What is apparent in Figure 2 is that the rate constants for three $C_2H_{3-x}Cl_x + O_2$ reactions (x = 0, 1, and 3) are quite similar, particularly at ambient temperature. However, there is a noticeable trend toward an increasingly negative activation energy as the degree of chlorine substitution increases, from −0.25 to −0.83 kcal mol^{-1} as x changes from 0 to 3.

The temperature dependence of these rate constants can be accounted for by the nature of the overall reaction mechanism;[12,19] initial association followed by either dissociation back to the original reactants or rearrangement and finally decomposition into the final observed products. (One explanation that accounts for the independence of the overall rate constants on pressure is that the lifetime of the $C_2H_{3-x}Cl_x–O_2$ adduct is short compared to the time between collisions.) The measured rate constant of a $C_2H_{3-x}Cl_x + O_2$ reaction is that of the association step multiplied by the fraction of the adducts formed that proceed on to the final products.[21] If the fraction is 1, then the measured rate constant is equivalent to the high-pressure limit rate constant for a more standard reversible addition reaction. It is likely that this fraction is near 1 for all three $C_2H_{3-x}Cl_x + O_2$ reactions at ambient temperature since the measured rate constants are close to (actually somewhat higher) than the high-pressure limit rate constant of the $C_2H_5 + O_2$ reaction[22,23] (the closest reversible $R + O_2$ reaction that can be used for comparison purposes).

While there is generally little temperature dependence in association rate constants, there can be a significant temperature dependence in the fraction of adducts that proceed to form new products.[21] Thus a significant negative activation energy for the measured rate constants implies that reformation of reactants becomes increasingly the more favored decomposition pathway for the $C_2H_{3-x}Cl_x–O_2$ adduct as temperature increases. For this to be the case, the potential energy barrier for the rearrangement of the $C_2H_{3-x}Cl_x–O_2$ adduct (leading to the formation of new products) must generally be lower than that for dissociation back to the original reactants (although the density of states for the two competing decomposition paths also determines this temperature dependence).

The trend in negative activation energies of the $C_2H_{3-x}Cl_x + O_2$ reactions with increasing chlorine substitution suggests that while the rearrangement barrier in all three cases is below that of the dissociation path, it becomes increasingly less so as more chlorine atoms are incorporated into the vinyl radical. This trend results in the $C_2Cl_3 + O_2$ association becoming more reversible with increasing temperature than is the case for the $C_2H_3 + O_2$ reaction. These changes in the *relative* heights of the two relevant potential energy barriers with chlorine substitution cannot be large since the rate constants and activation energies of the $C_2H_{3-x}Cl_x + O_2$ do not vary significantly.

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Pulse Radiolysis of 2,4,5-Trichlorophenol: Formation, Kinetics, and Properties of Hydroxytrichlorocyclohexadienyl, Trichlorophenoxyl, and Dihydroxytrichlorocyclohexadienyl Radicals

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Pulse radiolysis has been used to optically and kinetically characterize the transient free radicals formed by the reaction of H$^\bullet$, N$_3^\bullet$, or OH$^\bullet$ with 2,4,5-trichlorophenol (TCP-OH). The hydroxy-2,4,5-trichlorocyclohexadienyl radical (H-TCP-OH) formed by H$^\bullet$ addition to TCP-OH [$k = (1.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}] has an absorption maximum at 360 nm with $\epsilon_{360} = (4700 \pm 1000)$ M^{-1} cm^{-1}. The 2,4,5-trichlorophenoxyl radical (TCP-O$^\bullet$) formed by the reaction of N$_3^\bullet$ with TCP-O$^-$ [$k = (4.3 \pm 0.8) \times 10^9$ M^{-1} s^{-1}] has an absorption maximum at 430 nm with $\epsilon_{430} = (3600 \pm 600)$ M^{-1} cm^{-1}. The dihydroxy-2,4,5-trichlorocyclohexadienyl radical (HO-TCP-OH) formed by OH$^\bullet$ radical addition to TCP-OH [$k = (1.2 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}] has an absorption maximum at 320 nm with $\epsilon_{320} = (5300 \pm 250)$ M^{-1} cm^{-1}. The principal isomer formed by the reaction of OH$^\bullet$ with TCP-OH is the 1,6-dihydroxy-2,4,5-trichlorocyclohexadienyl radical, which has a pK_a of 4.8 ± 1.0. The solution absorption from each radical decays via second-order kinetics on the millisecond time scale.

Introduction

Chlorinated phenols represent an important class of pollutants that have been introduced into the environment as herbicides and fungicides. These compounds are generally resistant to chemical, photochemical, and biological degradation in the environment, making disposal, particularly of contaminated water, difficult. Lemaire and co-workers have found, however, that direct photolysis, using 290-nm light, initiates degradation of these toxic materials, leading to dechlorination via either ionic or radical intermediates, depending on the position of chlorine substitution. Dechlorination is generally considered a detoxification reaction; however, the intermediacy of free radicals in some of these pro-

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cesses opens the possibility of forming halogenated biphenyls, which may be more hazardous than the starting chlorophenols.[1]

The photocatalytic degradation of several chlorophenols has also been reported. With titanium dioxide powder as a sensitizer, irradiation of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4,5-trichlorophenol (TCP-OH) by simulated sunlight resulted in complete conversion of these materials to HCl and CO_2 with half-lives of 30–90 min. No dimeric products were detected.[2a,b] In contrast, Crosby and Wong report that in the absence of a sensitizer, irradiation of 2,4,5-T in a similar photoreactor results in only 8% conversion of starting material to products after 200 h.[3] These reports indicate that photocatalytic degradation using semiconductor powders as sensitizers may be a promising method for detoxifying polluted water.

The hydroxyl radical derived from TiO_2 photooxidation of water has been proposed as the reactive oxidant formed upon irradiation of aqueous suspensions of TiO_2.[4] Dihydroxychlorocyclohexadienyl radicals, formed by $OH^•$ addition to the aromatic ring, have been postulated as transient intermediates in the TiO_2-sensitized oxidation of chlorophenols and may, therefore, be important in photocatalytic degradation of a variety of chlorinated aromatic compounds.[2] This seems likely since Getoff and Solar recently found that $OH^•$ rapidly reacts with 2-chlorophenol with a rate constant of $1.2 \times 10^{10}\ M^{-1}\ s^{-1}$, yielding isomeric dihydroxychlorocyclohexadienyl radicals ($\lambda_{max} = 310$ nm).[5] If a mechanism involving $OH^•$ radical in the photocatalyzed oxidation of chlorophenols is to be understood, the structure, reactivity, and spectra of the dihydroxychlorocyclohexadienyl radical intermediates should be unambiguously characterized.

Pulse radiolysis provides a quantitative method for homogeneously producing both oxidizing ($OH^•$) and reducing (e_{aq}^-, $H^•$) radicals. Measurements of rate constants for $OH^•$ addition to substituted phenols show that $OH^•$ behaves as an electrophilic radical. The reactions of $H^•$, although a reducing radical, often resemble those of $OH^•$. $H^•$ also adds to the aromatic ring, producing cyclohexadienyl radicals similar to those formed by $OH^•$ addition.[6] The $OH^•$ radical may be used to prepare a less reactive, more selective, oxidant, i.e., $N_3^•$, by reaction with N_3^-. When phenoxides are present, $N_3^•$ reacts by electron transfer, producing phenoxyl radicals.[7] Phenoxyl radicals may also be formed by the elimination of water from dihydroxycyclohexadienyl radicals or by direct electron transfer in semiconductor-sensitized oxidations.[8]

In this investigation, we describe the properties of organic radicals formed when hydrogen, azide, or hydroxyl radicals react with 2,4,5-trichlorophenol (TCP-OH). The products of these reactions are the hydroxy-2,4,5-trichlorocyclohexadienyl radical (H-TCP-OH), the 2,4,5-trichlorophenoxyl radical (TCP-$O^•$), and the dihydroxy-2,4,5-trichlorocyclohexadienyl radical (HO-TCP-OH), respectively. A detailed study of the pH dependence of HO-TCP-OH optical and kinetic characteristics has allowed us to measure the pK_a of this radical. Spectral, kinetic, and chemical evidence suggest that the 1,6-dihydroxy-2,4,5-trichlorocyclohexadienyl radical is the major, if not the exclusive, radical formed by $OH^•$ addition to TCP-OH.

Experimental Section

Chemicals. 2,4,5-Trichlorophenol (TCP-OH) was obtained from Lancaster Synthesis ($\lambda_{max} = 310$ nm; $\epsilon_{310} = 4300\ M^{-1}\ cm^{-1}$ in water, pH 10). After having been recrystallized twice from hexanes and sublimed twice at room temperature at reduced pressure, the TCP-OH was found to be >99.99% pure by gas-liquid chromatography. Sodium azide and potassium phosphate (MCB), *tert*-butyl alcohol (Fisher Scientific), sodium hexachloroiridate(IV) hexahydrate, and potassium ferricyanide (Aldrich Chemical Co.) were used as received.

Electron Accelerator. Pulse radiolysis experiments were performed by using a 4-MeV (1–3 A) van de Graff accelerator. Pulse widths of 50, 100, and 250 ns allowed for radiation doses of 2.5–20 Gy per pulse.[9] Aqueous solutions (21 ± 1 °C) were irradiated in a flow cell with either a 1.0- or 2.4-cm analyzing path length. Transient absorptions were monitored by using a xenon lamp, grating monochromator, and photomultiplier tube arrangement. The absorbed radiation dose was determined by using the thiocyanate dosimeter, 10 mM KSCN in N_2O-saturated water ($G(OH^•) = G(SCN)_2^{•-} = 6.0$ molecules/100 eV; $\epsilon_{480} = 7600\ M^{-1}\ cm^{-1}$).[10] Absorption (millivolts) vs time data were recorded on a Biomation 8100 digitizer interfaced with a PDP 11/70 computer for data analysis.[11]

Solutions. Millipore filtered water was used for all solutions. The pH of solutions was adjusted with dilute aqueous KOH or H_2SO_4. Deoxygenation was accomplished by bubbling with either N_2O or N_2. The concentrations of solutes were chosen to ensure 90–100% capture of the desired primary radical in all experiments.

Calculations. AM1 calculations were performed by using the AMPAC package of semiemperical molecular orbital calculation programs on the Cray computer at the University of Texas at Austin.[12]

Results

Pulse Radiolysis of Aqueous Organic Solutions. The primary products formed by irradiation of water with high energy electrons may be summarized by eq 1. H_2O_2, H_3O^+, OH^-, and H_2 are

$$H_2O \xrightarrow{e^-} e_{aq}^-,\ H^•,\ OH^•,\ H_2O_2,\ H_3O^+,\ OH^-,\ H_2 \qquad (1)$$

stable, but e_{aq}^-, $H^•$ and $OH^•$ are highly reactive species and rapidly react with organic compounds, forming organic free radicals.

To create a system in which $OH^•$ is virtually the only radical reacting with an organic substrate, aqueous solutions (pH > 3) may be bubbled with nitrous oxide (N_2O). Besides eliminating dissolved oxygen, N_2O (25 mM) rapidly reacts with e_{aq}^-, quantitatively converting it to $OH^•$ (eq 2). The rate constant for this

$$N_2O + e_{aq}^- + H_2O \rightarrow OH^• + N_2 + OH^- \qquad (2)$$

reaction is $8.7 \times 10^9\ M^{-1}\ s^{-1}$,[13] and the G value for $OH^•$ in water (pH = 4) under these conditions is 6.0.[14] It is important to maintain the solution at a pH greater than 3, since this greatly reduces the extent to which e_{aq}^- reacts with H^+ (eq 3). Reaction

$$H_3O^+ + e_{aq}^- \rightarrow H^• + H_2O \qquad (3)$$

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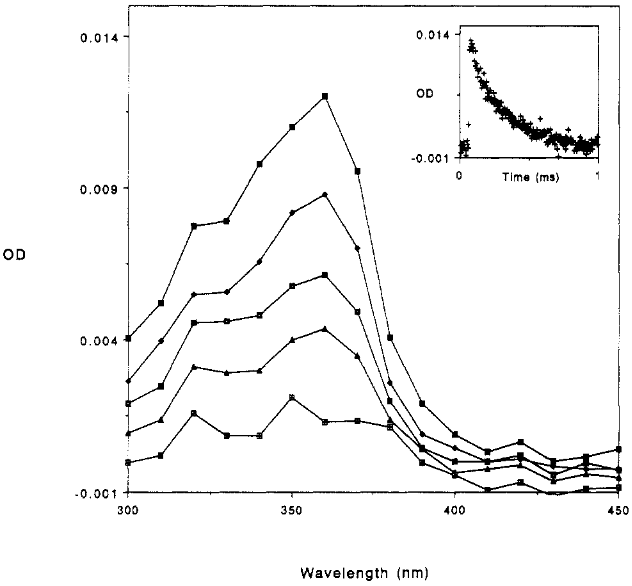


Figure 1. Transient absorption spectrum attributed to H-TCP-OH at 20 (■), 82.5 (◆), 160 (■), 267.5 (▲), and 652.5 (⊞) μs after irradiation of 5×10^{-4} M aqueous TCP-OH, pH = 1, in a 0.2 M *tert*-butyl alcohol solution; dose = 10 Gy per pulse. Inset: decay of optical density at 360 nm.

3 proceeds with a rate constant of 2.3×10^{10} M^{-1} s^{-1}.[13] A small primary yield of $H^\bullet$, $G(H^\bullet) = 0.55$, is however unavoidable but amounts to less than 10% of the radicals produced.[14]

The hydroxyl radical may be used to prepare less-oxidizing radicals such as $Br_2^{\bullet-}$, $(SCN)_2^{\bullet-}$, and $N_3^\bullet$ by reaction with Br^-, SCN^-, and N_3^-, respectively, e.g., eq 4. These radicals are often more discriminating reactants.

$$OH^\bullet + N_3^- \rightarrow OH^- + N_3^\bullet \qquad (4)$$

Azide radical formed by reaction 4, $k = 1.3 \times 10^{10}$ M^{-1} s^{-1} at pH 10, has an absorption maximum at 270 nm. $N_3^\bullet$ is particularly useful for producing phenoxyl radicals, since it reacts quantitatively [$G(OH^\bullet) = G(N_3^\bullet) = G(\text{phenoxyl})$] with phenoxides by electron transfer and does not interfere with observation of the phenoxyl radical's transient absorption.[7] The more reactive $OH^\bullet$ radical adds to the aromatic ring producing hydroxycyclohexadienyl radicals.

Reducing radical systems may be produced by a judicious choice of pH and concentration of $OH^\bullet$ radical scavenger. Solution pH determines whether e_{aq}^- or $H^\bullet$ is the reducing radical. According to eq 3, lower pH will favor $H^\bullet$ formation. The *G* value for $H^\bullet$ in acidic solutions containing sufficient *tert*-butyl alcohol to scavenge all $OH^\bullet$ radical is 3.0.[14] *tert*-Butyl alcohol is an ideal $OH^\bullet$ scavenger since it quickly reacts with $OH^\bullet$ radical, yielding a relatively inert alkyl radical (eq 5), $k = 5.2 \times 10^8$ M^{-1} s^{-1}.[15]

$$OH^\bullet + (CH_3)_3COH \rightarrow H_2O + (CH_3)_2C^\bullet H_2COH \qquad (5)$$

$H^\bullet$, however, reacts much more slowly with *tert*-butyl alcohol, $k = 1 \times 10^5$ M^{-1} s^{-1}.[16] Thus, aqueous solutions of *tert*-butyl alcohol provide a medium in which e_{aq}^- or $H^\bullet$, depending on pH, is the only radical that reacts with an organic substrate.

$H^\bullet$ Atom Adduct (H-TCP-OH). The absorption spectrum of the $H^\bullet$ adduct of TCP-OH(H-TCP-OH) was obtained in a nitrogen-saturated solution of 5×10^{-4} M TCP-OH at pH 1 with 0.2 M *tert*-butyl alcohol (Figure 1). This spectrum shows that H-TCP-OH has an absorption maximum at 360 nm.

The disappearance of adduct absorbance at 360 nm occurred via second-order kinetics with $2k/\epsilon = (5.4 \pm 0.6) \times 10^5$ s^{-1} (Figure 1, inset). An extinction coefficient at 360 nm was determined by extrapolating the second-order decay data, at four radiation doses, to time zero. The optical density at time zero (OD^0_{360}) was then divided by the concentration of radical produced [$G(H^\bullet) = G(\text{H-TCP-OH})$] and the optical path length. This procedure gave $\epsilon_{360} = (4700 \pm 1000)$ M^{-1} cm^{-1} and a second-order rate constant of $(1.3 \pm 0.3) \times 10^9$ M^{-1} s^{-1}.

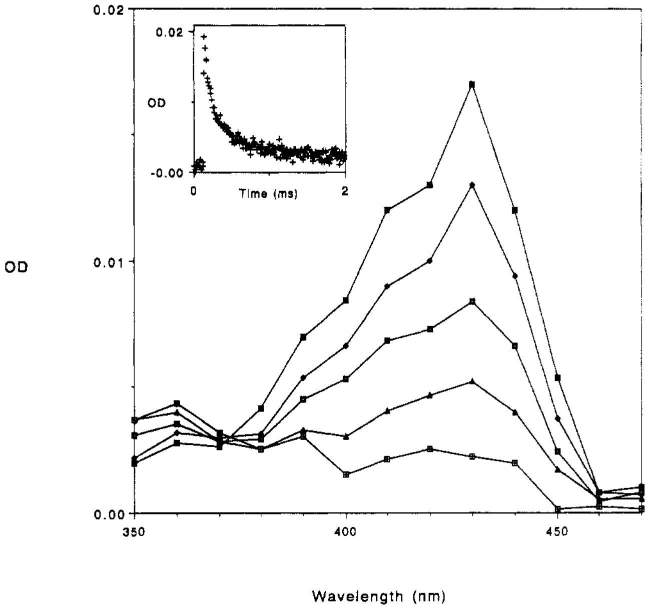
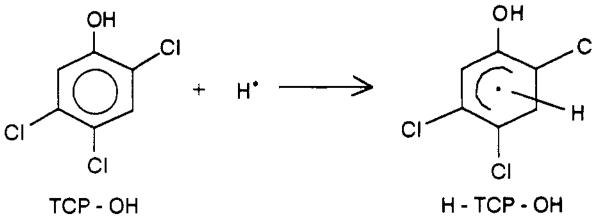


Figure 2. Transient absorption spectrum attributed to TCP-O at 20 (■), 60 (◆), 140 (■), 335 (▲), and 1160 (⊞) μs after irradiation of 7.4×10^{-5} M aqueous $TCP\text{-}O^-$, pH = 10, in a 0.01 M NaN_3 solution; dose = 10 Gy per pulse. Inset: decay of optical density at 430 nm.

By observation of the rate of increase of OD_{360} as a function of TCP-OH concentration, it was possible to determine the rate constant for the reaction shown in eq 6. The observed rate constant, k_{obsd}, varied from 9.2×10^4 to 2×10^5 s^{-1}, yielding a second-order rate constant for $H^\bullet$ addition to TCP-OH of $(1.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}.

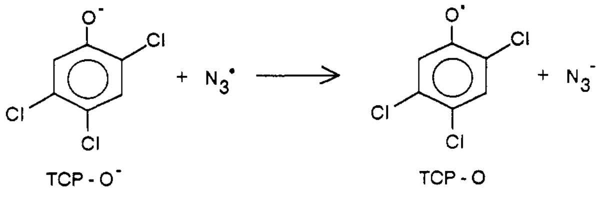


(6)

Phenoxyl Radical ($TCP\text{-}O^\bullet$). An absorption spectrum of $TCP\text{-}O^\bullet$ was obtained in a N_2O-saturated solution of 7.4×10^{-5} M $TCP\text{-}O^-$ ($pK_a = 7.4$) at pH 10 with 0.01 M NaN_3. The absorption maximum of $TCP\text{-}O^\bullet$ is centered around 430 nm (Figure 2).

Solution absorbance at 430 nm disappeared according to second-order kinetics with $2k/\epsilon = (4.3 \pm 0.6) \times 10^5$ s^{-1} (Figure 2, inset). The extinction coefficient at 430 nm was determined in the same manner as that of H-TCP-OH, assuming $G(TCP\text{-}O^\bullet) = G(N_3^\bullet)$. This calculation gave $\epsilon_{430} = (3600 \pm 600)$ M^{-1} cm^{-1} and a second-order decay rate constant of $(7.7 \pm 1.7) \times 10^8$ M^{-1} s^{-1}.

By measuring the rate of increase of optical density at 430 nm as a function of TCP-OH concentration, a rate constant for $N_3^\bullet$ oxidation of $TCP\text{-}O^-$ was determined. k_{obsd} ranged from 2.3×10^5 to 5.5×10^5 s^{-1}, yielding a bimolecular rate constant $k_2 = (4.3 \pm 0.8) \times 10^9$ M^{-1} s^{-1} for reaction 7.



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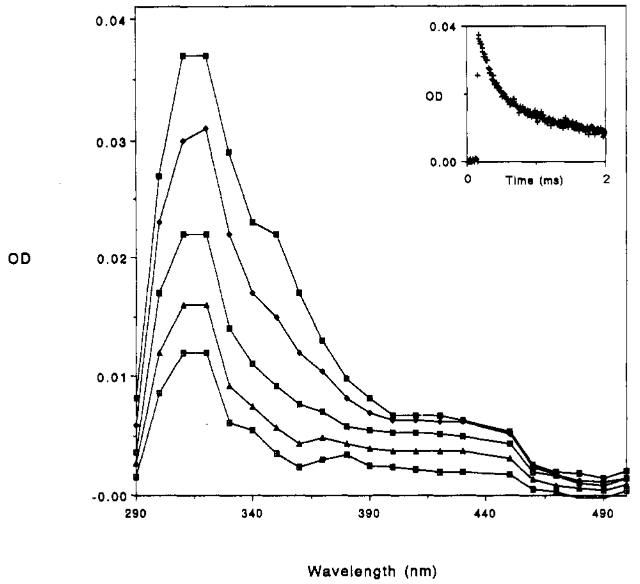
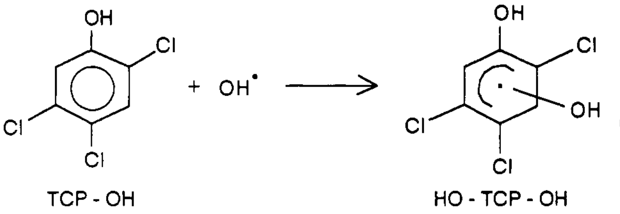


Figure 3. Transient absorption spectrum attributed to HO-TCP-OH at 35 (■), 145 (◆), 390 (■), 775 (▲), and 1400 (⊞) μs after irradiation of 2×10^{-4} M aqueous TCP-OH, buffered at pH = 3 in 10^{-3} M phosphate solution; dose = 8 Gy per pulse. Inset: decay of optical density at 320 nm.

OH• Radical Adduct (*OH-TCP-OH*). A N_2O-saturated solution of 2×10^{-4} M TCP-OH in 10^{-3} M phosphate buffer, pH = 4, was used to measure the absorption spectrum of the dihydroxytrichlorocyclohexadienyl radical (HO-TCP-OH) (Figure 3). The spectrum shows an absorption maximum at 320 nm, which decayed via second-order kinetics with $2k/\epsilon = (2.1 \pm 0.3) \times 10^5$ s^{-1} (Figure 3, inset). Assuming G(HO-TCP-OH) = G(OH•), the extinction coefficient at 320 nm was determined as before. The results are $\epsilon_{320} = (5300 \pm 250)$ M^{-1} cm^{-1} and $k_2 = (5.6 \pm 0.8) \times 10^8$ M^{-1} s^{-1}.

Again, the rate constant for OH• addition to TCP-OH was measured as the concentration of TCP-OH was varied between 4×10^{-6} and 2.5×10^{-5} M. In this concentration range, k_{obsd} at 320 nm increased from 7.5×10^4 to 3.0×10^5 s^{-1}, yielding a bimolecular rate constant of $(1.2 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} for reaction 8.



(8)

Determination of the pK_a of HO-TCP-OH. As we explored the pH dependence of HO-TCP-OH's spectral and kinetic characteristics, we found that both the protonated (HO-TCP-OH, λ_{max} = 320 nm) and deprotonated (HO-TCP-O$^-$, λ_{max} = 320 and 380 nm) forms of the dihydroxytrichlorocyclohexadienyl radical were observed in the pH region below the pK_a of TCP-OH. Since the radical and radical anion have different absorption spectra, we were able to determine the pK_a of HO-TCP-OH.

Qualitatively, as we increased the pH of solutions in which OH• is the primary radical reacting with TCP-OH, an absorption band centered around 380 nm began to appear in the transient spectrum and the intensity of the 320 nm absorption began to decrease (Figure 4). Quantitative evaluation of these spectral changes with pH was accomplished by varying the pH of N_2O-saturated solutions of 10^{-4} M TCP-OH in 10^{-3} M phosphate buffer and measuring the initial optical densities at 320 and 380 nm, OD^0_{320} and OD^0_{380}, respectively. These data are presented in Figure 5. To quantitatively evaluate the pK_a of HO-TCP-OH, the data in Figure 5 have been normalized to a uniform radiation dose corresponding to a total radical concentration of 4×10^{-6} M.

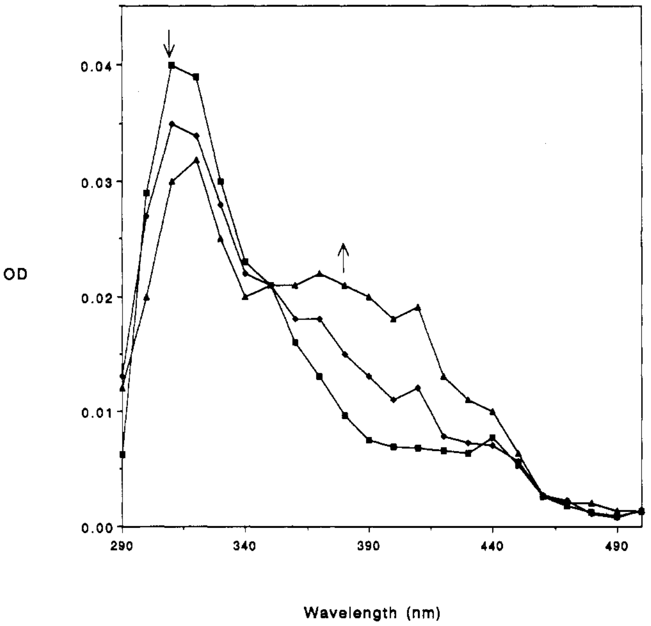


Figure 4. Transient absorption spectra at pH = 3.0 (■), pH = 4.6 (◆), and pH = 5.7 (▲). Spectra were recorded 40 μs after irradiation of 2×10^{-4} M aqueous TCP-OH in 10^{-3} M phosphate buffer; dose = 8 Gy per pulse. The spectrum at pH = 3.0 is attributed to HO-TCP-OH, while that at pH 5.7 is attributed to HO-TCP-O$^-$. The optical density at 320 nm is decreasing, while that at 380 nm is increasing around an isosbestic point at 350 nm.

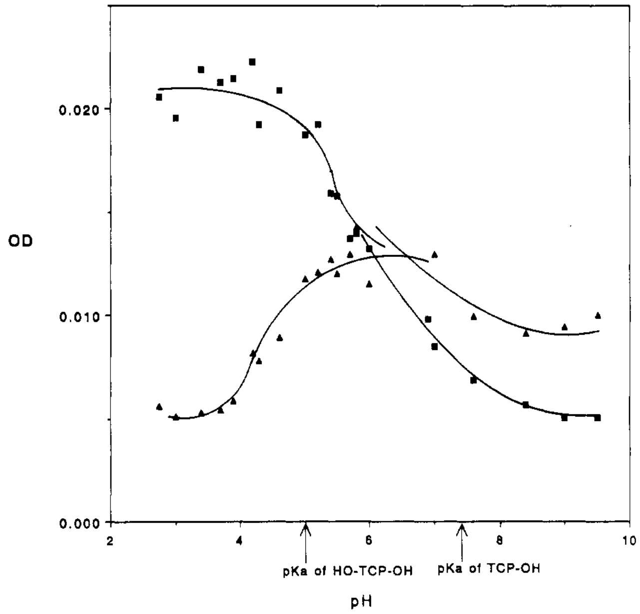
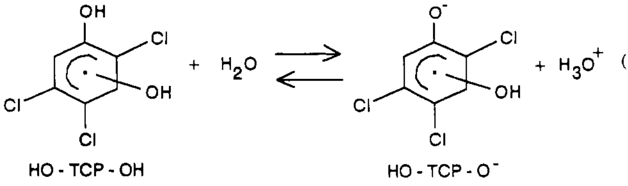


Figure 5. OD^0_{320} (■), and OD^0_{380} (▲) vs pH data. Optical densities have been normalized to values corresponding to a total radical concentration of 4×10^{-6} M.

The OD^0_{380} vs pH data illustrate that above pH 6.0 the dependence of optical density on pH is complicated by titration of the TCP-OH proton. Below pH 6.0, however, the observed changes in optical density reflect changes in the degree to which HO-TCP-OH is ionized (eq 9).



(9)

The extinction coefficients at 320 and 380 nm for the radical and radical anion were calculated from data in Figure 5.

TABLE I: Normalized Absorbance versus pH Data for HO-TCP-OH pK_a Determination

pH	OD^0_{320} × 10^2	OD^0_{380} × 10^2	$10^6[A^-]$,[a] M	$10^6[HA]$,[a] M	log $[A^-]/[HA]$	%[b]
3.0	1.96	0.51	0.044	3.59	−1.92	9.3
3.9	2.15	0.584	0.164	3.96	−1.39	3.2
4.2	2.23	0.817	1.06	3.59	−0.530	16
4.3	1.93	0.778	1.31	2.83	−0.334	3.5
4.6	2.09	0.893	1.53	3.02	−0.296	14
5.0	1.88	1.18	2.95	1.65	0.252	15
5.2	1.93	1.21	3.17	1.57	0.306	18
5.4	1.6	1.27	3.71	0.557	0.824	6.7
5.5	1.58	1.20	3.38	0.717	0.674	2.5
6.0	1.32	1.15	3.48	0.226	1.19	7.1

[a] $[A^-]$ and [HA] correspond to the concentrations of HO-TCP-O^- and HO-TCP-OH, respectively. [b] % = $100([A^-] + [HA])/(4 \times 10^{-6})$.

$\epsilon^{320}_{HOTCPOH}$ and $\epsilon^{380}_{HOTCPOH}$ are averages of $OD^0_\lambda/[\text{HO-TCP-OH}]l$ values for pH 3.0, 3.4, 3.7, and 3.9, (5300 ± 250) and (1350 ± 80) M^{-1} cm^{-1}, respectively. $\epsilon^{320}_{HOTCPO^-}$ and $\epsilon^{380}_{HOTCPO^-}$ are averages of $OD^0_\lambda/[\text{HO-TCP-OH}]l$ values for pH 5.7, 5.8, and 6.0, (3400 ± 100) and (3200 ± 350) M^{-1} cm^{-1}, respectively. It is clear from Figure 5 that between pH 3.0 and 4.0, the normalized OD^0_λ values are constant, indicating that HO-TCP-OH is fully protonated. In addition, within this pH range, the optical densities at 320 and 380 nm decay with rate constants that are identical within experimental error; $k_{320} = (5.6 \pm 0.8) \times 10^8$ M^{-1} s^{-1} and $k_{380} = (4.5 \pm 0.6) \times 10^8$ M^{-1} s^{-1}. Interpretation of the data at pH greater than 4.0 is more difficult, but the above values for $\epsilon^\lambda_{HOTCPO^-}$ seem reasonable in light of arguments below.

With these extinction coefficients and the normalized total optical densities at 320 and 380 nm it is possible to solve the following system of equations:

$$OD^0_{320} = l(\epsilon^{320}_{HOTCPOH}[\text{HO-TCP-OH}] + \epsilon^{320}_{HOTCPO^-}[\text{HO-TCP-O}^-]) \quad (10)$$

$$OD^0_{380} = l(\epsilon^{380}_{HOTCPOH}[\text{HO-TCP-OH}] + \epsilon^{380}_{HOTCPO^-}[\text{HO-TCP-O}^-])$$

for [HO-TCP-OH] and [HO-TCP-O^-] at various pHs.

With these calculated concentrations, a plot of log [HO-TCP-O^-]/[HO-TCP-OH] vs pH proved to be linear:

$$\log [\text{HO-TCP-O}^-]/[\text{HO-TCP-OH}] = \text{pH} - \text{p}K_a \quad (11)$$

with a slope of 1.08. This experimental slope agrees very well with the predicted value of 1.00. The intercept of the line with the log [HO-TCP-O^-]/[HO-TCP-OH] = 0 axis, (i.e., where [HO-TCP-O^-] = [HO-TCP-OH]), yields a pK_a for HO-TCP-OH of 4.8 ± 1.0 (Figure 6 and Table I).

Ir(IV) Oxidation of HO-TCP-OH. The model employed above for determining the pK_a of HO-TCP-OH assumes that a single isomer of the dihydroxytrichlorocyclohexadienyl radical is formed. To gain information on the nature and distribution of HO-TCP-OH isomers, we monitored the kinetics of HO-TCP-OH oxidation by $IrCl_6^{2-}$. These experiments were carried out in 3 × 10^{-3} M TCP-OH, pH 3.5, N_2O-saturated water with the concentration of $IrCl_6^{2-}$ (λ_{max} = 490 nm, $E°$ = 1020 mV vs NHE) varied from 2 × 10^{-4} to 5 × 10^{-4} M. The concentrations of $IrCl_6^{2-}$ were chosen based on our measurement of the rate constant for reaction of hydroxyl radical with $IrCl_6^{2-}$, $k = 9 \times 10^9$ M^{-1} s^{-1} and on the solubility of TCP-OH in water, approximately 3 × 10^{-3} M at 20 °C. Under these conditions, a single first-order decrease of the solution optical density at 490 and 320 nm was observed after an electron pulse. The observed rate constant was identical at each wavelength and varied from 2 × 10^3 to 1.6 × 10^4 s^{-1} between the lowest and highest concentration of $IrCl_6^{2-}$ used. The rate constant for oxidation of HO-TCP-OH by $IrCl_6^{2-}$, calculated from these results, is (4.9 ± 0.5) × 10^7 M^{-1} s^{-1}.

Similar experiments were performed using $Fe(CN)_6^{3-}$ (λ_{max} = 420 nm, $E°$ ~ 500 mV vs NHE) as oxidant. In this study the solution optical density at 420 nm also decreased after pulsed irradiation according to simple first-order kinetics. As expected, based on the more negative $E°$ of $Fe(CN)_6^{3-}$, the rate constant for oxidation was smaller ($k \sim 10^6$ M^{-1} s^{-1}).

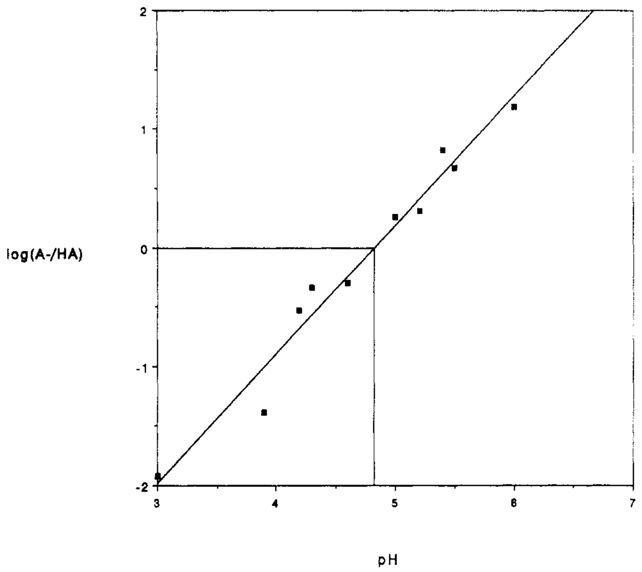
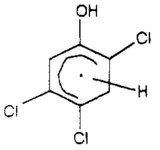
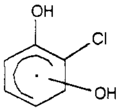
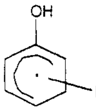


Figure 6. Plot of data in Table I according to eq 11: log $[A^-]/[HA]$ = 1.08 pH − 5.2, where $[A^-]$ = [HO-TCP-O-] and [HA] = [HO-TCP-O-H].

TABLE II: Comparison of H-TCP-OH Optical and Kinetic Properties with Values Published for Similar Radicals

radical	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	$10^{-9}k_{formation}$, M^{-1} s^{-1}	k_{decay}, M^{-1} s^{-1}
	360	4700 ± 1000	1.1 ± 0.2	(1.3 ± 0.3) × 10^9
	340[a]	3500 ± 100	1.5	2.8 × 10^8
	330[b]	3800 ± 800	1.8	NA[c]

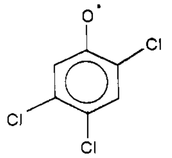
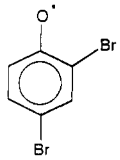
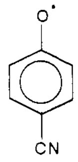
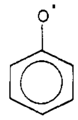
[a] Reference 5. [b] Reference 6. [c] Not applicable.

Discussion

Transient Radicals. The assignment of observed transient absorptions to particular radicals is based on that radical's chemical properties and on a comparison of its absorption and kinetic properties with literature values for similar radicals prepared under similar experimental circumstances. H-TCP-OH, HO-TCP-OH, and TCP-O• all react rapidly by second-order processes, making observation of a characteristic unimolecular H_2O elimination from HO-TCP-OH difficult to observe by optical techniques.[6] The fast dimerization and disproportionation reactions yield products that retain little information on the structural nature of the initial radical. Thus, no product analysis was undertaken. A comparison of the optical and kinetic properties of H-TCP-OH, TCP-O•, and HO-TCP-OH with published data on similar radicals is presented in Tables II–IV. Our assignments agree well with these results.

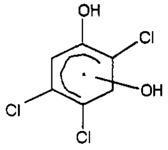
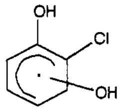
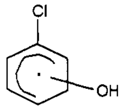
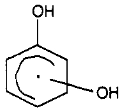
Regiochemistry of OH• Radical Attack. Information regarding the regiochemistry of the OH• radical attack has often been obtained by studying the distributions of isomeric phenols formed when various metal ions or quinones are used to oxidize the

TABLE III: Comparison of TCP-O Optical and Kinetic Properties with Values Published for Similar Radicals

radical	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	$10^{-9}k_{formation}$, $M^{-1}\ s^{-1}$	$10^{-8}k_{decay}$, $M^{-1}\ s^{-1}$
	430	3600 ± 600	4.3 ± 0.8	7.7 ± 1.7
	420[a]	3700	NA	1.0
	NA[b]	NA	3.8	NA
	400[c]	2200 ± 200	NA	NA

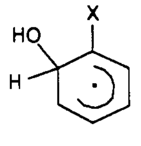
[a] Reference 22. [b] Reference 7. [c] Reference 6.

TABLE IV: Comparison of HO-TCP-OH Optical and Kinetic Properties with Values Published for Similar Radicals

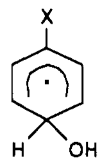
radical	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$	$10^{-10}k_{formation}$, $M^{-1}\ s^{-1}$	k_{decay}, $M^{-1}\ s^{-1}$
	320	5300 ± 250	1.2 ± 0.1	$(5.6 \pm 0.8) \times 10^8$
	300[a]	NA	1.2	NA
	320[b]	4000	NA	2.2×10^8
	330[c]	4400 ± 800	1.4	3.6×10^9

[a] Reference 5. [b] Reference 16. [c] Reference 6.

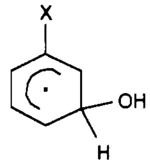
hydroxycyclohexadienyl radical before it can undergo its natural reactions.[17,18] Measurements of the rate constants for $Fe(CN)_3^{3-}$ oxidation of $HOC_6H_5X^{\bullet}$ indicate that ortho (I) and para (II) isomers are more readily oxidized than meta (III) isomers and that the rate constants for oxidation are sensitive to the nature of the substituent and the redox potential of the oxidant.[17] However, since these oxidations do not proceed at diffusion-controlled rates, the product phenols may not accurately represent the distribution of initially formed hydroxycyclohexadienyl radicals. However, by examining the kinetics of oxidation, it is



I



II

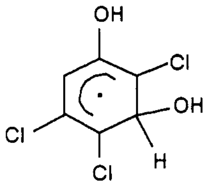


III

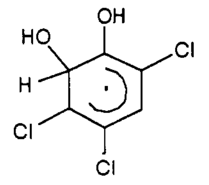
possible to kinetically distinguish isomers.

Buxton reports a single-exponential bleaching of OD_{490} when a series of $HOC_6H_5X^{\bullet}$'s is oxidized by $IrCl_6^{2-}$.[17] The rate constants for these reactions are diffusion limited. It was, therefore, impossible in his study to kinetically distinguish $HOC_6H_5X^{\bullet}$ isomers when $IrCl_6^{2-}$ is used as oxidant. However, with $Fe(CN)_6^{3-}$ as oxidant Buxton detected kinetically distinct isomers as a biexponential bleaching of OD_{420} when oxidation rate constants dropped below one-tenth of those for diffusion-controlled reactions. We, therefore, suggest that the observation of a single first-order decay of the optical densities at 320 and 490 nm in the experiments where $IrCl_6^{2-}$ was used to oxidize HO-TCP-OH provides evidence that at pH 3.5 a single isomer of HO-TCP-OH is formed. The rate constant we have measured, $(4.9 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$, is 2 orders of magnitude lower than that expected for a diffusion-controlled reaction in water. This hypothesis is also supported by the experiments using $Fe(CN)_6^{3-}$ as oxidant. If isomeric radicals were formed, two or more first-order processes and more complex kinetics would be observed in these oxidation studies.

If we exclude the possibility of $OH^{\bullet}$ attack at chlorine-substituted carbons, two isomers of HO-TCP-OH are possible:



3-HO-TCP-OH



6-HO-TCP-OH

AM1 calculations[12] indicate that the heat of formation of the α-hydroxy radical, 6-HO-TCP-OH, is more negative than that of the β-hydroxy radical, 3-HO-TCP-OH, by 5 kcal/mol. Although this is not a large energy difference, 3-HO-TCP-OH should be slightly more difficult to form. Simple electronic arguments also assert that the HO-TCP-OH isomer most likely formed would result from $OH^{\bullet}$ addition to position 6, which is activated by an adjacent hydroxyl substituent.

The straightforward decay kinetics of the optical densities at 320 and 380 nm in the absence of an oxidant also suggest a single isomer of HO-TCP-OH is formed. These observations do not exclude the unlikely possibilities that two or more isomers are present and decay with similar rates or that other isomers react so slowly that we fail to observe them on the time scale of these experiments (2 ms). Similar arguments apply to the oxidation studies.

A further argument that a single isomer of HO-TCP-OH is formed relies on the fit of the optical density vs pH data to a model developed for a single acid and the magnitude of the measured pK_a. The slope of the line described by eq 11 is sensitive to the values of the various extinction coefficients derived from our data. The largest errors in these extinction coefficients are associated with $\epsilon^{320}_{HOTCPO^-}$ and $\epsilon^{380}_{HOTCPO^-}$, which were measured in a pH region where interference by titration of the phenolic proton is important. If, as might be expected from examining Figure 5, the true value of $\epsilon^{320}_{HOTCPO^-}$ is 20% less and that of $\epsilon^{380}_{HOTCPO^-}$ is 20% more than those we reported, then the slope of eq 11 decreases to approximately 0.8, indicating a poor fit to the model.

There are few pK_a's reported in the literature for hydroxycyclohexadienyl radicals. Taniguchi and Schuler have determined that the pK_a of the hydroxycyclohexadienyl radical (IV) is approximately 14.6.[19] Anderson and Patel recently determined a

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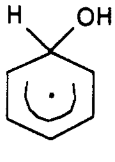
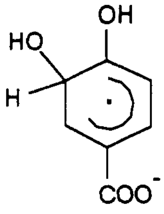


IV



V

pK_a of 8.4 for 4-carboxy-1,2-dihydroxycyclohexadienyl radical (V).[20] Our value of 4.8 for the pK_a of 1,6-dihydroxy-2,4,5-trichlorocyclohexadienyl radical seems reasonable in light of the further stabilization conferred on the radical anion by three chlorine substituents.

Note that the pK_a's of β-hydroxyalkyl radicals are generally several units higher than those of α-hydroxyalkyl radicals.[19,21] This suggests that in our experiments, we might not have been able to detect the titration of a proton from 3-HO-TCP-OH because of interference by the pK_a of the parent phenol.

Conclusions

Pulse radiolysis has been used to quantitatively generate and characterize the hydroxy-2,4,5-trichlorocyclohexadienyl radical (H-TCP-OH), the 2,4,5-trichlorophenoxyl radical (TCP-O$^\bullet$), and the 1,6-dihydroxy-2,4,5-trichlorocyclohexadienyl radical (6-HO-TCP-OH). The assignment of a particular isomeric structure to HO-TCP-OH is based on the isosbestic point in its transient spectrum, its straightforward decay kinetics, the single-exponential behavior of its oxidation by $IrCl_6^{2-}$ and $Fe(CN)_6^{3-}$, its more negative calculated heat of formation relative to the 3-HO-TCP-OH, and the excellent fit of our data to eq 11.

Now that HO-TCP-OH and TCP-O$^\bullet$ have been characterized, TCP-OH may be used as a mechanistic probe of TiO_2-photosensitized oxidation reactions. Using transparent TiO_2 colloids and laser flash photolysis, we seek to distinguish a mechanism involving direct transfer of an electron from adsorbed TCP-OH to the photoexcited surface from a mechanism involving electron transfer mediated by OH$^\bullet$ radical. The product of the direct electron-transfer mechanism should be the radical cation, TCP-OH$^{\bullet+}$, which would be expected to rapidly deprotonate yielding TCP-O$^\bullet$. The product of electron transfer mediated by OH$^\bullet$ would be HO-TCP-OH. Since in the present study we have demonstrated that TCP-O$^\bullet$ and HO-TCP-OH have distinct chemical properties, we should be able to distinguish these degradation pathways. Work on this project is well under way with promising preliminary results.

Acknowledgment. These experiments were performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the National Institute of Health and the University of Texas at Austin. We are grateful for invaluable discussion with Dr. Stephen Atherton and Elizabeth Gaillard and for Bill Naumann's expert operation of the electron accelerator. This work was supported by the National Science Foundation and the Robert A. Welch Foundation. We are also grateful for a NATO travel grant which allowed for collaboration between the University of Texas (Austin), Concordia University (Canada) and the University of Turin (Italy) on problems involving photocatalytic oxidation.

Registry No. TCP-OH, 95-95-4; H-TCP-OH, 118334-00-2; TCP-O, 118318-06-2; HO-TCP-OH, 118334-01-3; H, 12385-13-6; N_3, 12596-60-0; OH, 3352-57-6; $IrCl_6^{2-}$, 16918-91-5; $Fe(CN)_6^{3-}$, 13408-62-3.

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Hydrogen-Atom Abstraction from Methanol by OH

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Absolute rate coefficients for the reactions of OH with CH_3OH (k_1) and CD_3OH (k_2) were measured over the temperature range 293–866 K by using the laser photolysis/laser-induced fluorescence technique. The kinetic data, in the units cm^3 molecule^{-1} s^{-1}, are fitted to the three-parameter expressions $k_1(T) = 5.89 \times 10^{-20}T^{2.65} \exp(+883 \text{ cal mol}^{-1}/RT)$ and $k_2(T) = 1.28 \times 10^{-22}T^{3.48} \exp(+1275 \text{ cal mol}^{-1}/RT)$. The measured kinetic isotope effect, k_1/k_2, yields insight into the branching ratio for H-atom abstraction from the methyl versus the hydroxyl site in methanol.

Introduction

Hydroxyl-radical reactions are extremely important in both atmospheric and combustion chemistries because OH is a dominant reactive species in hydrocarbon oxidation.[1] Methanol reactivity impacts these chemistries because of the increasing use of clean-burning oxygenated fuels. The absolute rate coefficient, over a broad temperature range, of the reaction between OH and methanol is required input to atmospheric and combustion reaction models.[2,3] This reaction is also of fundamental interest since two separate H-atom abstraction channels may contribute to the overall reactivity, and the branching ratio for abstraction from the methyl versus the hydroxyl group will probably be strongly temperature dependent. In this paper, we report determinations of the absolute rate coefficients for the reactions

$$OH + CH_3OH \xrightarrow{k_1} \begin{cases} H_2O + CH_2OH \\ H_2O + CH_3O \end{cases} \tag{1}$$

$$OH + CD_3OH \xrightarrow{k_2} \begin{cases} HDO + CD_2OH \\ H_2O + CD_3O \end{cases} \tag{2}$$

The rate constants k_1 and k_2 are measured over the temperature range $293 \leq T \leq 866$ K at a pressure of 700 Torr of helium buffer gas.

Many previous investigations of the kinetics of reaction 1 have been published.[2-15] Several authors have reported room-temperature values of k_1,[4-13] and most studies agree well with an

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