

yield caused by other variations in experimental conditions must also, partly at least, involve the competition of (3) versus (4) and (5). Isotope effects indicate that, as would be expected, the (5), (6) sequence "is a more important path at low benzoyl peroxide concentration than at high. . ."<sup>4</sup> The presence of benzene as a competing substrate adds a  $\text{ArAr}'\text{H}\cdot$  species to undergo cross-combination (4) and cross-disproportionation (5) with the original *o*-, *m*-, and *p*- $\text{ArAr}'\text{H}\cdot$ ; yet, as illustrated in Table I, isomer distribution is unchanged, showing that in their interactions the various arylcyclohexadienyl radicals are converted randomly into biaryls or side-products. The same randomness is indicated by the constancy of relative reactivity, which requires that oxygen (to pick one experimental variable) increase the yield of biphenyl by exactly the same factor as the yield of substituted biphenyl, and yet by a factor that is different for each substrate mixture.

There is no inconsistency between the isotope effects<sup>4</sup> and the present findings. Whereas the ease of abstraction of hydrogen should certainly be affected by its atomic weight, consideration shows<sup>16</sup> that it is not at all unreasonable that ease of abstraction from the reactive species  $\text{ArAr}'\text{H}\cdot$  should be little affected by the nature or position of a substituent, or by steric factors. In any case, however it is explained, the evidence shows clearly that side-reactions have no significant effect on isomer distribution and relative reactivities measured by product analysis, and that such data provide valid rate factors for free radical aromatic substitution.

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RECEIVED AUGUST 16, 1962

#### SPONTANEOUS FORMATION OF RADICAL-ANIONS FROM NITROAROMATICS IN BASIC SOLUTION<sup>1,2</sup>

Sir:

*p*- and *o*-nitrotoluene spontaneously form radical-anions in the presence of potassium *t*-butoxide in *t*-butyl alcohol or dimethyl sulfoxide. A 0.0025 *M* solution of *p*-nitrotoluene in the presence of 0.06 *M* potassium *t*-butoxide in *t*-butyl alcohol under nitrogen gave a product containing about 0.0016 *M* unpaired spins (by comparison of e.s.r. absorption with that of diphenylpicrylhydrazyl) after 1 hr. at 30°. The e.s.r. spectrum obtained in dimethyl sulfoxide-*t*-butyl alcohol (4:1) containing excess potassium *t*-butoxide reproduces in all detail the seventy line spectrum reported for the *p*-nitrotoluene radical-anion in acetonitrile.<sup>3</sup> In *t*-butyl alcohol a forty line spectrum is observed (Fig. 1) which is consistent with a radical-anion with  $a_{\text{N}} = 12.7$ ,  $a_{\alpha\text{-H}} \sim a_{\text{o-H}} = 3.4 \pm 0.1$ ,  $a_{\text{m-H}} = 1.1 \pm 0.1$  gauss.<sup>4</sup>

(1) Reactions of Resonance Stabilized Anions. III.

(2) Grateful acknowledgment is made of support of this work by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

(3) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

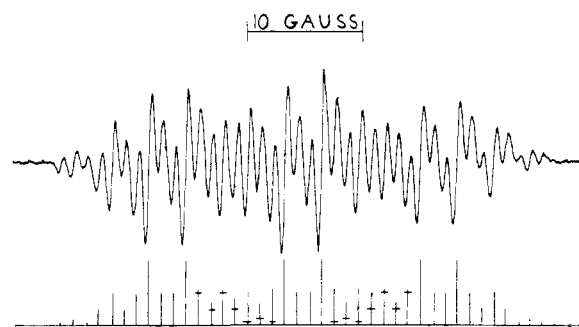


Fig. 1.—Radical-anion formed from reaction of potassium *t*-butoxide with *p*-nitrotoluene in *t*-butyl alcohol solution. Spectrum obtained with a Varian V-5400 EPR spectrometer using 100 kc. field modulation. Synthetic spectrum composed from hyperfine splitting constants given in text.

In *t*-butyl alcohol appreciable amounts of radicals are formed by the interaction of potassium *t*-butoxide with *p*-nitroethylbenzene, *o*-nitroethylbenzene, *o*-bromo-*p*-nitrotoluene, *p*-nitro-*o*-xylene, *o*-amino-*p*-nitrotoluene, *p*-nitrobenzyl alcohol, *p*-nitrobenzaldehyde, 2-nitrofluorene, *p*-nitroacenaphthalene and *m*-dinitrobenzene. Under these conditions all of the above compounds, as well as *o*- and *p*-nitrotoluene, react readily with oxygen to form a variety of products.<sup>5</sup> In the presence of excess *t*-butoxide ion no radicals, or only traces of radicals, were detected from *m*-nitrotoluene, nitrobenzene, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, tris-(*p*-nitrophenyl)-methane, *p*-nitrocumene, 2,2',4,4'-tetranitrodiphenylmethane, phenylnitromethane,  $\alpha$ -nitroacetophenone, 2-nitropropane, 2-nitro-1,3-indandione and *p*-nitrophenylacetonitrile. For these compounds little, if any, reaction with oxygen was observed and it seems safe to conclude that generally, aromatic nitro compounds which oxidize readily in basic solution spontaneously form free radicals in the absence of oxygen.

2,4-Dinitrotoluene spontaneously forms only a low concentration of radical-ions in the presence of excess base but forms significant amounts of radical-anions in deficient base. This result suggests that radical-anion formation often involves electron transfer between the ionized and unionized nitrocompound.<sup>6</sup>

If solutions of *p*-nitrotoluene (0.1 *M*) in *t*-butyl alcohol are acidified with excess water and then treated with oxygen, nearly all the starting material can be accounted for in recovered *p*-nitrotoluene and *p,p'*-dinitrobenzyl, provided the reaction time is short. After periods longer than those in Table I, the products become complex with the formation of polymeric substances containing azo or azoxy linkages.<sup>7</sup>

(4) These constants differ from those reported in acetonitrile solution.<sup>3</sup> Solvent effects on hyperfine splitting constants have been observed previously (E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962)); L. H. Piette, P. Ludwig and R. N. Adams, *ibid.*, **33**, 3904 (1961); Y. Deguchi, *Bull. Chem. Soc. Japan*, **35**, 260 (1962).

(5) Anthony J. Moye, Ph.D. Thesis, Iowa State University, 1961.

(6) In this connection it is pertinent to point out that the nitroalkanes (G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954)) as well as tris-(*p*-nitrophenyl)-methane react more readily with oxygen in the presence of deficient potassium *t*-butoxide in *t*-butyl alcohol than in the presence of excess base.

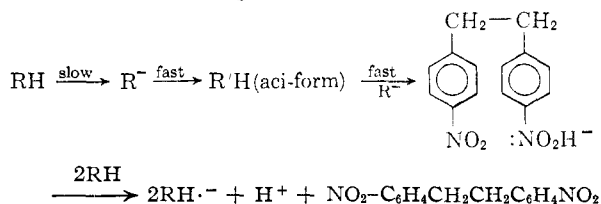
(7) For example, see A. G. Green, *J. Chem. Soc.*, **85**, 1424 (1904).

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

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

<sup>a</sup> Moles per liter. <sup>b</sup> 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.<sup>8</sup> 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'*-dinitrobenzyl is formed in reasonable yields in the presence of oxygen,<sup>5</sup> whereas the *p*-nitrobenzyl radical should react readily with oxygen,<sup>9</sup> we favor mechanisms wherein dimerization of the *p*-nitrobenzyl fragments precede radical formation, e.g.



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.<sup>10</sup> We will

(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).

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<sup>11</sup> should logically be formulated as a process involving free radicals as intermediates.

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

(12) Alfred P. Sloan Foundation Fellow.

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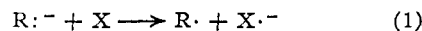
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#### EFFECT OF STRUCTURE ON THE RATE OF REACTION OF CARBANIONS WITH MOLECULAR OXYGEN<sup>1,2</sup>

Sir:

We have presented evidence indicating that reactions of molecular oxygen with carbanions often involve intermediate free radicals.<sup>3</sup> 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



wherein X may be O<sub>2</sub>, ROO<sup>·</sup>, RO<sup>·</sup>, OH<sup>·</sup>, or in certain cases a substance not containing unpaired electrons.<sup>3c</sup> 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.<sup>4</sup> 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<sup>·-</sup>. We have observed this decreased ease of oxidation in each instance wherein

(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. Schon, *ibid.*, **19**, 657 (1951); C. H. Leigh, A. H. Schon and M. Szwarc, *Proc. Roy. Soc. (London)*, **209A**, 197 (1951); G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).