functions.[5] Addition of sodium salicylate fails to accelerate the equilibration or to dilute the isotopic concentration; equilibration consequently must occur intramolecularly *via* **2**.

At 30° in water, pH 8.2, $\mu = 0.5$, the half-life of the equilibration of **1** to **1′** is 15 sec, and similarly rapid exchange occurs in organic solvents—in ethyl acetate at 0° in the presence of 1 equiv of triethylamine a first-order half-life of 7.5 min was observed. The insensitivity of the exchange process to solvent supports a simple mechanism involving equilibration among isomeric anions.

For water, reaction with **1** occurs *ca.* 10^4 times more slowly than equilibration of label, and direct information concerning product origin is inaccessible. However, with a nucleophile which can react with **1** at a rate which approximates k_1, measurement of equilibration of **1** with **1′** and labeling of **3** will allow direct calculation of k_2 if reaction occurs predominantly from **1**, or of k_{-1}/k_3 if from **2**.

$\mathbf{1} + \mathbf{1'} \rightarrow \mathbf{3} + \mathbf{3'}$

$$\ln\left(\frac{[\mathbf{1}]_0}{[\mathbf{1}] + [\mathbf{1'}]}\right) = \left(\frac{k_1}{\dfrac{k_{-1}}{k_3} + 1} + k_2\right)t = k_{\text{obsd}}t \qquad (1)$$

Disappearance of **1**

$$\ln\left(\frac{[\mathbf{1}]_0}{[\mathbf{1}]}\right) = (k_1 + k_2)t \qquad (2)$$

$\mathbf{1} \rightarrow \mathbf{1'}$

$$\ln\left(\frac{[\mathbf{1}] + [\mathbf{1'}]}{[\mathbf{1}]}\right) = \left(\frac{k_1}{\dfrac{k_3}{k_{-1}} + 1}\right)t \qquad (3)$$

Label fraction in products

$$\frac{[\mathbf{3}]}{[\mathbf{1'}] + [\mathbf{3'}]} = \frac{k_2}{k_1} \qquad (4)$$

The three pertinent experimental ratios, measured for a series of reactions of **1** with aqueous hydrazine, are given in Table I, along with values for k_{obsd}, k_1, and k_2 calculated from eq 1–4.

Table I. Reaction of **1** with Aqueous Hydrazine[a]

$[N_2H_4]$, *M*	A	B	C	k_{obsd}, min^{-1}	k_2, min^{-1}	k_1, min^{-1}
0.021	0.97	0.51	0.91	0.034	0.045	2.5
0.046	0.91	0.58	0.92	0.088	0.099	2.5
0.071	0.86	0.63	0.90	0.15	0.14	2.4
0.095	0.79	0.67	0.92	0.24	0.21	2.6
0.144	0.63	0.65	0.92	0.46	0.40	2.6
0.193	0.48	0.65	0.93	0.73	0.64	2.8
0.292	0.25	0.60	0.91	1.38	1.16	2.6
0.341	0.16	0.57	0.91	1.82	1.56	2.7

[a] $t = 1.0$ min, 30°, pH 8.15, $\mu = 0.5$. A = ([I] + [**1′**])/[**1**]$_0$; B = [**3′**]/([**3**] + [**3′**]); C = [**1′**]/([**1**] + [**1′**]).

The constancy of the ratio [**1′**]/([**1′**] + [**1**]) indicates that k_3/k_{-1}, which should increase at least as rapidly as $[N_2H_4]$, must be markedly less than unity over this concentration range. Moreover, the equivalence of k_2, calculated from eq 2 and 4, with k_{obsd} establishes direct attack of hydrazine on **1** as the mechanism of hydrazinolysis. The kinetic irrelevance of salicylic anhydride (**2**), established under conditions in which **2** approaches its equilibrium concentration with respect to **1**, requires that **2** be regarded as a *normal* intermediate in the sense of the accompanying communication; for **2**, intrinsic reactivity fails to compensate inferior concentration.

Two generalizations arise from this work. (1) Aside from its symmetry, **1** is a normal representative of its class, and similarly rapid equilibrations with anhydride isomers are expected for other acylsalicylic acids. (2) With hydrazine, **1** appears to be exactly as reactive as a simple phenolic ester;[6] however, because of hydrogen bonding and the likelihood of intramolecular catalysis, **2** is anticipated both to be present at higher concentration and to be more reactive than expected for the intrinsic stability of an aromatic anhydride. As models for the relative reactivity of equilibrated phenolic esters and anhydrides, **1** and **2** appear to offer a choice particularly weighted toward **2**. The failure to observe reactions *via* anhydrides in this and in related systems implies that carboxylates cannot serve as nucleophilic catalysts for ester hydrolysis, even with the assistance of an agent which allows the intermediary anhydride to reach its limiting concentration. This conclusion is in harmony with the results of Gold,[8] for all but highly activated phenolic esters, and with the thermodynamic and kinetic data of Jencks.[9,9a]

(6) The term k_{obsd} may be represented as $(1.4 + 12[N_2H_4])[N_2H_4]$, in good agreement with more accurate data obtained by a uv method. These coefficients may be compared with the values 0.65 M^{-1} min^{-1} and 19.0 M^{-2} min^{-1} observed by Bruice and Benkovic[7] for hydrazinolysis of phenyl acetate under comparable conditions. See also ref 2 for a discussion of pertinent issues.

(7) T. C. Bruice and S. J. Benkovic, *J. Amer. Chem. Soc.*, **86**, 418 (1964).

(8) A. R. Butler and V. Gold, *J. Chem. Soc.*, 1334 (1962); D. G. Oakenfull, T. Riley, and V. Gold, *Chem. Commun.*, 385 (1966).

(9) J. F. Kirsh and W. P. Jencks, *J. Amer. Chem. Soc.*, **86**, 833, 837 (1964).

(9a) NOTE ADDED IN PROOF. Data concerning the contrary case of cyclic anhydrides have been summarized by T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, 90, 3808 (1968). The main conclusions of this study have been established independently by Fersht and Kirby [A. R. Fersht and A. J. Kirby, *ibid.*, 90, 5818, 5826, 5833 (1968)].

(10) Fellow of the A. P. Sloan Foundation, 1968–1970. The authors gratefully acknowledge support from the National Institutes of Health (GM 13453) and the National Science Foundation (GP 8329).

(11) National Institutes of Health Predoctoral Fellow, 1965–1968.

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Electron Spin Resonance of Aliphatic Hydrocarbon Radicals in Solution

Sir:

We wish to report a convenient and versatile technique for examining the esr spectra of a variety of short-lived free radicals in solution. The method is particularly useful for the study of alkyl and other organic free radicals in nonaqueous systems, where the more conventional flow techniques are difficult to apply.

Radicals (R·) are generated by ultraviolet irradiation of a static solution of di-*t*-butyl peroxide in the presence of a hydrogen donor (RH). The thoroughly degassed sample is contained in a small fused silica tube (4-mm

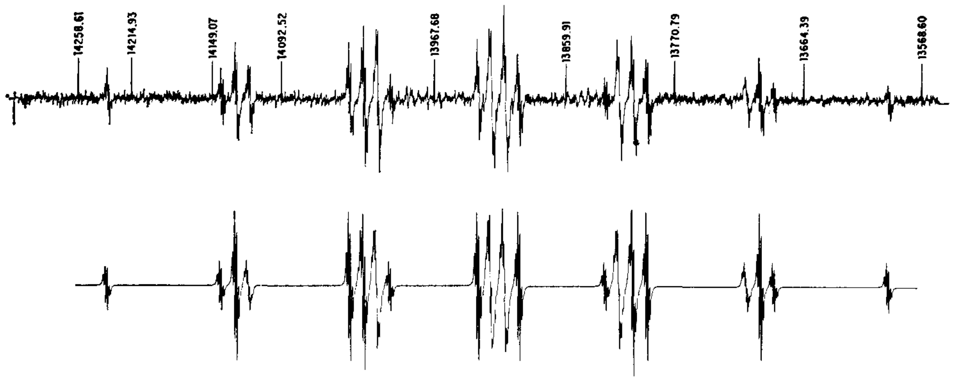


Figure 1. Esr spectrum of the *sec*-butyl radical at −90°. The proton nmr frequency markers are in kcps. The computer-simulated spectrum includes second-order effects.

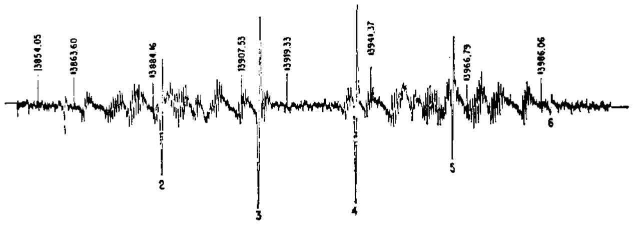


Figure 2. Esr spectrum of cyclopentadienyl radical (labeled lines) in cyclopropane solution at −130°. The line widths are *ca.* 0.08 G. The additional fine structure (the wing lines are not included) is due to the allylic radical resulting from the addition of *t*-butoxyl to cyclopentadiene.

i.d. and 0.5-mm wall thickness), and less than 0.5 g of material is needed. The tube is irradiated directly in the microwave cavity of the spectrometer by a 2-kW high-pressure mercury lamp (PEK Labs AIB). Generally, the best signal-to-noise ratios are obtained at the lowest temperatures than can be maintained without solidification. Under these conditions alkyl radicals can be observed for prolonged periods over a range of temperatures.

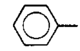
The ultraviolet spectrum of di-*t*-butyl peroxide shows regularly increasing and structureless absorption from 3400 to 2200 Å.[1] Photolysis in this region produces *t*-butoxy radicals (eq 1) with a primary quantum yield

$$(CH_3)_3COOC(CH_3)_3 + h\nu \longrightarrow 2(CH_3)_3CO \qquad (1)$$

of unity.[2,3] Our esr studies are consistent with this oxy radical species being responsible for the generation of alkyl radicals (eq 2). Other studies have demonstrated that *t*-butoxy radicals are rather selective in hydrogen-transfer processes such as (2).[4]

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (2)$$

Table I. Esr of Alkyl Radicals from Hydrocarbons[a]

Hydrocarbon	Temp, °C	Radical	Coupling constant,[e] G a_α	a_β	a_γ
Propane	−162	$CH_3\dot{C}HCH_3$	22.1_5	24.7_4	
Butane	−90	$CH_3\dot{C}HCH_2CH_3$	21.9_0	24.6_3 (CH_3) 27.2_0 (CH_2)	0.39
Pentane	−101	$CH_3CH_2\dot{C}HCH_2CH_3$[f]	21.6_9	27.6_1	0.44
		$CH_3\dot{C}HCH_2CH_2CH_3$	21.8_8	24.8_0 (CH_3) 24.8_0 (CH_2)[j]	Nd[i]
Cyclobutane	−85		21.3_0	36.7_7	1.0_9
Isobutane	−157	$(CH_3)_3\dot{C}$		22.7_1	
Isopentane	−114	$(CH_3)_2\dot{C}CH_2CH_3$[g]		18.0_8 (CH_2) 22.8_0 (CH_3)	Nd[i]
Toluene[b]	−93	 $-\dot{C}H_2$[h]	16.3_0	5.1_5 (*o*) 1.7_7 (*m*) 6.1_8 (*p*)	
Allene	−128	$H_2C{=}C{=}\dot{C}H$	12.6_2 (CH) 18.9_0 (CH_2)		
Methylacetylene	−122	$H_2C{=}C{=}\dot{C}H$	12.6_8 (CH) 18.9_2 (CH_2)		
Cyclopentadiene[c,d]	−133		6.04		
Cycloheptatriene[c]	−61	C_7H_7	3.9_1		

[a] Photolysis of a solution (*ca.* 10% by volume) of di-*t*-butyl peroxide in hydrocarbon, unless noted otherwise. [b] Solution was 30% by volume in ethane. [c] Solution was 50% by volume cyclopropane. [d] Allyl radical by *t*-butoxyl addition also present. [e] *Cf.* ref 5; A. Carrington and I. C. Smith, *Mol. Phys.*, 9, 137 (1965); G. Liebling and H. McConnell, *J. Chem. Phys.*, 42, 3931 (1965); A. Carrington and I. C. P. Smith, *Mol. Phys.*, 7, 99 (1963). [f] Approximately equal amounts of both radicals. [g] Approximately 15% 3-methyl-2-butyl radical formed. [h] All 54 lines resolved. [i] Not determined. [j] Tentative value.

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(1) E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 337 (1950).

(2) (a) L. M. Dorfman and Z. W. Salsburg, *ibid.*, **73**, 255 (1951); (b) D. H. Volman and W. M. Graven, *ibid.*, **75**, 3112 (1953); (c) G. R. McMillan, *ibid.*, **82**, 3018 (1960).

(3) Based on studies in the gas phase. No doubt cage effects will modify this value in solutions (*cf.* E. S. Huyser and R. M. VanScoy, *J. Org. Chem.*, **33**, 3524 (1968)).

(4) For a discussion of hydrogen abstraction by *t*-butoxyl see: (a) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967); (b) K. Ingold, *ibid.*, **15**, 49 (1967); (c) P. Gray, R. Shaw, and J. C. Thynne, *Progr. Reaction Kinetics*, **4**, 63 (1967).

This simple technique for the production of alkyl radicals for esr study enjoys the advantages of ease and especially selectivity over the classic radiolytic method of Fessenden and Schuler.[5] The esr spectrum generally observed belongs to that alkyl radical produced by abstraction of hydrogen from the weakest bond (*i.e.*, allyl, benzyl > *t*-alkyl > *sec*-alkyl ≫ *p*-alkyl). Radicals produced by scission of the carbon chain inherent in electron radiolysis are absent. Except where several hydrogens have nearly the same reactivities (*e.g.*, 2- and 3-pentyl from pentane), the esr spectrum is generally uncomplicated by the presence of several radical species. A typical example (Figure 1) is the spectrum of the *sec*-butyl radicals produced from *n*-butane. A variety of free radicals produced from some representative hydrocarbons is given in Table I, with the appropriate coupling constants.

Isotropic spectra characteristic of freely tumbling alkyl radicals in solution can be obtained even for the higher melting or readily polymerizable hydrocarbons. Methane, ethane, and cyclopropane, which do not produce radicals in sufficient concentrations to be observed under these conditions, can be conveniently employed as solvents or diluents.[6,7] The esr spectrum of cyclopentadienyl radical in cyclopropane solution (Figure 2) illustrates the characteristic narrow lines attainable.[9,10]

The highly selective production of alkyl radicals by this method offers a potentially valuable tool for the detailed study of a variety of free-radical structures and dynamics.[11]

Acknowledgments. J. K. K. expresses his gratitude to the Central Research Department for the hospitality extended to him during the course of this work.

(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1967).

(6) Under these conditions we have not observed the methyl radicals formed by fragmentation of *t*-butoxyls.

(7) Radicals have recently been observed in the γ radioloysis of di-*t*-butyl peroxide in rigid matrices.[8] Broad lines and a mixture of radical species were reported, apparently by an electron-transfer process.

(8) T. Shida, *J. Phys. Chem.*, **72**, 723 (1968).

(9) Cyclopentadienyl radicals in solution have also been observed previously by R. W. Fessenden, *et al.* (*J. Am. Chem. Soc.*, **86**, 3591 (1964); "Radiation Research," G. Silini, Ed., North Holland Publishing Co., Amsterdam 1967, p 99).

(10) The complete equivalence of the five protons precludes a static Jahn–Teller distortion of the molecule at this temperature (*cf.* G. F. Liebling and H. M. McConnell, *J. Chem. Phys.*, **42**, 3931 (1965)).

(11) After this work was accepted for publication J. Q. Adams (*J. Am. Chem. Soc.*, **90**, 5363 (1968)) reported an esr study of α-hydroxy alkyl radicals generated by photolysis of di-*t*-butyl peroxide in the presence of alcohols. A flow technique similar to that of R. Livingston and H. Zeldes (*J. Chem. Phys.*, **44**, 1245 (1966)) was employed.

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Isomerization and Electron Spin Resonance of Allylic Radicals

Sir:

The photolysis of a propylene solution of di-*t*-butyl peroxide produces allyl radicals (I). The esr spectrum of the allyl radical is shown in Figure 1. The spectral assignments are based on internal consistency with the methyl-substituted allyl radicals (*vide infra*).[1] Our coupling constants agree with those of Fessenden and Schuler,[3] who were able to extract the allyl lines from a complex spectrum obtained from the radiolysis of cyclopropane.[4]

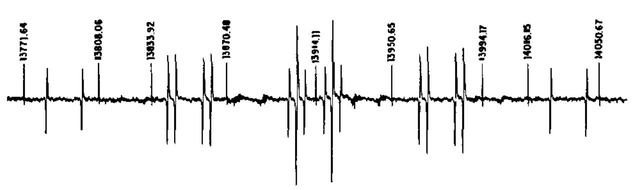
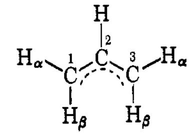


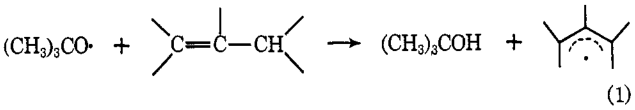
Figure 1. Esr spectrum of the allyl radical at −130°. The nmr frequency markers are in kcps.



I

coupling constants, G
$a_{1,3\alpha H} = 14.81$
$a_{1,3\beta H} = 13.90$
$a_{2H} = 4.06$

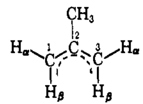
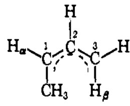
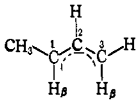
Hydrogen atoms in the allylic position can also be selectively abstracted from a series of butenes by the technique described in the previous communication.[5] Thus, the esr spectrum obtained from isobutylene can be unambiguously assigned to the 2-methallyl radical (II). *cis*-Butene-2 affords the *cis*-1-methallyl radical (III) (Figure 2). Similarly, *trans*-butene-2 gives *trans*-1-methallyl radical (IV) (Figure 3).[6]



(1)

The esr spectrum of *cis*-1-methallyl from the pho-

Table I. Methallyl Radicals from Butenes

Butene	Methallyl radical	Coupling constants, G
Isobutylene	 II	$a_{CH_3} = 3.19$ $a_{1,3\alpha H} = 14.68$ $a_{1,3\beta H} = 13.82$
cis-Butene-2	 III	$a_{CH_3} = 14.01$ $a_{1\alpha H} = 14.17$ $a_{2H} = 3.83$ $a_{3\alpha H} = 14.94$ $a_{3\beta H} = 13.52$
trans-Butene-2	 IV	$a_{CH_3} = 16.43$ $a_{1,3\beta H} = 13.83$ $a_{2H} = 3.85$ $a_{3\alpha H} = 14.78$

(1) It is to be noted that Hinchliffe and Atherton's semiempirical calculations[2a] lead to $a_{\beta H} > a_{\alpha H}$ for the methylene protons. More recent calculations by Pople, *et al.*,[2b] lead to the same prediction but with a much smaller difference between the two positions.

(2) (a) A. Hinchliffe and N. M. Atherton, *Mol. Phys.*, **13**, 89 (1967); (b) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968).

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

(4) The spectrum was successfully dissected into six radical components: cyclopropyl, isopropyl, allyl, methyl, and two unidentified species formed in minor amounts.[3]

(5) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968).