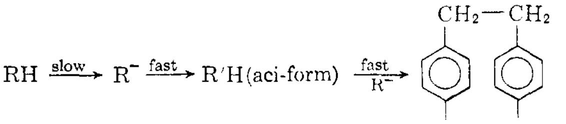
TABLE I

PRODUCTS OF THE REACTION OF *p*-NITROTOLUENE IN POTASSIUM *t*-BUTOXIDE–*t*-BUTYL ALCOHOL SOLUTION

Time, min.	*p*-Nitrotoluene[a]	Potassium *t*-butoxide[a]	Recovered *p*-nitrotoluene[b]	Dimer[b]
5	0.08	0.23	68	21
10	.08	.23	56	35
20	.08	.23	42	55
15	.10[c]	.30		60

[a] Moles per liter. [b] Percentage of starting *p*-nitrotoluene. In the presence of 0.12 *M* nitrobenzene.

When *p*-nitrotoluene in *t*-butyl alcohol is treated with potassium *t*-butoxide the solution is lemon-yellow if a trace of oxygen is present. After a short period of time, depending on how well the solution has been degassed, a blood-red coloration develops at about the same time that the e.s.r. signal becomes detectable. It seems reasonable to attribute the yellow coloration to the *p*-nitrobenzyl carbanion and the red product to the *p*-nitrotoluene radical-ion.[8] In *t*-butyl alcohol, but not in dimethyl sulfoxide, a red precipitate soon develops after which the concentration of radical-ion in solution remains constant as the paramagnetic precipitate increases. Over a concentration range of 0.004 to 0.32 *M* *t*-butoxide ion and 0.002 to 0.01 *M* *p*-nitrotoluene in *t*-butyl alcohol, the initial rate of radical-ion formation (homogeneous solution) is first order in both *p*-nitrotoluene and potassium *t*-butoxide. This relationship holds over concentration ranges wherein the concentration of *p*-nitrobenzyl carbanion, if present at the equilibrium concentration, would not be directly proportional to the concentration of base and *p*-nitrotoluene if appreciable ionization had occurred. It appears that the rate of radical formation is equal to the rate of ionization of *p*-nitrotoluene after a steady state concentration of the anion has been achieved. Since *p*,*p*′-dinitrobibenzyl is formed in reasonable yields in the presence of oxygen,[5] whereas the *p*-nitrobenzyl radical should react readily with oxygen,[9] we favor mechanisms wherein dimerization of the *p*-nitrobenzyl fragments precede radical formation, *e.g.*



$$\xrightarrow{2RH} 2RH\cdot^- + H^+ + NO_2\text{–}C_6H_4CH_2CH_2C_6H_4NO_2$$

In dimethyl sulfoxide–*t*-butyl alcohol (4:1) weak e.s.r. signals were detected from many nitroaromatics including nitrobenzene, 2,4.6-trinitrotoluene and 2,2′,4,4′-tetranitrodiphenylmethane in excess or deficient base and a slow reaction with oxygen was observed. These reactions may be in part a catalyzed oxidation of the solvent involving the methylsulfinylcarbanion, similar to the nitrobenzene catalyzed oxidation of fluorene.[10] We will show in future publications that there is considerable scope to electron-transfer processes involving such carbanions, nitranions or mercaptide anions and a wide variety of organic acceptors. It seems pertinent to suggest that the rearrangement of *o*-nitrotoluene to anthranilic acid[11] should logically be formulated as a process involving free radicals as intermediates.

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[8] In dimethyl sulfoxide solution, wherein the radical buildup is much more rapid, the radical-ion appears to be green-blue.

[9] Unpublished work with Mr. R. Williamson.

[10] G. A. Russell, E. G. Jansen, H.-D. Becker and F. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962).

[11] R. Scholl, *Monatsh. Chem.*, **34**, 1011 (1913).

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EFFECT OF STRUCTURE ON THE RATE OF REACTION OF CARBANIONS WITH MOLECULAR OXYGEN[1,2]

Sir:

We have presented evidence indicating that reactions of molecular oxygen with carbanions often involve intermediate free radicals.[3] If this is the case, the ease of oxidation of ionizable organic compounds (RH) in basic solutions should depend not only on the degree of conversion to the carbanions but also on the relative stability of the carbanions and the corresponding radicals, factors which influence the ease of electron transfer

$$R:^- + X \longrightarrow R\cdot + X\cdot^- \qquad (1)$$

wherein X may be O_2, ROO·, RO·, OH·, or in certain cases a substance not containing unpaired electrons.[3c] Qualitatively, the rates of oxidation of numerous substances in *t*-butyl alcohol or *t*-butyl alcohol–dimethyl sulfoxide mixtures in the presence of an excess of potassium *t*-butoxide can be rationalized readily in these terms.

In *t*-butyl alcohol solution (RH = 0.1 *M*, potassium *t*-butoxide = 0.3 *M*) the relative rates of oxygen absorption are *p*-nitrotoluene > *p*-nitroethylbenzene > *p*-nitrocumene (not oxidized), a sequence reflecting the ease of ionization of prim. > sec. > tert. benzylic hydrogen atoms. In dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution, where ionization is significant for all the compounds, oxidation occurs so rapidly that a rate sequence has not been established.

Substituents recognized to provide stabilization when directly conjugated with a pair of electrons are known to have but little effect on stabilizing the corresponding radicals.[4] Thus, provided the degree of ionization of RH is high in all cases, further substitution of groups such as nitro, cyano, carbonyl, etc., in R would be expected to increase the degree of ionization of RH but to decrease the ease of oxidation of $R:^-$. We have observed this decreased ease of oxidation in each instance wherein

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[1] Reactions of Resonance Stabilized Anions. IV.

[2] Grateful acknowledgment is hereby made of support of this work by grants from the National Science Foundation and the Alfred P. Sloan Foundation.

[3] (a) G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954); (b) G. A. Russell, E. G. Jansen, H.-D. Becker and F. Smentowski, *ibid.*, **84**, 2652 (1962); (c) G. A. Russell and E. G. Janzen, *ibid.*, **84**, 4153 (1962).

[4] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948); M. Szwarc and J. J. Roberts, *ibid.*, **16**, 609 (1948); M. Szwarc, C. H. Leigh and A. H. Sehon, *ibid.*, **19**, 657 (1951); C. H. Leigh, A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **209A**, 197 (1951); G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

a series of appropriately substituted compounds have been compared in a common solvent under conditions such that the extent of ionization was considerable. For instance, in *t*-butyl alcohol solution containing excess potassium *t*-butoxide the rates of oxidation are: *p*-nitrotoluene > 2,4-dinitrotoluene > 2,4,6-trinitrotoluene; *p*-nitrodiphenylmethane > *p,p'*-dinitrodiphenylmethane >> 2,2',4,4'-tetranitrodiphenylmethane (stable); *p*-nitrotriphenylmethane > tris-(*p*-nitrophenyl)-methane; phenylacetonitrile > *p*-nitrophenylacetonitrile; thiophenol >> *p*-nitrothiophenol (stable); while in dimethyl sulfoxide–*t*-butyl alcohol mixtures (80–20), aniline >> *p*-nitroaniline (stable), and *p*-nitrocumene > 2,4-dinitrocumene. Under conditions wherein ketones are oxidized readily in basic solution, many β-dicarbonyl compounds are stable,[5] presumably due to the fact that the second carbonyl group stabilizes the enolate anion more than the radical and thereby decreases the ease with which reaction 1 will occur. In a similar manner we have observed that in dimethyl sulfoxide–*t*-butyl alcohol solutions (80–20%) in the presence of a two-fold excess of potassium *t*-butoxide, the relative rates of oxygen absorption are

$\mathrm{CH_3C_6H_4NO_2\text{-}}p > \mathrm{CH_2(C_6H_4NO_2\text{-}}p)_2 > \mathrm{CH(C_6H_4NO_2\text{-}}p)_3$ (all in *t*-butyl alcohol)
$\mathrm{CH_3COCH_3 > CH_2(COCH_3)_2,\ CH_2(CH_3CO)CO_2C_2H_5}$
$\mathrm{CH_3COC_6H_5 > CH_2(COC_6H_5)_2}$ (stable)
$\mathrm{CH_2(C_6H_5)CO_2C_2H_5 > CH(C_6H_5)(CO_2C_2H_5)_2}$ (stable)
$\mathrm{CH_3SO_2CH_3,\ CH_2(SO_2CH_3)_2,\ CH(SO_2CH_3)_3}$ (all stable)
$\mathrm{CH_3COC_6H_5 > CH_2(NO_2)COC_6H_5}$ (stable)
$\mathrm{CH_2(C_6H_5)COC_6H_5 > CH(C_6H_5)(CN)COC_6H_5}$ (stable)

In aliphatic series one usually expects radical stabilities of tert. > sec. > prim. whereas carbanion stabilities are usually prim. > sec. > tert. Thus, other factors being equal, the conversion of a tert.-carbanion to a tert.-radical should always occur more readily than the conversion of a prim.-carbanion to a prim.-radical. In every appropriate case we know of this relationship holds. Thus, in *t*-butyl alcohol solution 2,4-dinitrocumene is oxidized more readily than 2,4-dinitrotoluene. In dimethyl sulfoxide–*t*-butyl alcohol mixtures (80–20) these relative rates are observed

$\mathrm{(CH_3)_2CHCOCH(CH_3)_2 > CH_3CH_2COCH_2CH_3 > CH_3COCH_3}$
$\mathrm{(CH_3)_2CHSO_2CH(CH_3)_2 > CH_3CH_2SO_2CH_2CH_3 \gg CH_3SO_2CH_3}$ (stable)
$\mathrm{(CH_3)_2CHCN > CH_3CH_2CN > CH_3CN}$
$\mathrm{(CH_3)_2CHCO_2C_2H_5 > CH_3CH_2CO_2C_2H_5 \gg CH_3CO_2C_2H_5}$ (stable)
$\mathrm{(CH_3)_2CHCOC_6H_5 > CH_3CH_2COC_6H_5 > CH_3COC_6H_5}$[6]
$\mathrm{(CH_3)_2CHNO_2 > CH_3CH_2NO_2 > CH_3NO_2}$[6]

Substitution of a phenyl group for a hydrogen atom does not have a consistent effect on the ease of oxidation of the resulting carbanion. The phenyl group is recognized to be important in stabilizing both radicals and carbanions and one might expect these effects to cancel in regard to the ease of occurrence of reaction 1. However, in most cases the phenyl-substituted compound oxidizes more readily than the unsubstituted compound, indicating that in general the phenyl group stabilizes a radical more than a carbanion. The following relative rates of oxidation have been observed in dimethyl sulfoxide–*t*-butyl alcohol (80–20) containing excess potassium *t*-butoxide

$\mathrm{(C_6H_5)_2CHCN > C_6H_5CH_2CN > CH_3CN}$
$p\text{-}\mathrm{NO_2C_6H_5CH_3} > p\text{-}\mathrm{NO_2C_6H_5CH_2C_6H_5} > p\text{-}\mathrm{NO_2C_6H_5CH(C_6H_5)_2}$ (all in *t*-butyl alcohol)
$\mathrm{(C_6H_5)_2CHCO_2C_2H_5 > C_6H_5CH_2CO_2C_2H_5 \gg CH_3CO_2C_2H_5}$ (stable)
$\mathrm{C_6H_5CH_2COCH_2C_6H_5 > CH_3COCH_3}$
$\mathrm{C_6H_5CH_2SO_2CH_2C_6H_5 \gg CH_3SO_2CH_3}$ (stable)
$\mathrm{C_6H_5COCH(C_6H_5)_2 > C_6H_5COCH_2C_6H_5 > C_6H_5COCH_3}$
$\mathrm{C_6H_5CH_2OH > (C_6H_5)_2CHOH > CH_3OH}$
$\mathrm{CH_3NO_2 \gg C_6H_5CH_2NO_2}$ (stable)

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[5] W. E. Doering and R. M. Haines, *J. Am. Chem. Soc.*, **76**, 482 (1954).

[6] These series were oxidized in the presence of deficient base. The oxidations are more rapid in deficient base than in the presence of excess potassium *t*-butoxide (see ref. 3c).

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THE FORMATION OF RADICAL-ANIONS BY ELECTRON TRANSFER BETWEEN ANIONS AND THEIR UNSATURATED ANALOGS IN DIMETHYL SULFOXIDE SOLUTION[1,2]

Sir:

We have shown in a previous publication[3] that electron transfer between carbanions and organic electron acceptors (π), such as the nitroaromatics, often occurs readily.

$$\mathrm{R}:^- + \pi \longrightarrow \pi\cdot^- + \mathrm{R}\cdot \longrightarrow \text{products}$$

Experimentally this irreversible process is not as conveniently studied as the reversible electron transfer reaction between a dianion and its unsaturated analog.

$$\pi^{=} + \pi \rightleftarrows 2\pi\cdot^- \text{ or } \pi\mathrm{H}^- + \pi \rightleftarrows 2\pi\cdot^- + \mathrm{H}^+$$

It is known that in basic solution electron transfer occurs between hydroquinones and quinones[4] and between benzoin and benzil.[5] Dianions prepared from alkali metals and an olefin will in certain cases react with more of the olefin to produce radical-ions. Such reactions have been observed for stilbene,[6a] tetraphenylethylene[6b] and cyclooctatetraene.[6c] Calculations indicate that in the alkali metal adducts of aromatic hydrocarbons[7] the radical-anion is favored over a mixture of dianion and unreacted hydrocarbon.[7] It is also recognized that dianions, obtained by the addition

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[1] Reactions of Resonance Stabilized Anions. V.

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[3] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4143 (1962).

[4] T. H. James and A. Weissberger, *ibid.*, **60**, 98 (1938); L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granick, *ibid.*, **60**, 1678 (1938); J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49**, 1433 (1953); H. Diebler, M. Eigen and P. Matthies, *Z. Naturforsch.*, **16B**, 629 (1961).

[5] A. Weissberger, H. Mainz and E. Strasser, *Ber.*, **62**, 1942 (1929); A. Weissberger, *ibid.*, **65**, 1815 (1932); L. Michaelis and E. S. Fletcher, *J. Am. Chem. Soc.*, **59**, 1246 (1936); J. L. Ihrig and R. G. Caldwell, *ibid.*, **78**, 2097 (1956).

[6] (a) D. E. Paul, D. Lipkin and S. I. Weissman, *ibid.*, **78**, 116 (1956); (b) J. F. Garst and R. S. Cole, Abstracts of Papers, 142nd Meeting of the Am. Chem. Soc., Atlantic City, 1962, p. 5-Q; (c) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960).

[7] N. S. Hush and J. Blackledge, *ibid.*, **23**, 514 (1955); C. J. Hoijtink, E. DeBoer, P. H. van der Heij and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).