Electron Paramagnetic Resonance of *t*-Butoxy Radical Reactions with Alcohols

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Abstract: The presence of alkoxy radicals, RO·, in solution has been inferred from reaction products but never directly confirmed by spectroscopy. The first-formed free radicals in the reactions of alkoxy radicals with other molecules in solution have been the subject of much speculation. In the work reported here, epr was used to characterize free-radical products of reactions between various alcohols and a presumed *t*-butoxy radical, $(CH_3)_3CO\cdot$, generated in a flow system by photolysis of di-*t*-butyl peroxide in an isooctane at room temperature. In each case, the epr of the reaction mix revealed only the presence of a free radical resulting from removal of an α proton from the alcohol. The $(CH_3)_3CO\cdot$ radical was not detected. In reactions with alcohols, the *t*-butoxy radical apparently produces the same free radicals as the presumed ·OH from photolyzed H_2O_2. These observations on the reaction of the *t*-butoxy radical with alcohols serve as a logical bridge between the previous studies of ·OH reactions and future work on alkoxy radical reactions. The reactions between $(CH_3)_3CO\cdot$ and species other than alcohols have been followed with epr using the technique described here.

Alkoxy radicals, RO·, are thought to play an important role in autoxidation. The chemical analyses of the end products of many oxidation reactions have been found to support reaction mechanisms which infer the presence of RO· radicals. However, the existence of RO· radicals in solution has never been confirmed by spectroscopy. Nevertheless, the first-formed free radicals in the reaction of RO· with various molecules have been the subject of much speculation.[1] The transient free-radical species, characterized by epr, in the reactions of a presumed *t*-butoxy radical, $(CH_3)_3CO\cdot$, with various alcohols are reported here.

The only previous epr studies of oxy radical reactions in solution have been those in which a presumed ·OH radical was generated either chemically or by photolysis. The chemical method

$$\mathrm{Ti^{III}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Ti^{IV}} + \mathrm{OH^-} + \cdot\mathrm{OH}$$

allowed the ·OH to react with many species in fast-mixing flow systems.[2-6] From alcohols the ·OH radical abstracted both α and β protons, where the proton labeling is the usual one.

$$\underset{\gamma}{-\mathrm{CH_2}}-\underset{\beta}{\mathrm{CH_2}}-\underset{\alpha}{\mathrm{CH_2}}-\mathrm{OH}$$

Other workers found that the ·OH radicals from photolysis of H_2O_2 in alcohols showed little tendency to abstract β protons in nonaqueous solutions.[7] Addition of water to the mixtures increased the abstraction of β protons by the ·OH radical.[8]

In the work reported here, mixtures of an isooctane, di-*t*-butyl peroxide, and an alcohol were photolyzed within the microwave cavity of an epr spectrometer in an attempt to follow directly the reactions of the *t*-butoxy radical from the cleaved peroxide. Alcohol free radicals formed by the loss of an α proton, presumably abstracted by the *t*-butoxy radical, were characterized by their epr spectra. The $(CH_3)_3CO\cdot$ radical was not detected, but its presence was assumed on the basis of the observed free-radical reaction products. The technique can be extended to follow RO· reactions with other species. These observations on the reaction of the *t*-butoxy radical with alcohols serve as a logical bridge between the previous studies of ·OH reactions and future work on alkoxy radical reactions.

Many reactions of alkoxy radicals should be similar to the reactions of ·OH. However, the use of an alkoxy radical rather than ·OH permits the reactions to be carried out in nonpolar solvents, avoiding the complicating effects of protonation in aqueous solutions. In addition, compounds insoluble in aqueous solution can often react with an alkoxy radical in nonpolar solvents.

Experimental Section

Materials. The di-*t*-butyl peroxide was obtained in 97% purity from the U. S. Peroxygen Corp., anhydrous methyl alcohol from Mallinckrodt, and absolute ethyl alcohol from the Commercial Solvents Corp. The rest of the alcohols were Baker and Adams reagent grade. The isooctane was Phillips 2,2,4-trimethylpentane (99 mole % minimum).

Sample Preparation. The sample solutions were prepared from di-*t*-butyl peroxide, hereinafter called R_2O_2, reagent grade alcohols, and the isooctane. Hydroperoxides were removed from the R_2O_2 by shaking a 20% by volume R_2O_2-in-isooctane solution with portions of aqueous acidified potassium iodide. The iodine remaining in the isooctane solution was removed by shaking with portions of aqueous potassium iodide. The isooctane solution was then washed with water and partially dried by passage through several layers of filter paper. Two types of solutions were used: (1) 5% by volume R_2O_2 in alcohol and (2) 20% by volume R_2O_2 and 10% by volume alcohol in isooctane. The same free radicals were produced by both types of solution in the early studies, but the type 2 solution gave better signal-to-noise ratios. For this reason, only type 2 solutions have been used in the later work. The solutions were bubbled with nitrogen for 0.5 hr to remove dissolved oxygen before irradiation.

Apparatus. A conventional Varian X-band epr spectrometer with 100-kc field modulation was used in conjunction with a Varian 6-in. magnet to record the first derivative of the absorption spectrum. The hyperfine splitting intervals were measured using a Varian TE 104 dual cavity with potassium peroxylamine disulfonate as the reference standard. The cavity was cooled by a stream of chilled nitrogen to oppose the heating effect of the light source used for the photolysis.

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Table I. Epr Hyperfine Coupling Constants for the Free Radicals Produced by the Reaction of Alcohols with $\cdot OH$ and with $(CH_3)_3CO\cdot$

		Proton hyperfine coupling constants, gauss[a]								
		C_α–H			C_β–H			C–OH		
Alcohol	Free radical	$\cdot OH$[c]	$\cdot OH$[d]	$(CH_3)_3CO\cdot$[e]	$\cdot OH$[d]	$\cdot OH$[d]	$(CH_3)_3CO\cdot$[e]	$\cdot OH$[c]	$\cdot OH$[d]	$(CH_3)_3CO\cdot$[e]
Methanol	$\cdot CH_2OH$	17.2	17.38	16.9					1.15	1.2
Ethanol	$CH_3\dot{C}HOH$	15.0	15.37	15.1	22.0	22.19	21.9			
1-Propanol	$CH_3CH_2\dot{C}HOH$		15.1	14.8		21.4	21.0			
2 Propanol	$(CH_3)_2\dot{C}OH$				20.0	19.66	19.3		0.70	0.65
1-Butanol	$CH_3CH_2CH_2\dot{C}HOH$		15.3	15.0		20.0	19.8			
2-Methyl-1-propanol[b]	$(CH_3)_2CH\dot{C}HOH$	12.7	14.74	14.9	20.0	21.41	22.0			

[a] Proton labeling convention is $-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-OH$. [b] Assigned by comparison with other coupling constants in this table. [c] Reference 2. Chemically produced $\cdot OH$. [d] Reference 7. Measured at 26° using photolyzed H_2O_2. [e] Measured at 26° using photolyzed di-*t*-butyl peroxide. Error in hyperfine coupling constants is ±0.1 G.

No effort was made to obtain the minimum line width. The narrowest lines compatible with sufficient resolution and signal-to-noise ratio were accepted. Consequently, the observed line widths range between 0.2 and 1.0 G, although the 6-in. magnet was homogeneous enough to provide minimum line widths less than 0.1 G. Microwave power levels (10–40 mW) were chosen to optimize signal-to-noise ratios.

The light-initiated chemical reactions occurred in a one-stream flow system constructed of Teflon and glass. As it flowed through a fused-silica cell placed in the microwave cavity, the solution was irradiated by a mercury arc, whose light passed through the 50% transmission grid furnished with the Varian V-4531 cavity. The fused-silica cells, fabricated in our laboratory, were similar in design to the one sold by Varian (V-4548) but had optical path lengths in the range 0.5–3.0 mm. The best signal-to-noise ratios were obtained from the 2.0-mm cell. Only Suprasil No. 1 fused silica (Amersil Quartz Division, Engelhard Industries) was used in the construction of the cells to avoid the spurious paramagnetic resonance signals arising from prolonged ultraviolet irradiation of impurities in ordinary fused silica.[7]

The light source for the irradiation was a PEK Labs 500-2 mercury short-arc lamp in a PEK Labs M916 housing with first-surface parabolic mirror and clear fused-quartz condensing lens system, which allowed focusing to a minimum distance of 12 in. A detailed description of the Livingston and Zeldes apparatus,[7] kindly provided by Dr. Henry Zeldes, combined with crude calculations of light-gathering geometry and light intensity indicated that the irradiation apparatus reported here provides an ultraviolet light intensity roughly four times greater than the apparatus used by Livingston and Zeldes. The lamp was changed only when a reduction of signal-to-noise ratio in the epr spectra indicated reduced ultraviolet output. Lamps were used for as long as 80 hr with no difficulty.

General Considerations. The purpose of this work was to identify by epr the free radicals produced in the reaction of alcohols with $(CH_3)_3CO\cdot$ from photolyzed di-*t*-butyl peroxide. Consequently, the optimization of resolution and signal-to-noise ratio were the dominant experimental problems. The spectra were weak in many cases; amplifier filter time constants of 1 and 3 sec were frequently necessary.

The epr spectra were described adequately by the usual high-field spin-Hamiltonian. No *g*-value measurements were made, since the identity of the chemical species could be determined from the hyperfine splitting patterns. Many *g*-value measurements have been made by others on alcohol radicals.[7]

The epr spectra were dependent upon flow rate only to the extent that too slow a flow rate reduced the spectrum amplitude. Consequently, the minimum flow rate was chosen which resulted in optimum signal-to-noise ratio, roughly 3 ml/min in most cases.

All spectra reported here were obtained at room temperature. An unsuccessful attempt was made to increase the radical signals by observation at low temperatures. However, as the solution temperature was lowered below room temperature, the free-radical signal-to-noise ratio in the spectrum grew progressively worse. Apparently, the chance of an $RO\cdot$ radical, produced by the photolytic decomposition of the peroxide, escaping from the solvent "cage" is less at low temperatures where diffusion from the cage is slower. The $\cdot OH$ radicals from photolyzed H_2O_2 did not show this effect,[7,8] presumably because the "cage" walls were formed by the molecules from which $\cdot OH$ attack produced the observed free radicals.

Results

The reactions of $RO\cdot$ with alcohols produced the same observable radicals when carried out either with 5% R_2O_2 in the alcohol or with 20% R_2O_2 and 10% alcohol in the isooctane. For the 5% R_2O_2 in alcohol the reaction mechanisms, in part, are probably

$$R_2O_2 + h\nu \longrightarrow 2RO\cdot$$

$$RO\cdot + RCH_2OH \longrightarrow ROH + R\dot{C}OH$$

However, for dilute R_2O_2 and alcohol in isooctane, additional reactions of isooctane alkyl radicals are probably also involved; namely

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

$$R\cdot + RCH_2OH \longrightarrow RH + R\dot{C}HOH$$

In Table I are listed the hyperfine coupling constants of the alcohol radicals produced by the reaction of $\cdot OH$ and $(CH_3)_3CO\cdot$ radicals with the respective alcohols. The epr spectra for the alcohol radicals produced in the three different ways show the same patterns, differing only slightly in the magnitude of the hyperfine splitting. These small differences are of the size expected for solvent effects in going from aqueous to alcoholic to hydrocarbon solvents.

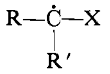
The radicals had the general structure

$$R\text{-}\underset{\gamma}{C}H_2\text{-}\underset{\beta}{C}H_2\text{-}\underset{\alpha}{\dot{C}}H\text{-}OH$$

where the Greek labels are used in reference to both the carbon atoms and their attached protons. At room temperature the presumed *t*-butoxy radical abstracted only α protons, forming the same radicals produced by the presumed $\cdot OH$ radical from photolysis in the absence of water. This was encouraging evidence that $RO\cdot$ was the active species from R_2O_2.

Discussion

The most important conclusion to be drawn from this work is that alkoxy radicals, in particular the *t*-butoxy radical, abstract protons from other molecules in solution at room temperature, producing transient free-radical species which can be detected by epr. The structure of the transient species indicates that they may be the first-formed free radicals in the reactions. The possibility of abstracting protons in nonpolar solvents opens the door to the production of free radicals of many new types, until now unavailable. Several new types of radicals with the following structure, where



$$R{-}\dot{C}{-}X \atop {\;\;\;|\atop \;\;\;R'}$$

X = OR, SR, SSR, CHO, and NO_2, have been and are being studied by the author. Some useful qualitative insight can be obtained from the familiar σ–π interaction approximations.

Experimental hyperfine coupling constants for α protons have been successfully explained by the McConnell relation[9]

$$A_\alpha^{H} = Q_\alpha \rho_c^{\pi} \quad (1)$$

where A_α^H is the α-proton hyperfine coupling constant, ρ_c^π is the spin density in the p_z orbital of the α-carbon atom, and Q_α is a constant, 23 G in the case of the methyl radical.[10] The small α-proton hyperfine coupling constants in the alcohol radicals suggest that the α-carbon atom has nearly planar sp^2 bond hybridization.[10] Then, using Q_α = 23 G, the spin densities of the α-carbon atoms in methyl and ethyl alcohol radicals are 0.74 and 0.66, respectively. Partial delocalization of the unpaired electron onto the oxygen atom would not be surprising in these radicals, since the oxygen could form a π-electron system with the α-carbon atom.

The coupling constants for β protons have also been rationalized by a McConnell relation like eq 1, in which Q_α is replaced by $Q(\theta)$; where[11]

$$Q(\theta) = B_0 + B_2 \cos^2 \theta \quad (2)$$

In (2), θ is the angle between the axis of the p_z orbital and the C–H bond, both projected onto a plane perpendicular to the C–Ċ bond. Both experiment and theory suggest that the value of the constant B_0 is very small compared to the value of the constant B_2.[12] Consequently, (2) can be simplified to

$$Q(\theta) = B \cos^2 \theta \quad (3)$$

If hindered internal rotation occurs in the free radical, the expression for the β-proton coupling constant becomes

$$A_\beta^{H} = \langle Q(\theta)\rangle \rho_c^{\pi} = B\langle \cos^2\theta\rangle \rho_c^{\pi} \quad (4)$$

where $\langle Q(\theta)\rangle$ is the quantum mechanical average over the statistically weighted internal-rotation states of the molecule.[13,14] For free rotation $\langle\cos^2\rangle = {}^1/_2$. Then the experimental data for the ethyl alcohol free radical suggest that $B \simeq 45$ G. This value can be compared with $B \simeq 59$ G for the ethyl radical.[10] The difference may be due to the approximations made in calculating the spin densities and obtaining eq 4.

The onset of hindered internal rotation in a family of free radicals can be detected by comparing the A_β^H/A_α^H ratios, since[13,14]

$$A_\beta^{H}/A_\alpha^{H} = (B/Q_\alpha)\langle\cos^2\theta\rangle \quad (5)$$

A change in A_β^H/A_α^H indicates a change in $\langle\cos^2\theta\rangle$, if B and Q_α can be regarded as very nearly constant for the radical family. The ratios for the series $CH_3\dot{C}HOH$, $CH_3CH_2\dot{C}HOH$, and $(CH_3)_2CH\dot{C}HOH$ are 1.45, 1.42, and 1.48, respectively. Within experimental error, no hindered internal rotation is occurring about the C–Ċ bond.

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