence of an additional decay pathway for 2-propanol radical recombination has been previously observed in some organic solvents,[23] but not in water. These measured k_8 rate constants also follow very good Arrhenius behavior, see Figure 5a, and are well described by the equation

$$\log k_8 = [(9.93 \pm 0.24) - (30{,}000 \pm 1400)/2.303RT] \tag{21}$$

The specific mechanism of this first-order reaction pathway was not resolved in this study. A search of the literature revealed an analogous first-order decay component in the recombination of acetone radicals[36] which was attributed to the internal bond cleavage/rearrangement reaction

$$^{\bullet}\mathrm{CH_2COCH_3} \rightarrow {}^{\bullet}\mathrm{CH_3} + \mathrm{CH_2CO} \tag{22}$$

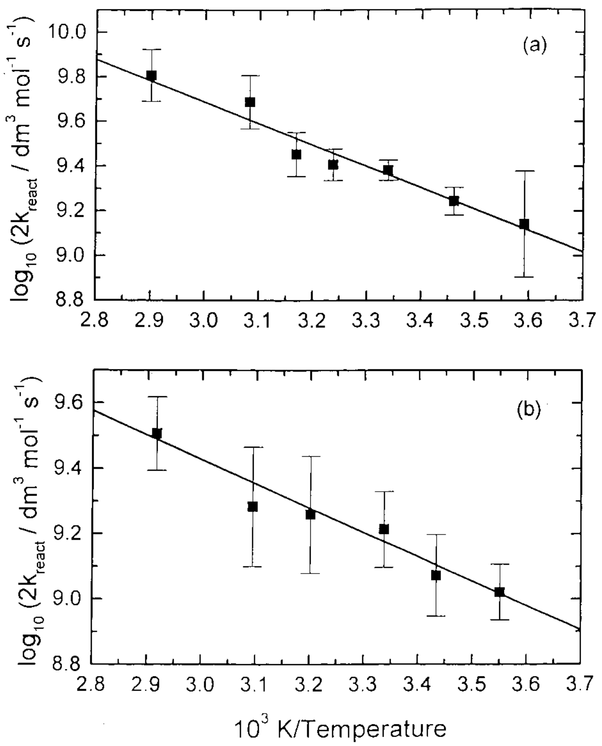

Figure 4. (a) Arrhenius plot for calculated 2-propanol $2k_{\mathrm{react}}$ values with solid line corresponding to predicted values of eq 20 in text. (b) *tert*-butyl alcohol calculated $2k_{\mathrm{react}}$ data, with fitted line given by eq 28 in text. Error bars for both sets of data correspond to one standard deviation.

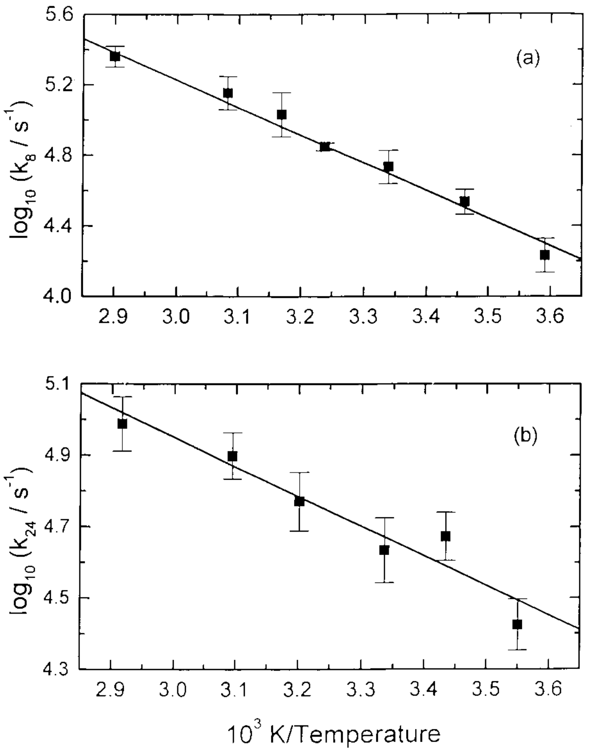

Figure 5. (a) Arrhenius plot for fitted first-order component of 2-propanol radical reaction in aqueous solution. Error bars correspond to one standard deviation obtained by averaging several decay curve values. Solid line is the predicted values of eq 21 in text. (b) Analogous Arrhenius plot for first-order component of *tert*-butyl alcohol radical reaction, with solid line corresponding to eq 32 in text.

However, the equivalent pathway for the 2-propanol radical seems unlikely, as it would involve the conversion of a tertiary carbon-centered radical into a primary one, although it is plausible for the observed first-order decay component of the *tert*-butyl alcohol radical (see below). One possible explanation is 2-propanol radical reaction with an impurity in the solution. Some support for this assignment is given by the activation energy of 30.0 ± 1.4 kJ mol^{-1} for this process, which is similar to values obtained for impurity hydrogen atom abstraction reactions of the 2-propanol radical in the organic solvents 2-butanol, tetrahydrofuran, and *tert*-butylmethylester of 31, 25 and 23 kJ mol^{-1} respectively.[23] However, the standard system cleaning precautions undertaken, the purity of all the chemicals used and the significantly lower activation energy for the analogous process in *tert*-butyl alcohol radical recombination (see later) makes this pathway suspect. Another possible pathway for this first-order process is an internal radical rearrangement, perhaps giving a resonance stabilized radical with appreciable spin population on the oxygen atom. Alternatively there could be a slow reaction of the 2-propanol radical with N_2O occurring. Further experiments are currently in progress to elucidate this first-order reaction component in the 2-propanol radical decay.

It should also be noted that the curve fitting procedures to obtain these temperature-dependent rate constants did not take account of any cross radical reactions, such as 2-propanol radical reaction with the product of the first-order decay. From computer simulation of the overall 2-propanol radical decay under our "worst case" experimental conditions, at the highest temperature and lowest dose where the first-order decay pathway was maximized, assuming that such cross reactions occurred with a rate constant of $2k = 5 \times 10^9$ $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ gave a fitted 2-propanol radical recombination rate constant of $2k_7 = 5.1 \times 10^9$ $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$. This value is comparable with the original value of $2k_7 = (4.18 \pm 0.64) \times 10^9$ $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ obtained under these conditions, and therefore it is inferred that such cross-reactions are not important under most conditions in this study.

***tert*-Butanol Recombination.** Analogous temperature-dependent rate constant data were also obtained for *tert*-butyl alcohol radical recombination in aqueous solution. Typical decay curves obtained for this system are shown in Figure 1b, at temperatures of 18.1 and 50.1 °C. As observed for 2-propanol radical recombination, these decays also exhibited mixed order kinetics, therefore these data was again fitted using eq 6 with rate constants corresponding to the reactions

$$2^{\bullet}\mathrm{CH_2C(CH_3)_2OH} \rightarrow \mathrm{(CH_3)_3CO} + \mathrm{(CH_3)_2CHOH} \qquad (23a)$$

$$\rightarrow \mathrm{CH_2C(CH_3)_2OH} + \mathrm{(CH_3)_2CHOH} \qquad (23b)$$

$$\rightarrow \mathrm{(CH_3)_2C(OH)CH_2CH_2(OH)C(CH_3)_2} \qquad (23c)$$

and

$$^{\bullet}\mathrm{CH_2C(CH_3)_2OH} \rightarrow \text{products} \qquad (24)$$

where $2k_{23} = 2k_{23a} + 2k_{23b} + 2k_{23c}$. Initial radical concentrations were determined as for 2-propanol, using the calculated initial yield value in Table 1. For the two decay curves shown in Figure 1b, fitted rate constants of $2k_{23} = (8.69 \pm 0.91) \times 10^8$ $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}/k_{24} = (4.31 \pm 0.62) \times 10^4\ \mathrm{s}^{-1}$ and $2k_{23} = (1.51 \pm 0.26) \times 10^9$ $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}/k_{24} = (7.03 \pm 1.27) \times 10^4\ \mathrm{s}^{-1}$ were obtained for the data at 18.1 and 50.1 °C, respectively.

This combined fitting was performed on the data obtained over the temperature range 8.5−69.8 °C, to give the averaged $2k_{\mathrm{obs}}$ rate constants listed in Table 2. The Arrhenius plot for the second-order component of this radical decay is shown in Figure 2b, and is well described by the equation

$$\log 2k_{23} = [(11.80 \pm 0.16) - (15830 \pm 920)/2.303RT] \tag{25}$$

corresponding to an activation energy of 15.83 ± 0.92 kJ mol^{-1}. Also shown in this plot are the previous room-temperature measurements for this recombination process,[25,37,38] again very good agreement is seen between all determinations. The overall ratio of *tert*-butyl alcohol radical disproportionation to combination has been measured as 4.7 in water at 23 °C,[39] and so specific rate constants of $(2k_{23a} + 2k_{23b}) = (8.41 \pm 0.91) \times 10^8$ and $2k_{23c} = (1.79 \pm 0.19) \times 10^8\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ can be calculated at this temperature.

For the calculation of the Smoluchowski diffusion-controlled rate constant, the *tert*-butyl alcohol radical was once again approximated by the alcohol. Diffusion coefficients of this alcohol have again been experimentally determined in aqueous solution,[28,40,41] these literature values are shown in Figure 3b. A nonlinear dependence is observed over the larger temperature range of determination, and the values required in this study were derived from the fitted equation

$$\log D = -5.066 - 2.577 \times 10^3/T + 8.133 \times 10^5/T^2 - 1.189 \times 10^8/T^3 \tag{26}$$

with T being the absolute temperature. However, for the calculation of the reaction radius no equivalent density data could be found for *tert*-butyl alcohol. Therefore this parameter was estimated by the following procedure. The critical volume of *tert*-butyl alcohol in water V_{C} was calculated using the method of Lyderson,[42,43] and this was converted into the molal volume ϕ using the empirical relationship of Tyn and Calus,[43,44]

$$\phi = 0.285 V_{\mathrm{C}}^{1.048} \tag{27}$$

which could be simply corrected to the molar volume V_{X} and then substituted into eq 18. The validity of this procedure was tested by performing this calculation for 2-propanol at 25 °C, which gave $r_{\cdot\mathrm{R}} = 2.88 \times 10^{-10}$ m. As this calculated value is slightly higher than the reaction radius of 2.75×10^{-10} m derived using experimental data, the ratio of these two values, 0.955, was used to correct the calculated *tert*-butyl alcohol reaction radius of 3.12×10^{-10} m to give the used value of 2.98×10^{-10} m for this radical. As this calculation is only applicable at room temperature (assumed to be 22 °C), the same temperature dependence determined for 2-propanol was also assumed for *tert*-butyl alcohol, to give the final values listed in Table 2.

On the basis of the measured diffusion coefficients and calculated reaction radii, the Smoluchowski $2k_{\mathrm{diff}}$ rate constants were then calculated using eq 14, these values are also given in Table 2. Again these rate constants are seen to be much larger than the measured $2k_{\mathrm{obs}}$ rate constants in this study, indicating that this recombination is also only partially diffusion controlled. The $2k_{\mathrm{react}}$ rate constants were again calculated using eq 19, with specific values given in Table 2 and shown in Figure 4b.

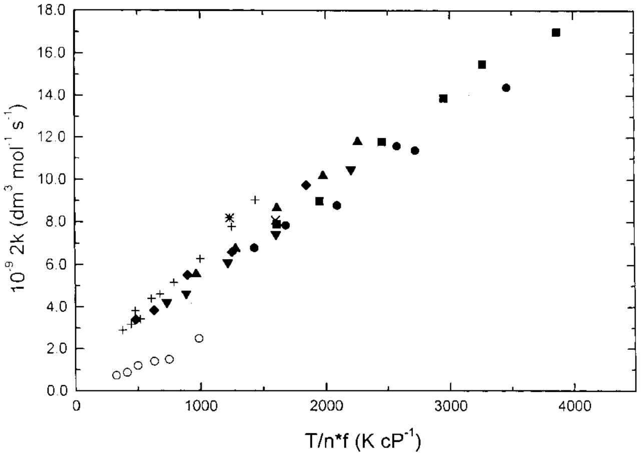

Figure 6. Microfriction corrected second-order termination rate constants for *tert*-butyl alcohol radicals[30] in C_7H_{16} (g), C_8H_{18} (n), $C_{10}H_{22}$ (▲), $C_{12}H_{26}$ (▼), $C_{14}H_{30}$ (◇), $C_{16}H_{34}$ (+), C_6H_6 (*), and isobutane (×) in comparison to the water (○) values of this study.

The good Arrhenius behavior observed was found to be well fitted by the equation

$$\log 2k_{23}^{\mathrm{react}} = [(11.66 \pm 0.21) - (14300 \pm 1200)/2.303RT] \tag{28}$$

with the specific activation energy for this process being 14.3 ± 1.2 kJ mol^{-1}. Once again this analysis suggests that the recombination of this radical in water is controlled by its reactivity, not diffusion.

An extensive study of temperature-dependent *tert*-butyl alcohol radical recombination rate constants in a wide range of *n*-alkane solvents has been previous performed,[30] with all values found to be effectively diffusion-controlled, provided microfriction factors[45] were taken into account. This correction is made to the Stokes−Einstein relationship, eq 16, for the case where the reaction radius of the solute (r) is of comparable magnitude to that of the solvent (r_{s})[46] and takes the form

$$D_{\cdot\mathrm{R}} = \frac{kT}{6\pi\eta r_{\cdot\mathrm{R}} f} \tag{29}$$

with

$$10f = \left(0.4 + \frac{r}{r_{\mathrm{s}}}\right)(3.6 + 1.6T_{\mathrm{r}} - T_{\mathrm{r}}^{\mathrm{s}}) \tag{30}$$

where T_{r} and T_{rs} are the reduced temperatures

$$T_{\mathrm{r}} = \frac{T - T_{\mathrm{F}}}{T_{\mathrm{B}} - T_{\mathrm{F}}} \tag{31}$$

calculated from the freezing (T_{F}) and boiling (T_{B}) points of the solute and solvent, respectively. Figure 6 shows all of the previously determined $2k_{\mathrm{obs}}$ values for the range of *n*-alkane solvents, with a very good linear relationship observed. Also shown in this figure is the microfriction-corrected data of this study for *tert*-butyl alcohol radical recombination in water, which is seen to be much lower than all of the other data. This again indicates that this reaction is not diffusion-controlled, thus further supporting the findings of this study.

The temperature dependence of the fitted first-order rate constants for this radical reaction (see averaged values in Table 2) also gave a good Arrhenius plot (Figure 5b), being well described by the equation

$$\log k_{24} = [(7.44 \pm 0.39) - (15900 \pm 2300)/2.303RT] \quad (32)$$

corresponding to an activation energy of 15.9 ± 2.3 kJ mol^{-1}, about half of the value determined for the 2-propanol radical. The lower activation energy for this first-order process compared to the 2-propanol radical suggests a different loss mechanism, and in this case we can invoke a radical transformation pathway. Using the work of Zeldes and Livingston[36] as a reference point, we can envision fragmentation of the *tert*-butyl alcohol radical to form a methyl radical and an acetone molecule, analogous to the transformation from the 2-keto-1-propyl radical to the methyl radical and acetaldehyde that was observed in their work.

Summary

Temperature-dependent rate constants for the second-order recombination of 2-propanol and *tert*-butyl alcohol radicals have been measured in aqueous solution. The Arrhenius behavior of these two reactions was found to be well described by the equations

$$\log 2k_7 = [(12.46 \pm 0.21) - (18800 \pm 1200)/2.303RT] \quad (13)$$

and

$$\log 2k_{23} = [(11.80 \pm 0.16) - (15830 \pm 920)/2.303RT] \quad (25)$$

respectively. Comparison with Smoluchowski encounter rate calculations showed that radical reactivity controlled these aqueous recombinations. At higher temperatures an additional first-order decay component was also found to be important, for these corresponding pathways the temperature-dependent rate constants were found to be

$$\log k_8 = [(9.93 \pm 0.24) - (30000 \pm 1400)/2.303RT] \quad (21)$$

and

$$\log k_{24} = [(7.44 \pm 0.39) - (15900 \pm 2300)/2.303RT] \quad (32)$$

for 2-propanol and *tert*-butyl alcohol.

Acknowledgment. We thank Mike Thomas and Mark Richmond for their assistance in maintaining and running the Van de Graaff accelerator.

References and Notes

(1) von Sonntag, C. Free-radical reactions of carbohydrates as studied by radiation techniques. In *Advances in Carbohydrate Chemistry and Biochemistry*; Tipson, R. S., Horton, D., Eds.; Academic Press: New York, 1980; Vol. 37, pp 7−77.

(2) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513. Updates to this compilation are appear at the URL: http://www.rcdc.nd.edu.

(3) Asmus, K. D.; Möckel, H.; Henglein, A. *J. Phys. Chem*. **1973**, *77*, 1218.

(4) Héberger, K.; Fischer, H. *Int. J. Chem. Kinet*. **1993**, *25*, 913.

(5) Batchelor, S. N.; Fischer, H. *J. Phys. Chem*. **1996**, *100*, 9794.

(6) Neta, P.; Grodkowski, J.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1996**, *25*, 709. Updates to this compilation appear at URL: http://www.rcdc.nd.edu.

(7) Eriksen, T. E. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 208.

(8) Madden, K. P. Manuscript to be published.

(9) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(10) Madden, K. P.; McManus, H. J. D.; Fessenden, R. W. *Rev. Sci. Instrum*. **1994**, *65*, 49.

(11) Verma, N. C.; Fessenden, R. W. *J. Chem. Phys*. **1973**, *58*, 2501.

(12) Capellos, C.; Bielski, B. H. J. *Kinetic Systems: Mathematical Description of Chemical Kinetics in Solution*; Wiley-Interscience: New York, 1972.

(13) Blank, B.; Henne, A.; Laroff, G. P.; Fischer, H. *Pure Appl. Chem*. **1975**, *41*, 475.

(14) Henne, A.; Fischer, H. *Helv. Chim. Acta* **1975**, *58*, 1596.

(15) Pimblott, S. M.; LaVerne, J. A. *Radiat. Res.* **1990**, *122*, 12.

(16) LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem*. **1991**, *95*, 3196.

(17) Pimblott, S. M.; LaVerne, J. A. *Radiat. Res*. **1992**, *129*, 263.

(18) LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem*. **1992**, *96*, 8904.

(19) LaVerne, J. A.; Pimblott, S. M. *Rad. Res*. **1993**, *135*, 16.

(20) Farhataziz; Rodgers, M. A. J., Eds. Radiation Chemistry. Principles and Applications; VCH: New York, 1982.

(21) Schuler, R. H.; Hartzell, A. L.; Behar, B. *J. Phys. Chem*. **1981**, *85*, 192.

(22) Lide, D. R., Ed. Handbook of Chemistry and Physics, 71st ed.; CRC Press: Boca Raton, FL, 1990.

(23) Lehni, M.; Fischer, H. *Int. J. Chem. Kinet*. **1983**, *15*, 733.

(24) Shastri, L. V.; Mittal, L. J.; Mittal, J. P. *Radiat. Phys. Chem*. **1986**, *28*, 359.

(25) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem*. **1977**, *81*, 99.

(26) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem*. **1969**, *73*, 3794.

(27) North, A. M. The Collision Theory of Chemical Reactions in Liquids; Methuen, London, 1964.

(28) Gary-Bobo, C. M.; Weber, H. W. *J. Phys. Chem*. **1969**, *73*, 1155.

(29) Pratt, K. C.; Wakeham, W. A. *Proc. R. Soc. London A* **1975**, *342*, 401.

(30) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet*. **1976**, *8*, 341.

(31) Schuh, H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(32) Daniels, F.; Mathews, J. H.; Williams, J. W.; Bender, P.; Murphy, G. W.; Alberty, R. A. Experimental Physical Chemistry, 4th ed.; McGraw-Hill: New York, 1949.

(33) Friedman, M. E.; Scheraga, H. A. *J. Phys. Chem*. **1965**, *69*, 3795.

(34) Noyes, R. M. Effects of diffusion rates on chemical kinetics. In *Progress in Reaction Kinetics*; Pergamon Press: London, 1961; Vol. 1.

(35) Weston, R. E.; Schwarz, H. A. Chemical Kinetics; Prentice-Hall: Englewood Cliffs, NJ, 1972.

(36) Zeldes, H.; Livingston, R. *J. Chem. Phys*. **1966**, *45*, 1946.

(37) Waltz, W. L. Private communication.

(38) Von Piechowski, M.; Thelen, M. A.; Hoigne, J.; Buehler, R. E. *Bunsen-Ges. Phys. Chem*. **1992**, *96*, 1448.

(39) Blank, B.; Henne, A.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 920.

(40) Ito, N.; Saito, K.; Fujiyama, T. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 991.

(41) Tominaga, T.; Matsumoto, S. *J. Chem. Eng. Data* **1990**, *35*, 45.

(42) Lyderson, A. L. Engineering Experimental Station Report 3; University of Wisconsin College of Engineering: Madison, Wisconsin, 1955.

(43) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. The Properties of Gases and Liquids, 3rd ed.; McGraw-Hill: New York, 1977.

(44) Tyn, M. T.; Calus, W. F. *Processing* **1975**, *16*, 21.

(45) Sprenol, A.; Wirtz, K. *Naturforsch*. **1953**, *8a*, 522.

(46) Einstein, A. *Z. Elektrochem*. **1908**, *14*, 235.