Oxidation of Carbanions. II. Oxidation of *p*-Nitrotoluene and Derivatives in Basic Solution[1,2]

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The reactions of *p*-nitrotoluene and a number of ring and/or α-substituted derivatives of *p*-nitrotoluene with molecular oxygen in *t*-butyl alcohol containing potassium *t*-butoxide have been studied on the basis of reaction products, rates, stoichiometry, and concentrations of reagents. It is concluded that the oxidation of *p*-nitrotoluene itself represents a secondary process resulting from the spontaneous electron-transfer reactions that occur in basic solutions in the absence of oxygen. Substituents that decrease the rate of ionization of *p*-nitrotoluene also decrease the rate of oxidation in basic solution. Substituents which increase the acidity of *p*-nitrotoluene do not universally increase the rate of oxidation in basic solution. Substituents such as α-cyano or 2,6-dinitro stabilize the *p*-nitrobenzyl anion to such an extent that oxidation occurs slowly if at all. Similar results were obtained for a series of nitro-substituted di- and triphenylmethanes.

An examination of *o*- and *p*-nitrotoluene and many derivatives of *p*-nitrotoluene in the presence of strong base but absence of oxygen has demonstrated the spontaneous formation of radical anions derived by reduction of the parent nitrotoluene by ionization products of the nitrotoluene.[3] It was concluded that in the absence of oxygen the rate of formation of *p*-nitrotoluene radical anion is limited by the rate of ionization of *p*-nitrotoluene in *t*-butyl alcohol containing potassium *t*-butoxide,[3a] but is a function of both *p*-nitrotoluene and *p*-nitrobenzyl anion concentrations in 1:1 mixtures of dimethyl sulfoxide and *t*-butyl alcohol containing potassium *t*-butoxide.[3b]

The rapid reaction of *o*- and *p*-nitrotoluenes with molecular oxygen in basic solution is intimately connected with this spontaneous oxidation–reduction reaction which in the absence of oxygen produces *p,p'*-dinitrobibenzyl from *p*-nitrotoluene,[3] and anthranilic acid (among other products) from *o*-nitrotoluene.[4] The spontaneous electron-transfer reaction appears to control the products of oxidation of *p*-nitrotoluene (*i.e.*, *p,p'*-dinitrobibenzyl)[5] but for other derivatives, particularly those with substituents at the α-carbon atom, the spontaneous reaction appears to afford simply a source of radical intermediates which yield oxygenation products of the starting nitrotoluene derivative.[6]

Results

Oxidation of *p*-Nitrotoluene.—The reaction of *p*-nitrotoluene with molecular oxygen in basic solutions yields *p,p'*-dinitrobibenzyl, *p,p'*-dinitrostilbene (an oxidation product of the bibenzyl), and *p*-nitrobenzoic acid. The ratio of products formed depends upon the concentration of oxygen in solution, the concentration of *p*-nitrotoluene, and the concentration of base. Since under "normal" stirring conditions the reaction solutions are not saturated with oxygen with respect to its partial pressure in the vapor phase, the ratio of products can also be dependent upon the degree of agitation. Thus, the oxidation of *p*-nitrotoluene is one of variable stoichiometry, even when the concentration of oxygen in solution is maintained at a constant value.

Figure 1 shows typical oxidation curves observed for *p*- and *o*-nitrotoluene. The oxygen absorptions were measured under conditions wherein the rate was partially controlled by the rate of solution of oxygen. With the most vigorous agitation we have employed the rate curve for *p*-nitrotoluene closely approximates the one given in Figure 1 for *o*-nitrotoluene.

Table I summarizes the final yields of dimeric products formed in the oxidation of various initial concentrations of *p*-nitrotoluene. The yield of dimer increases with an increase in the initial concentration of *p*-nitrotoluene at constant concentrations of base. From the first five entries in Table I it can be calculated that for instantaneous *p*-nitrotoluene concentrations of 0.16 *M* in the presence of 0.35 *M* potassium *t*-butoxide, the dimeric product is the only oxidation product. Between 0.12 *M* and 0.16 *M* *p*-nitrotoluene 11 times as much *p*-nitrotoluene is converted to dimer as to acid; between 0.08 and 0.12 *M* *p*-nitrotoluene 3.2 times as much *p*-nitrotoluene is converted to dimer as to acid; between 0.04 and 0.08 *M* *p*-nitrotoluene the conversion to dimer exceeds conversion to acid by 70% while between 0.0 and 0.04 *M* *p*-nitrotoluene concentrations 40% more *p*-nitrotoluene is converted to acid than to dimer.

Figure 2 and Table II demonstrate that *p*-nitrobenzoic acid is not formed by oxidation of the initially formed *p,p'*-dinitrobibenzyl. Figure 3 demonstrates that, in the oxidation of 0.17 *M* *p*-nitrotoluene, *p*-nitrobenzoic acid is not formed during the initial stage of the reaction but becomes an important reaction product only when the concentration of *p*-nitrotoluene has

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(1) For part I, see G. A. Russell and A. G. Bemis, *J. Am. Chem. Soc.*, **88**, 5491 (1966). This paper is part XXVII in the series, Reaction of Resonance-Stabilized Anions. For part XXVI, see G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, in press.

(2) This research was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) (a) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962); (b) G. A. Russell and E. G. Janzen, *ibid.*, in press.

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

(5) H. O. House, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 367.

(6) H. Klinger [*Ber.*, **15**, 866 (1882); **16**, 421 (1883)] reported an acidic fraction in the products resulting from the basic treatment of *p*-nitrotoluene. The oxidative coupling reaction of *p*-nitrotoluene-*o*-sulfonic acid was noted by F. Bender and G. Schultz [*ibid.*, **19**, 3234 (1886)] and applied to *p*-nitrotoluene by O. Fischer and E. Hepp [*ibid.*, **26**, 2231 (1893)] and A. G. Green [*J. Chem. Soc.*, 85, 1424 (1904)]. Dimerization of *o*-nitrotoluene in basic solution by oxygen has been reported by A. Lapworth [*ibid.*, **79**, 1265 (1901)], F. W. Bergstrom, I. M. Granara, and V. Erickson [*J. Org. Chem.*, **7**, 98 (1942)], R. Huisgen [*Ann.*, **559**, 141 (1948)], and H. A. Stansbury and W. R. Proops [*J. Org. Chem.*, **26**, 4162 (1961)]. In addition to molecular oxygen the coupling can be effected by hypochlorite [C. Ris and C. Simon, *Ber.*, **30**, 2618 (1897)] or iodine [A. H. Green and J. Baddiley, *J. Chem. Soc.*, **93**, 1721 (1908)]. The oxidative coupling has been reported to occur for *o*-nitroethylbenzene [R. Oda and T. Tsuruta, *Repts. Inst. Chem. Res. Kyoto Univ.*, **16**, 6 (1948)] and *p*-nitropropylbenzene [Huang-Minlon, *J. Am. Chem. Soc.*, **70**, 2802 (1948)].

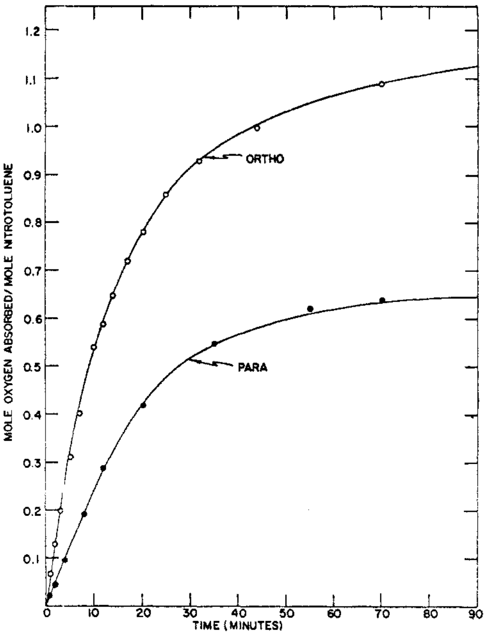

Figure 1.—Oxygen absorption of *o*- and *p*-nitrotoluene in *t*-butyl alcohol containing 0.352 *M* potassium *t*-butoxide at 26°; 25 ml of solution was vigorously stirred with a magnetic stirring bar in a 50-ml erlenmeyer flask to develop a well-defined vortex in the presence of oxygen at 700 mm: ○, 0.13 *M* *o*-nitrotoluene; ●, 0.19 *M* *p*-nitrotoluene.

TABLE I

YIELD OF DIMER IN OXIDATION OF *p*-NITROTOLUENE

[*p*-Nitrotoluene]$_0$, mole/l.	Base/ [*p*-nitrotoluene]$_0$	Oxygen absorbed^a	Dimer^a
0.22	1.6	0.71^b	0.39
0.17	2.1	0.96^b	0.32
0.13	2.7	1.10^b	0.31
0.080	4.4	1.26^b	0.26
0.047	7.5	1.48^b	0.22
0.25	2.5		0.29^c
0.20	3.2		0.28^c
0.15	4.2		0.23^c
0.10	6.4		0.11^c
0.05	13		low^c

[a] Moles/mole of *p*-nitrotoluene. [b] Oxidations performed in 25 ml of 0.352 *M* potassium *t*-butoxide in *t*-butyl alcohol solution for a period of 180 min at 26°. A magnetic stirring bar developed a well-defined vortex in a 50-ml erlenmeyer flask containing an atmosphere of oxygen at 750 mm. [c] Oxidation performed in 15 ml of 0.62 *M* potassium *t*-butoxide in *t*-butyl alcohol. The solution was vigorously shaken (300 cpm) in a 50-ml erlenmeyer flask mounted on a motor-driven rack in a 25° thermostat in the presence of oxygen at 700 mm.

been reduced by the dimerization reaction. Also the extrapolation to zero time of the dimer curve clearly indicates that the formation of *p,p'*-dinitrobibenzyl requires the absorption of 1 mole of oxygen per mole of the bibenzyl. Additional evidence for the

$$2(p\text{-}NO_2C_6H_4CH_2^-) + O_2 \longrightarrow p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p + O_2^{-2} \quad (1)$$

formation of the peroxide dianion is furnished by the observation that addition of catalytic amounts of lead acetate to an oxidation decreased the oxygen absorption without otherwise affecting the reaction products.

$$2K_2O_2 + 2(CH_3)_3COH \xrightarrow{Pb^{II}} 2KOH + 2KOC(CH_3)_3 + O_2 \quad (2)$$

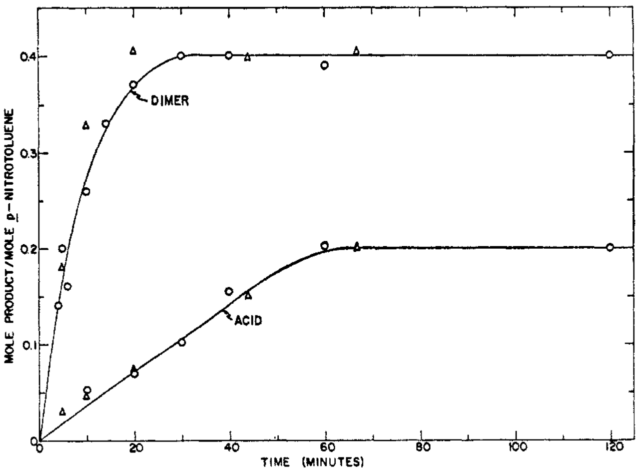

Figure 2.—Products of oxidation of *p*-nitrotoluene as a function of time (see Figure 1 for reaction conditions): ○, 0.16 *M* *p*-nitrotoluene, 0.23 *M* potassium *t*-butoxide; △, 0.16 *M* *p*-nitrotoluene, 0.48 *M* potassium *t*-butoxide.

TABLE II

PRODUCTS OF OXIDATION OF *p*-NITROTOLUENE^a

[KOCMe$_3$] mole/l.	Time, min	Oxygen absorbed^b	Products^b Dimer^c	Acidic^d
0.12	6	0.09	0.03	
0.12	12	0.15	0.05	
0.12	18	0.22	0.09	
0.12	30	0.28	0.10	0.10
0.12	60	0.33	0.12	0.18
0.12	120	0.48	0.13	0.27
0.12	180	0.58	0.14	0.34
0.12	300	0.55	0.15	0.38
0.12	330	0.60	0.14	
0.35	4	0.11	0.16	
0.35	6	0.16	0.32	0.05
0.35	10	0.29		
0.35	14	0.37	0.33	0.10
0.35	30	0.50	0.40	0.17
0.35	40	0.65	0.40	
0.35	60	0.71	0.39	0.21
0.35	120	0.75	0.40	0.20
0.35	240	0.73	0.39	0.22
0.51	5	0.17	0.18	0.03
0.51	10	0.34	0.33	0.05
0.51	20	0.56	0.40	0.08
0.51	44	0.71	0.40	0.15
0.51	67	0.83	0.41	0.20
0.93	330	1.75	0.41	0.19

[a] 0.17 *M* *p*-nitrotoluene in *t*-butyl alcohol at 26°. Oxidations performed in 25 ml of solvent in a 50-ml erlenmeyer flask under oxygen at 750 mm. A magnetic stirring bar developed a well-defined vortex. [b] Moles/mole of *p*-nitrotoluene. [c] *p,p'*-Dinitrobibenzyl except at times >60 min and base >0.35 *M* whence a mixture of *p,p'*-dinitrobibenzyl and *p,p'*-dinitrostilbene were formed. [d] *p*-Nitrobenzoic acid.

Table III lists observed and calculated oxygen stoichiometry on the basis of reactions 1, 2, and 3. The discrepancies in Table III are more apparent at the high base concentrations wherein an appreciable conversion of the bibenzyl to the stilbene occurred.

$$p\text{-}NO_2C_6H_4CH_2^- + {}^3/_2O_2 \longrightarrow p\text{-}NO_2C_6H_4CO_2^- + H_2O \quad (3)$$

The ratio of dimer to acid decreased with an increase in oxygen pressure. Table IV presents some pertinent results.

TABLE III

OXYGEN BALANCE IN THE OXIDATION OF p-NITROTOLUENE[a]

[KOCMe$_3$], mole/l.	Time, min	Products[b] Dimer[c]	Products[b] Acid[d]	Oxygen absorbed[b] Found	Oxygen absorbed[b] Calcd[e]
0.14	120	0.13	0.27	0.48	0.54
0.14	240	0.15	0.35	0.57	0.66
0.33	30	0.40	0.10	0.50	0.55
0.33	60[f]	0.39	0.21	0.71	0.71
0.45	180[f]	0.37	0.26	0.85	0.76
0.45	180[f,g]	0.36	0.27	0.66	0.59
0.52	44	0.40	0.15	0.71	0.63
0.52	67	0.41	0.20	0.83	0.71
0.77	330[f]	0.41[h]	0.19	1.75	

[a] 0.18 *M* p-nitrotoluene in *t*-butyl alcohol at 26°. Oxidations performed in 25 ml of solvent in a 50-ml erlenmeyer flask under oxygen at 750 mm. A magnetic stirring bar developed a well-defined vortex. [b] Moles/mole of *p*-nitrotoluene. [c] *p,p'*-Dinitrobibenzyl. [d] *p*-Nitrobenzoic acid. [e] On the basis of eq 1–3. [f] Oxidation complete. [g] Containing 0.002 *M* lead subacetate. [h] Mainly *p,p'*-dinitrostilbene.

TABLE IV

EFFECT OF OXYGEN PRESSURE ON PRODUCTS OF OXIDATION OF p-NITROTOLUENE[a]

Stirring concn[b]	Oxygen pressure, min	[*p*-Nitro-toluene]$_0$, mole/l.	[KOC-(CH$_3$)$_3$]/[*p*-nitro-toluene]$_0$	Time, min	Dimer,[c] %	Dimer[d]/acid
1	150	0.28	3.1	360	88.3	3.8
1	150	0.18	3.2·	120	87.6	3.5
2	150	0.17	1.7	120	77.2	1.68
3	150	0.17	3.8	120	60.3	0.76
3	700	0.24	2.2	120	51.4	0.53
3	700	0.24	2.2	120	47.9	0.46
4	755	0.15	2.6	360	43.8	0.39
4	755	0.15	14.3[e]	1100	23.0	0.15
5	860	0.18	3.0	120	37.8	0.30
3	860	0.18	50[f]	660	28.2	0.20
3	860	0.18	3.0	120	33.2	0.24
3	2050	0.096	6.0	120	17.6	0.11
3	2050	0.25	1.7	120	22.1	0.14
3	2050	0.18	3.0	5	25.1	
4	2050	0.18	3.8	150	25.6	0.17
5	2050	0.17	4.0	150	29.8	0.21
3	3040	0.19	3.1	180	21.8	0.14
4	3040	0.36	1.6	120	21.7	0.14
5	3040	0.36	1.6	180	21.2	0.13
5	3040	0.19	3.1	60	21.6	0.14
5	3040	0.10	6.0	60	21.2	0.13

[a] In *t*-butyl alcohol at 27°. [b] Condition 1, slow stirring by magnetic stirring bar, 25 ml of solution in 50-ml erlenmeyer flask, no vortex; condition 2, same as condition 1 except fast stirring, vortex visible; condition 3, 50 ml of solution in 250-ml Parr hydrogenation apparatus, driven at 220 cpm; condition 4, 15 ml of solution in a flask mounted on a motor-driven reciprocating rack, 300 cpm; condition 5, same as condition 3 except driven at 160 cpm. [c] By weight. [d] Mole ratio of *p,p'*-dinitrobibenzyl to *p*-nitrobenzoic acid. [e] Methanolic potassium hydroxide. [f] Methanol containing 30% by weight of potassium hydroxide.

The first four experiments of Table IV emphasize the sensitivity of the reaction products to oxygen pressure and hence to the stirring conditions. The experiments at 2050 and 3040 mm of oxygen pressure were performed under vigorous agitation and showed little effect on products of an increase in the shaking rate. The ultimate yield of *p,p'*-dinitrobibenzyl in oxygen saturated solutions initially 0.17 *M* in *p*-nitrotoluene thus decreases from about 60% at 150 mm of saturation pressure to 33% at 860 mm and 22% at 3040 mm.

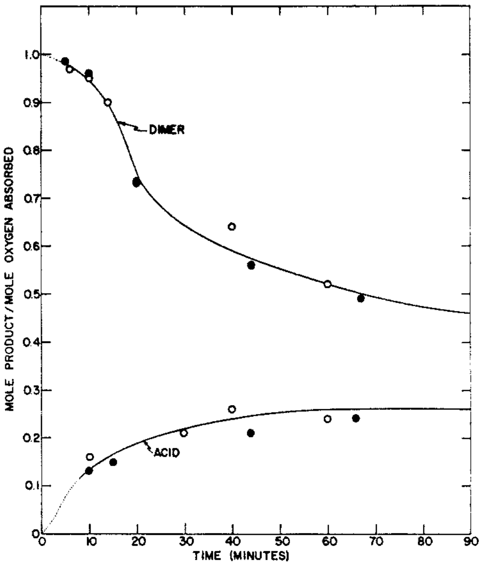

Figure 3.—Products of oxidation of *p*-nitrotoluene as a function of time and oxygen absorbed at 26° (see Figure 1 for reaction conditions): ○, 0.16 *M* *p*-nitrotoluene, 0.34 *M* potassium *t*-butoxide; ●, 0.16 *M* *p*-nitrotoluene, 0.48 *M* potassium *t*-butoxide.

The effects of solvents in the oxidation of *p*-nitrotoluene in basic solution correspond to those expected for a reaction controlled mainly by the rate of ionization of the *p*-nitrotoluene or by the concentration of the *p*-nitrobenzyl anions. The rate was much faster in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing potassium *t*-butoxide than in pyridine (80%)-*t*-butyl alcohol (20%). Both of the mixed solvents gave a considerably faster rate than pure *t*-butyl alcohol. As illustrated in Table V the yields of dimeric products varied with the solvent. In pyridine or dimethyl sulfoxide solution the dimeric product was usually a mixture of the bibenzyl and stilbene except in those cases where the stilbene was the only dimer produced. Moreover, in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) the stilbene is oxidized to *p*-nitrobenzoic acid in the presence of excess base. This behavior possibly also occurred in pyridine solution containing 0.60 *M* lithium *t*-butoxide. The oxidation

TABLE V

OXIDATION PRODUCTS OF p-NITROTOLUENE[a]

Solvent, % by vol. *t*-BuOH	Solvent, % by vol. Py	Solvent, % by vol. DMSO	[*p*-Nitro-toluene]$_0$, mole/l.	[KOCMe$_3$], mole/l.	Products, % Di-meric[b]	Products, % Acidic[c]
100			0.18	0.35	78	22
20	80		0.15	0.20	87	10
20	80		0.16	0.20	87	10
	100		0.15	0.66[d]	56	30
100			0.10	0.20	48	
80		20	0.10	0.20	70	
50		50	0.10	0.20	104[e]	Trace
20		80	0.10	0.20	74	19
20		80	0.096	0.15	71	32
		100	0.10	0.20	32	
20		80	0.075[f]	0.15	83	15
20		80	0.036[f]	0.15		100

[a] At 27° in a wrist-action stirrer, 1 atm of oxygen. [b] Mixture of *p,p'*-dinitrobibenzyl and *p,p'*-dinitrostilbene. [c] *p*-Nitrobenzoic acid. [d] Lithium *t*-butoxide. [e] *trans-p,p'*-Dinitrostilbene, mp 303–305°. [f] *p,p'*-Dinitrobibenzyl.

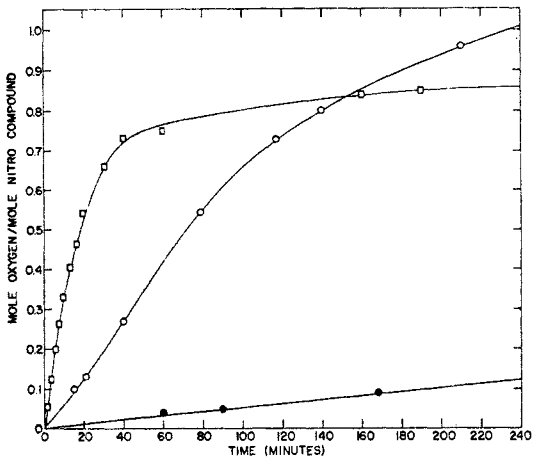

Figure 4.—Rate of oxygen absorption of 0.18 M p-nitrotoluene, □, p-nitroethylbenzene, ○, and p-nitrocumene, ●, in t-butyl alcohol at 27° containing 0.289 M potassium t-butoxide. See Figure 1 for reaction conditions.

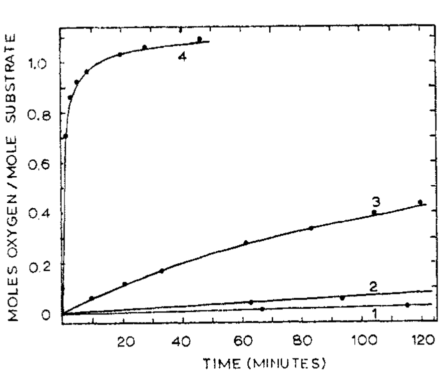

Figure 5.—Oxidation of p-nitrocumene at 27°: (1) 0.19 M p-nitrocumene, 0.43 M lithium t-butoxide in pyridine; (2) 0.16 M p-nitrocumene, 0.46 M potassium t-butoxide in t-butyl alcohol; (3) 0.19 M p-nitrocumene, 0.28 M Triton B in pyridine; (4) 0.11 M p-nitrocumene, 0.25 M lithium t-butoxide in dimethyl sulfoxide. Reaction mixtures were vigorously agitated in a wrist-action shaker (see footnote d, Table VI) in the presence of oxygen at 750 mm.

of the stilbene to the benzoic acid probably involves an addition mechanism of the following type.

$$\begin{aligned}&p\text{-}NO_2C_6H_4CH{=}CHC_6H_4NO_2\text{-}p + B^- \longrightarrow\\&\quad [p\text{-}NO_2C_6H_4CHBCHC_6H_4NO_2]^- \longrightarrow\\&\qquad p\text{-}NO_2C_6H_4CHBCOC_6H_4NO_2\text{-}p \longrightarrow\\&\qquad\quad p\text{-}NO_2C_6H_4C(OO^-)BCOC_6H_4NO_2\text{-}p \longrightarrow\\&\qquad\qquad\qquad p\text{-}NO_2C_6H_4COB + p\text{-}NO_2CC_6H_4CO_2^-\end{aligned}$$

Catalysis in the Oxidation of p-Nitrotoluene.—Figure 4 summarizes the rate of oxidation of p-nitrotoluene in t-butyl alcohol (80%)-methanol (20%) containing the potassium alkoxides. In this solvent the oxidation is very slow presumably because of the low rate of ionization of p-nitrotoluene and the rapid reprotonation of the p-nitrobenzyl anion by methanol. The presence of a better electron acceptor than p-nitrotoluene itself, such as m-dinitrobenzene, leads to a considerable acceleration in the rate of oxidation. The product is still a mixture of the bibenzyl and acid. The catalyst can be regenerated by reaction with molecular oxygen.[7]

$$ArNO_2\cdot^- + O_2 \longrightarrow ArNO_2 + O_2\cdot^-$$

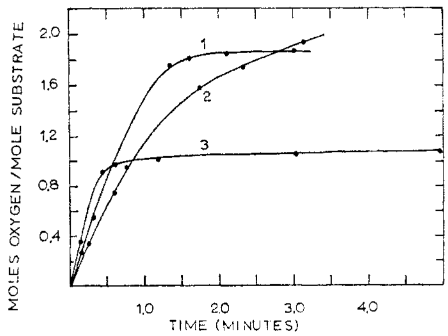

Figure 6.—Oxidation of 0.10 M p-nitrotoluene (1), p-nitroethylbenzene (2), and p-nitrocumene (3) in the presence of 0.2 M potassium t-butoxide at 27° in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) solution. See Figure 5 for reaction conditions.

Oxidation of p-Nitroethylbenzene and p-Nitrocumene.—In t-butyl alcohol containing potassium t-butoxide, p-nitrocumene is stable to oxygen although 2,4-dinitrocumene is oxidized readily to give 2,4-dinitrophenol among other products. p-Nitroethylbenzene is oxidized less readily than p-nitrotoluene to give excellent yields of p-nitrobenzoic acid. Since p-nitroacetophenone is readily oxidized under the reaction conditions, the reaction apparently involves

$$[p\text{-}NO_2C_6H_4CHCH_3]^- \xrightarrow{O_2} [p\text{-}NO_2C_6H_4CH(OOH)CH_3] \xrightarrow{-H_2O} p\text{-}NO_2C_6H_4COCH_3$$

No dimer could be detected in this oxidation; it was shown that authentic $meso$-p,p'-dinitro-α,α'-dimethylbibenzyl was stable to the reaction conditions. The rate sequence (see Figure 4) of nitrotoluene > p-nitroethylbenzene ≫ p-nitrocumene, apparently reflects the ease of ionization of the substrates involved.

p-Nitrocumene is oxidized to p-nitro-α,α'-dimethylbenzyl alcohol in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide. Figure 5 illustrates the ease of oxidation of p-nitrocumene in a number of solvents.

In Figure 6 the rates of oxidation of p-nitrotoluene, p-nitroethylbenzene, and p-nitrocumene are illustrated for dimethyl sulfoxide (80%)-t-butyl alcohol (20%) solutions. The initial rates are rather similar but are in the order p-nitrocumene > p-nitrotoluene > p-nitroethylbenzene. It appears that in this solvent ionization is rapid and extensive for all substrates and the rates of oxidation reflect other factors.

Formation of Paramagnetic Products in the Oxidation of p-Nitrotoluene and Derivatives.—In t-butyl alcohol or dimethyl sulfoxide (80%)-t-butyl alcohol (20%) the spontaneous formation of p-nitrotoluene radical anion is observed in the presence of base but absence of oxygen. In pure dimethyl sulfoxide containing an excess of potassium t-butoxide the initial reaction in the absence of oxygen appears to give a mixture of radical anions without a characteristic hyperfine pattern. However, in 100% dimethyl sulfoxide when exposed to traces of oxygen a high concentration of radical anion can be obtained. The same radical anion is obtained by oxidizing p-nitrophenylacetate anion and spontaneously (but very slowly) from p-nitrobenzoic acid itself. We thus believe the radical anion to be the p-nitrobenzoate radical dianion.

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(7) G. A. Russell and A. G. Bemis, *Inorg. Chem.*, in press.

The esr spectrum changes with base concentration; so we are apparently dealing with an equilibrium between dianion and monoanion. The spectra ob-

$$p\text{-}NO_2C_6H_4CO_2\cdot^{2-} \rightleftarrows p\text{-}NO_2C_6H_4CO_2H\cdot^{-}$$

served at high and low base concentrations are given in Figure 7.

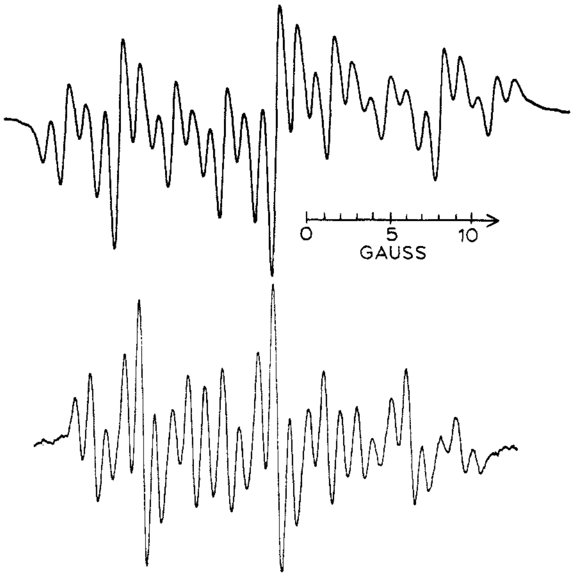

Figure 7.—*p*-Nitrobenzoate radical anions in dimethyl sulfoxide solution: top, spectrum observed at potassium *t*-butoxide concentrations of 0.3–0.5 *M*; bottom, spectrum observed at a potassium *t*-butoxide concentration of 0.05 *M*. The top spectrum (27 lines) is consistent with $a^{N} = 9.85$, $a_{meta}^{H} = 3.31$, $a_{ortho}^{H} = 1.07$ gauss. The bottom spectrum (25 lines) is consistent with $a^{N} = 8.37$, $a_{ortho}^{H} = 3.14$, and $a_{meta}^{H} = 0.96$ gauss. Both spectra show considerable line broadening.

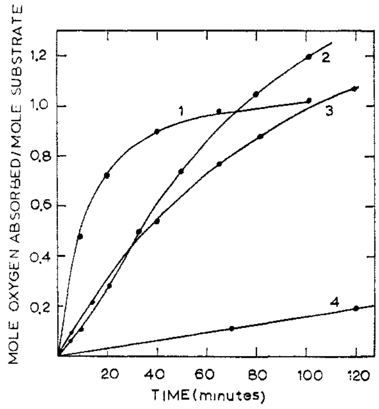

Figure 8.—Oxidation of *p*-nitrotoluene and derivatives at 26° and 700 mm of oxygen pressure, in *t*-butyl alcohol solution: (1) 0.16 *M* *p*-nitrotoluene, 0.35 *M* potassium *t*-butoxide, rapid agitation of 50 ml of solution (220 cpm) in a 250-ml Parr hydrogenation apparatus; (2) 0.11 *M* 2,4-dinitrotoluene, 0.39 *M* potassium *t*-butoxide, stirring condition of Figure 1; (3) 0.09 *M* 2,4-dinitrocumene, 0.39 *M* potassium *t*-butoxide, stirring conditions of Figure 1; (4) 0.11 *M* 2,4,6-trinitrotoluene, 0.39 *M* potassium *t*-butoxide, stirring conditions of Figure 1.

TABLE VI

RATES OF OXIDATION OF 2,4-DINITROTOLUENE AND 2,4,6-TRINITROTOLUENE[a]

Substrate, mole/l.	Solvent (%)	[KOC-(CH$_3$)$_3$], mole/l.	Maximum rate,[b] mole of oxygen/mole of substrate/min
2,4-Dinitrotoluene, (0.03)	*t*-BuOH	0.27	0.039
2,4-Dinitrotoluene, 0.10	*t*-BuOH	0.30	0.031
2,4-Dinitrotoluene, 0.02	*t*-BuOH	0.025	0.011
2,4-Dinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.50	0.70
2,4-Dinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.20	0.45
2,4-Dinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.10	0.22
2,4-Dinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.050	0.075
m-Dinitrobenzene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.050	0.005
2,4,6-Trinitrotoluene, 0.10	*t*-BuOH	0.39	0.002
2,4,6-Trinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.20	0.032
2,4,6-Trinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.10	0.027
2,4,6-Trinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.075	0.075
2,4,6-Trinitrotoluene,[c] 0.10	DMSO (80)–*t*-BuOH (20)	0.050	0.045
sym-Trinitrobenzene, 0.15	*t*-BuOH	0.39	0.004[e]

[a] 700 mm of oxygen pressure, 27°. [b] Autocatalysis apparent for 2,4-dinitrotoluene in *t*-butyl alcohol, 2,4,6-trinitrotoluene in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) and *sym*-trinitrobenzene in *t*-butyl alcohol. [c] In a wrist-action stirrer.[d] [d] G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, Advances in Chemistry Series, Vol. 51, American Chemical Society, Washington, D. C. 1965, p 112. [e] After an 80-min induction period.

Oxidation of Polynitrotoluenes.—2,4-Dinitrotoluene oxidized considerably slower than *p*-nitrotoluene and at about the same rate as 2,4-dinitrocumene (Figure 8). 2,4,6-Trinitrotoluene oxidized much more slowly than 2,4-dinitrotoluene in *t*-butyl alcohol containing potassium *t*-butoxide. No coupling products were found from either of the polynitrotoluenes. Trace amounts of 2,4-dinitrophenol were formed in the oxidation of 2,4-dinitrotoluene as evidenced by the distinctive reversible indicator behavior of 2,4-dinitrophenol as a function of pH. The oxidations of 2,4-dinitrobenzene and 2,4,6-trinitrobenzene were much faster in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) than in *t*-butyl alcohol solution. In the mixed solvents the rates of oxygen absorption were ~10 times those observed in *t*-butyl alcohol solution. In the mixed solvents the effect of the ratio of base to substrate was investigated. It was found that the rate of oxidation of 2,4-dinitrotoluene increased with the concentration of potassium *t*-butoxide while 2,4,6-trinitrotoluene went through a maximum at a base to 2,4,6-trinitrotoluene ratio of about 0.75. Table VI summarizes pertinent data.

m-Dinitrobenzene oxidized in *t*-butyl alcohol or dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution while *sym*-trinitrobenzene oxidized in an autocatalytic manner in *t*-butyl alcohol. In the mixed solvents trinitrobenzene rapidly formed an insoluble addition product with the base. In fact, the oxidation of *m*-dinitrobenzene in *t*-butyl alcohol solution may well involve oxidation of intermediate adducts of the Meisenheimer type ($B^- = OH^-, OR^-$),[8a] while in

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(8) (a) R. Foster and R. K. Mackie, *J. Chem. Soc.*, 3796 (1963), and references cited therein; (b) R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 1131 (1962); **19**, 691 (1963).

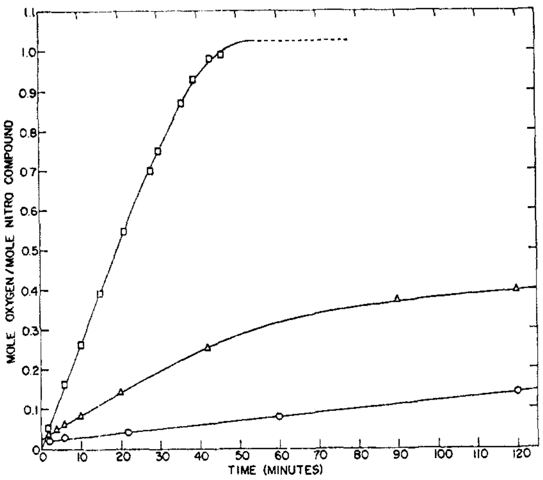
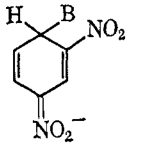


Figure 9.—Rates of oxidation of 0.13 *M* *p*-nitrodiphenylmethane derivatives in *t*-butyl alcohol containing potassium *t*-butoxide at 25° and 700 mm of oxygen pressure (see Figure 1 for stirring conditions): □, *p*-nitrodiphenylmethane, 0.35 *M* base; △, bis(4-nitrophenyl)methane, 0.29 *M* base; ○, bis(2,4-dinitrophenyl)methane, 0.29 *M* base.

dimethyl sulfoxide solutions a Janovsky-type[8b] adduct or methylated product may be involved. This is supported by the observation that the major product produced in the slow oxidation of nitrobenzene in DMSO-(80%)-*t*-butyl alcohol (20%) solutions containing excess potassium *t*-butoxide is *p*-nitrobenzoic acid arising from a Janovsky adduct where B = CH_3SOCH_2 or from *p*-nitrotoluene.[9]



Oxidation of Nitro-Substituted Polyphenylmethanes.—The oxidations of mono-*p*-nitrodiphenylmethane, bis-(*p*-nitrophenyl)methane, bis(2,4-dinitrophenyl)methane, mono-*p*-nitrotriphenylmethane, and tris(*p*-nitrophenyl)methane were studied. No dimeric products were formed and the corresponding ketones and carbinols were the major oxidation products isolated in *t*-butyl alcohol solution from the diphenylmethanes and triphenylmethanes, respectively. In *t*-butyl alcohol containing potassium *t*-butoxide the relative rates of oxidation (Figure 9) were *p*-nitrodiphenylmethane > bis(*p*-nitrophenyl)methane > bis-(2,4-dinitrophenyl)methane. This behavior is interpreted as being due to resonance stabilization in the carbanions that is not present in the radicals. Thus the ease of reactions such as

$$(Ar)(Ar')CH:^- \xrightarrow[ROO\cdot]{O_2 \text{ or}} (Ar)(Ar')CH\cdot$$

decreases as Ar and Ar′ are changed from Ar = phenyl, Ar′ = *p*-nitrophenyl; Ar = Ar′ = *p*-nitrophenyl; and Ar = Ar′ = 2,4-dinitrophenyl.

The autoxidation of bis(2,4-dinitrophenyl)methane was studied in DMSO (80%)-*t*-butyl alcohol (20%) solution containing potassium *t*-butoxide. The rates of oxidation were roughly 200 times as rapid as in *t*-butyl alcohol and increased with increasing concentrations of base even though the bis(2,4-dinitrophenyl)methane should have been completely ionized with any excess base.[10] It appears that the rates given in Table VII may reflect the oxidation of a Janovsky-type adduct for bis(2,4-dinitrophenyl)methane in DMSO containing solvents. The rate of oxidation of mono-*p*-nitrotriphenylmethane greatly exceeds that of tris(*p*-nitrophenyl)methane, presumably because of the greater stability of the tris(*p*-nitrophenyl)methide ion. The major oxidation products are the corresponding carbinols. The oxidation of tris(*p*-nitrophenyl)methane in the presence of excess base is catalyzed by ferric chloride and by nitrobenzene (Table VIII). Although tris(*p*-nitrophenyl)methane must be nearly completely ionized in the presence of a slight excess of *t*-butoxide ion in *t*-butyl alcohol solutions [pK_a = 14.6 (hydrazine),[10] 17.4 (ethanol)][11] the oxidation proceeds ~100 times faster in DMSO (80%)-*t*-butyl alcohol (20%) solution than in *t*-butyl alcohol. Apparently in DMSO solvents the carbanion is less solvated *via* hydrogen bonding and is more reactive in electron-transfer reactions, such as[12]

$$(p\text{-}NO_2C_6H_4)_3C:^- + ROO\cdot \longrightarrow ROO^- + (p\text{-}NO_2C_6H_4)_3C\cdot$$

In *t*-butyl alcohol the oxidation gives mainly the carbinol as had been previously found in ethanol solution.[13] Actually, the rate of oxidation of tris(*p*-nitrophenyl)methane is considerably greater in ethanol-potassium hydroxide than in *t*-butyl alcohol containing potassium *t*-butoxide. Here catalysis apparently involves the presence of un-ionized tris(*p*-

TABLE VII

OXIDATION OF BIS(2,4-DINITROPHENYL)METHANE AT 27°

Concn, mole/l.	Solvent (%)	[KOC-(CH_3)$_3$], mole/l.	Initial rate, mole of oxygen/mole of substrate/min
0.14	*t*-BuOH	0.29	0.001
0.10	DMSO (80)-*t*-BuOH (20)	0.075	0.13
0.10	DMSO (80)-*t*-BuOH (20)	0.10	0.17
0.10	DMSO (80)-*t*-BuOH (20)	0.20	0.25
0.10	DMSO (80)-*t*-BuOH (20)	0.50	0.33

TABLE VIII

OXIDATION OF TRIS(*p*-NITROPHENYL)METHANE AT 27°

Concn, mole/l.	Solvent (%)	[KOC-(CH_3)$_3$], mole/l.	Initial rate, mole of oxygen/mole of substrate/min
0.11[a]	*t*-BuOH	0.39	0.017
0.02	EtOH	0.35[b]	0.11
0.12	*t*-BuOH	0.35	0.001
0.12	*t*-BuOH	0.35	0.003[c]
0.033	*t*-BuOH	0.033	0.007
0.033	*t*-BuOH	0.10	0.0015
0.033	*t*-BuOH	0.10	0.013[d]
0.10	DMSO (80)-*t*-BuOH (20)	0.05	0.55
0.10	DMSO (80)-*t*-BuOH (20)	0.20	0.30

[a] Mono-*p*-nitrotriphenylmethane. [b] Potassium hydroxide. [c] 0.001 *M* ferric chloride. [d] 0.3 *M* nitrobenzene.

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(9) G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

(10) pK_a = 15.8 (sulfolane), 15.9 (hydrazine): N. C. Deno, *J. Am. Chem. Soc.*, **74**, 2039 (1952).

(11) R. S. Stearns and G. W. Wheland, *ibid.*, **69**, 2025 (1947).

(12) The possible intervention of a Janovsky-type adduct and its subsequent oxidation in DMSO may also be involved.[8]

(13) M. F. Hawthorne and G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

nitrophenyl)methane and an increase in the concentration or basicity of the base employed can retard the rate of oxidation by reduction of the amount of un-ionized tris(*p*-nitrophenyl)methane present at equilibrium. In line with this interpretation the oxidation of tris(*p*-nitrophenyl)methane can be catalyzed at high base concentrations by nitrobenzene or by Fe^{III}. Similar observations have been made in the oxidation of 2-nitropropane[14] and in the spontaneous disproportionation reaction of 2,4-dinitrotoluene.[3] The mechanism of nitrobenzene catalysis in the oxidation of anions derived from fluorene and acetophenone has been interpreted in terms of electron-transfer initiations.[14]

$$R:^- + ArNO_2 \longrightarrow R\cdot + ArNO_2\cdot^-$$

Oxidation of α-Substituted *p*-Nitrotoluene Derivatives.—A number of α-substituted *p*-nitrotoluene derivatives were oxidized in *t*-butyl alcohol or dimethyl sulfoxide (20%)-*t*-butyl alcohol (80%) solutions containing potassium *t*-butoxide. *p*-Nitrobenzyl alcohol and *p*-nitrobenzylphenyl ether were oxidized to *p*-nitrobenzoic acid. The initial rates of oxidation are summarized in Table IX. The rates appear to reflect two effects, the ease of ionization of the substrate and the ease of loss of one electron from the resulting carbanion. These two effects work in opposite directions. The sequence *p*-nitrodiphenylmethane > *p*-nitrotoluene > *p*-nitroethylbenzene apparently reflects the ease of ionization of the benzylic hydrogen atoms. On the other hand the very low reactivity of *p*-nitrophenylacetonitrile must reflect the resonance stabilization of the carbanion and its inertness in electron transfer reactions of the following type.[15]

$$R:^- \xrightarrow{O_2,\ ROO\cdot,\ ArNO_2} R\cdot$$

Table IX

Rates of Oxidation of α-Substituted *p*-Nitrotoluene Derivatives (p-$NO_2C_6H_4CH_2R$) at 27°

R	Substrate concn, mole/l.	Solvent (%)	[KOC(CH_3)$_3$], mole/l.	Initial rate, mole of oxygen/mole of substrate/min
H	0.17	*t*-BuOH	0.29	0.037
H	0.10	DMSO (20)–*t*-BuOH (80)	0.20	1.3
CH_3	0.20	*t*-BuOH	0.29	0.007
CH_3	0.10	DMSO (20)–*t*-BuOH (80)	0.20	0.120
C_6H_5	0.15	*t*-BuOH	0.35	0.053
OC_6H_5	0.10	DMSO (20)–*t*-BuOH (80)	0.20	1.3
O^-	0.10	DMSO (20)–*t*-BuOH (80)	0.20	0.22
O^-	0.17	*t*-BuOH	0.34	0.032
CO_2^-	0.10	DMSO (20)–*t*-BuOH (80)	0.20	0.90
CN	0.10	DMSO (20)–*t*-BuOH (80)	0.20	Very slow
CN	0.16	*t*-BuOH	0.29	0.001
CN[a]	0.14	*t*-BuOH	0.39	0.063

[a] Phenylacetonitrile.

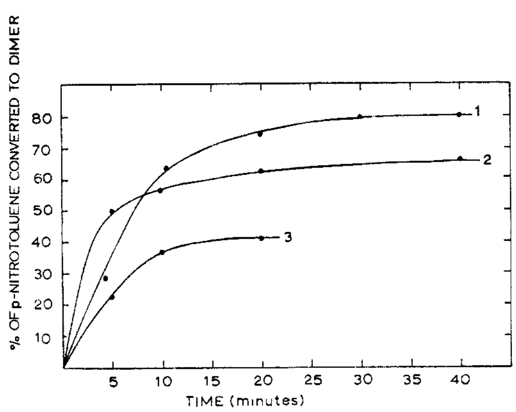
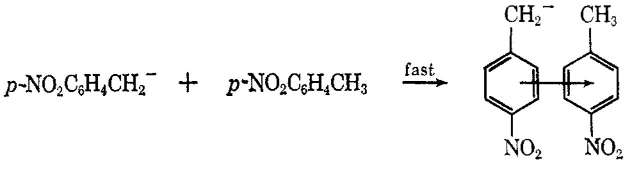


Figure 10.—Yield of dimer (*p,p'*-dinitrobibenzyl and *p,p'*-dinitrostilbene) as a function of time: (1) oxidation of 0.20 *M* *p*-nitrotoluene in *t*-butyl alcohol containing 0.35 *M* potassium *t*-butoxide at 27° and 700 mm of oxygen pressure (see Figure 1 for stirring conditions); (2) oxidation of 0.09 *M* *p*-nitrotoluene in *t*-butyl alcohol containing 0.27 *M* potassium *t*-butoxide; 50 ml of solution was shaken at 220 cpm in a Parr hydrogenation apparatus under 2050 mm of oxygen pressure; (3) spontaneous reaction of 0.10 *M* *p*-nitrotoluene in *t*-butyl alcohol, containing 0.21 *M* potassium *t*-butoxide at 27°.[1]

Discussion

The formation of *p,p'*-dinitrobibenzyl from *p*-nitrotoluene in the presence of strong base but absence of oxygen[3] and the formation of dimer in the presence of oxygen are related phenomena. Figure 10 shows that the initial rates of formation of the bibenzyl in the two processes are quite similar. The formation of the bibenzyl in the absence of oxygen has been formulated as involving the following sequence.[3b] The charge-transfer complex 1[16] is rapidly destroyed to yield *p,p'*-dinitrobibenzyl and *p*-nitrotoluene radical anion. Molecular oxygen can replace the un-ionized *p*-nitrotoluene as an electron acceptor in this process as well as convert the *p*-nitrotoluene radical anion into *p*-nitrotoluene so that a higher ultimate yield of dimer can be achieved in the presence of oxygen than in its absence. The *p*-nitrobenzoic acid can be formed in a competing process whose rate is dependent upon oxygen pressure. Under the reaction conditions both *p*-nitrobenzyl alcohol and *p*-nitrobenzaldehyde rapidly yielded *p*-nitrobenzoic acid.

$$p\text{-}NO_2C_6H_4CH_3 \xrightarrow[\text{slow}]{B^-} p\text{-}NO_2C_6H_4CH_2^-$$



1

$$1 + 2(p\text{-}NO_2C_6H_4CH_3) \longrightarrow p\text{-}NO_2C_6H_4CH_2CH_2C_6H_4NO_2\text{-}p + 2(p\text{-}CH_3C_6H_4NO_2\cdot^-)$$

$$p\text{-}NO_2C_6H_4CH_2^- + O_2 \longrightarrow p\text{-}NO_2C_6H_4CH_2OO^- \longrightarrow p\text{-}NO_2C_6H_4CHO + OH^-$$

Mechanisms involving the coupling of *p*-nitrobenzyl radicals in the presence of molecular oxygen can be excluded by the known rapidity of the reaction of molecular oxygen with alkyl radicals, including those

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[14] See Table VI, footnote *d*.

[15] G. A. Russell, A. J. Moye, and K. Nagpal, *J. Am. Chem. Soc.*, **84**, 4154 (1962).

[16] Spectroscopic evidence for intermediate complexes of this type has been presented: J. M. Miller and H. Pobiner, *Anal. Chem.*, **36**, 238 (1964).

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\cdot \longrightarrow \begin{cases} \xrightarrow[k_o]{\text{O}_2} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OO}\cdot \\ \xrightarrow[k_d]{p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\cdot} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p \end{cases}$$

of the *p*-nitrobenzyl type.[17] Reasonable estimates for k_0 can be obtained using the polystyrenyl radical as a model;[17] $k_0 = 5 \times 10^7$ l/mole sec at 30°.[18] The termination rate constant for benzyl radicals is reported as $k_d = 4 \times 10^7$ l/mole sec at 25°.[19] To obtain an equimolar mixture of *p*-nitrobenzoic acid and *p,p'*-dinitrobibenzyl at an oxygen concentration of $\sim$0.02 *M* (solution saturated with oxygen at 700 mm)[20] would require a concentration of *p*-nitrobenzyl radicals in the range of 0.2 mole/l. At this concentration of radicals, and with the value of k_0 cited, the reaction would have to be explosive.[21] Since the adsorption of oxygen proceeds at a fast but reasonable rate, a mechanism involving coupling of *p*-nitrobenzyl radicals must be excluded.

An alternative mechanism involving *p*-nitrobenzyl radicals deserves consideration. Possibly *p*-nitrobenzyl radicals are rapidly trapped by carbanions and this reaction can compete with the trapping of radicals by molecular oxygen. It appears that this mechanism

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 + (\text{CH}_3)_3\text{CO}^- \xrightarrow[\text{slow}]{t\text{-(CH}_3)_3\text{COH}} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^-$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3 \overset{\text{fast}}{\rightleftharpoons} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\cdot + [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3]\cdot^-$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\cdot + p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^- \xrightarrow{\text{fast}} [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]\cdot^-$$

$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p]\cdot^- \begin{cases} \xrightarrow{p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p + [p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3]\cdot^- \\ \xrightarrow{\text{O}_2} p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p + \text{O}_2\cdot^- \end{cases}$$

$$p\text{-NO}_2\text{C}_6\text{H}_5\text{CH}_2\cdot + \text{O}_2 \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_5\text{CH}_2\text{OO}\cdot \longrightarrow \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_5\text{CO}_2^-$$

can be rationalized with an ionization rate controlled process in the absence of oxygen. Factors that increase the rate of formation of the *p*-nitrobenzyl anion, such as an increase in the concentration of potassium *t*-butoxide or *p*-nitrotoluene, should also increase the yield of dimer in the oxidation process. Upon increasing the oxygen pressure, a larger fraction of the *p*-nitrobenzyl radicals will be trapped by oxygen and the yield of dimer will be decreased. However, the stoichiometry of the bibenzyl-forming process should be

$$2(p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3) \approx 2\text{O}_2 \approx p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p$$

since oxygen reacts with nitroaromatic radical anions to yield potassium superoxide (KO_2).[7] This stoichiometry is inconsistent with the observed stoichiometry (Figure 3). The reaction of **1** with molecular oxygen and base may conceivably require only one molecule of oxygen (to yield K_2O_2). Possible reaction sequences are discussed elsewhere.[3b]

Further evidence inconsistent with the formation of the *p,p'*-dinitrobibenzyl in this manner is the absence of crossed reaction products in the oxidation of *p*-nitrotoluene in the presence of high concentrations of carbanions stable to molecular oxygen, such as the 2-nitro-2-propyl anion, bis(2,4-dinitrophenyl)methide anion, or the 2,4,6-trinitrobenzyl anion. Not only are cross reaction products not observed but the oxidation of *p*-nitrotoluene does not induce the oxidation of the other carbanions, an observation not particularly consistent with a free-radical chain oxidation.

The kinetics of the oxidation of *p*-nitrotoluene in methanolic potassium hydroxide have been discussed by Tsuruta, Fueno, and Furukawa.[22] However, we believe that their conclusions have little meaning since these authors did not take into account the formation of *p*-nitrobenzoic acid, the variable reaction stoichiometry, the spontaneous formation of radical anions and *p,p'*-dinitrobibenzyl in the absence of oxygen, or the fact that methanolic base undergoes cooxidation with the *p*-nitrotoluene.

With the exception of *p*-nitrophenylacetic acid none of the other *p*-nitro derivatives investigated in this work underwent the oxidative dimerization reaction although in the absence of oxygen many of them spontaneously produce radical anions.[3] The oxidation pathway leading to acids, ketones, or alcohols predominates over the dimerization pathway. In these cases the trapping of the substituted *p*-nitrobenzyl radical by oxygen may completely overshadow the trapping of the radical by the carbanion. In the case of α-substituted derivatives, such as *p*-nitrocumene, 2,4-dinitrocumene, *p*-nitrodiphenylmethane, *p,p'*-dinitrodiphenylmethane, bis(2,4-dinitrophenyl)methane, *p*-nitrotriphenylmethane, *p*-nitrobenzylate anion, or *p*-nitrobenzyl phenyl ether, there may be considerable steric hindrance to the formation of a bond between the α-carbon atoms and **1** may decompose to yield a benzyl-type radical and a nitroaromatic radical anion.

The substitution of powerful carbanion stabilizing groups in the α or *ortho* positions of *p*-nitrotoluene greatly decreases the ease of oxidation of the resulting carbanion because it is now more difficult for the carbanion to lose an electron. Thus, in *t*-butyl alcohol solution we find that, in the presence of potassium *t*-butoxide, *p*-nitrotoluene or phenylacetonitrile is readily oxidized whereas phenylnitromethane or *p*-nitrophenylacetonitrile is stable. Similarly, in all solvents studied the rates of oxidation were *p*-nitrotoluene > 2,4-dinitrotoluene > 2,4,6-trinitrotoluene.

For 2,4,6-trinitrotoluene, and tris(*p*-nitrophenyl)methane we find that the rate of oxidation passes through a maximum as the ratio of base to nitroaromatic is increased. The same effect has been found in the oxidation of 2-nitropropane[14,23] and in the spontaneous formation of 2,4-dinitrotoluene radical anion

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[17] G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2354 (1964).

[18] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *ibid.*, **73**, 5395 (1951); A. A. Miller and F. R. Mayo, *ibid.*, **78**, 1017 (1956).

[19] R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960).

[20] C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

[21] The reaction $\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$ is exothermic. When $\text{R}\cdot$ = cyclohexyl an exothermicity of 25.5 kcal/mole can be calculated (G. A. Russell, in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p 108) which reads to an exothermicity of $\sim$10 kcal/mole for R = benzyl or *p*-nitrobenzyl; see also S. W. Benson, *J. Am. Chem. Soc.*, **87**, 972 (1965); C. L. Ayers, E. G. Janzen, and F. J. Johnston, *ibid.*, **88**, 3531 (1965).

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from 2,4-dinitrotoluene in the presence of base.[3] These results are consistent with an oxidation process in which some initiation step involves a reaction of the carbanion derived from the nitro compound with the un-ionized nitro compound, or its *aci* form, or some complex thereof. At high ratios of base to nitro compound ionization is complete and no acceptor molecules remain in solution. Under these conditions oxidations of tris(p-nitrophenyl)methane can be catalyzed by the addition of electron acceptors, such as ferric ion, nitrobenzene, or m-dinitrobenzene, that are less susceptible to deprotonation.[14] These results are consistent with the following mechanism (RH = p-nitrotoluene derivative, $ArNO_2$ = added catalyst).

$$RH \overset{B^-}{\rightleftharpoons} R^-$$

$$R^- + RH \rightleftharpoons R\cdot + RH\cdot^-$$

$$R^- + ArNO_2 \rightleftharpoons R\cdot + ArNO_2\cdot^-$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$RH\cdot^-(ArNO_2\cdot^-) + O_2 \longrightarrow RH(ArNO_2) + O_2\cdot^-$$

$$ROO\cdot + O_2\cdot^- \longrightarrow ROO{:}^- + O_2$$

Experimental Section

Oxidation Apparatus and Procedure.—Oxidation rates and products were determined (except as noted below) by use of an all-glass system equipped with a mercury manometer, a 50-ml gas buret, and connections for establishing a vacuum and introducing oxygen. The reaction vessel was a 50-ml ₸ erlenmeyer flask. Stirring was provided by a 20 × 8 mm glass-covered iron turned by a magnet mounted on an inverted Waco stirring motor rated at 600 rpm. A well-defined vortex with frothing was developed. Substrate and catalyst (where necessary) were weighed into the flask and 25 ml of a standard solution of base in the desired solvent was added. The system was alternately flushed and evacuated with dry, carbon dioxide free oxygen several times. Finally, the system was filled with oxygen to the desired pressure, magnetic stirring was started, and oxygen uptake at room temperature (26 ± 2°) was followed at constant oxygen pressure maintained by manual adjustment of a mercury leveling bulb. Experiments at higher oxygen pressure were performed in a Parr hydrogenation apparatus at various shaking speeds using 50 ml of t-butoxide–t-butyl alcohol solutions in a 250-ml heavy walled pressure bottle. In general, the oxidation rates (and/or products) reported in Tables V–IX and Figures 5 and 6 were obtained under conditions of vigorous agitation employing a wrist-action shaker previously described (Table VI, footnote *d*).

Isolation of Oxidation Products.—Product yields in the oxidation of p-nitrotoluene were determined at the conclusion of each oxidation by pouring the reaction mixture into ice–water, quantitatively collecting the precipitate in a weighed, sintered-glass crucible, and titrating the filtrate potentiometrically with standard acid. The contents of the crucible were washed with cold methanol to remove any unreacted nitro compound, followed by several washings with hot water. The crucible and contents were dried overnight (usually 12–15 hr) at 110°, cooled to room temperature, and weighed. This procedure permitted quantitative recovery of products on the basis of starting materials for reactions that had gone to completion. For the shorter experiments (<2 hr, <0.5 M base) the p,p'-dinitrobibenzyl melted sharply at 182–184° uncor. For longer reaction times and at higher concentrations of base, the yellow bibenzyl derivative was contaminated with pale green p,p'-dinitrostilbene. The green color of the stilbene underwent an irreversible thermochromic change when heated above 80°. Oxidations performed in dimethyl sulfoxide–t-butyl alcohol mixtures yielded dimeric products consisting mainly of the stilbene derivative which increased to a maximum of 100% in a 1:1 mixtue of these solvents. The *trans*-p,p'-dinitrostilbene melted at 304–305° (lit.[24] mp 304–306°). p-Nitrobenzoic acid was isolated by filtering the aqueous filtrate after potentiometric titration. The acid so isolated melted at 233–237° and after recrystallization caused no depression of the melting point of authentic p-nitrobenzoic acid.

Products from other oxidations were isolated in a similar fashion. The oxidation of p-nitroethylbenzene yielded only p-nitrobenzoic acid, even though *meso*-2,3-bis(p-nitrophenyl)-butane was completely insoluble under the reaction conditions.

The products of oxidation of p-nitrocumene were isolated from a large-scale experiment. Since a preliminary experiment with 0.32 M p-nitrocumene and 0.64 M potassium t-butoxide in 25 ml of dimethyl sulfoxide (50%)–t-butyl alcohol (50%) indicated that an almost instantaneous uptake of oxygen (molar ratio of oxygen absorbed to p-nitrocumene ≅ 1:1) occurred under these conditions, the proportion of dimethyl sulfoxide was reduced in the large-scale experiment to avoid any danger from a very rapid reaction. p-Nitrocumene (33.0 g, 0.20 mole) was placed in a 1-l. flask flushed with nitrogen and to it was added a solution of 47.3 g (0.42 mole) of commercial potassium t-butoxide in 480 ml of t-butyl alcohol and 120 ml of dimethyl sulfoxide at 0°. The vigorously stirred reaction mixture was then immediately allowed to react with oxygen stored in a large rubber balloon (capacity about 10 l.). However, hardly any absorption of oxygen was apparent after 20–25 min. Hence, the flask was warmed to room temperature (25°) and 120 ml more of dimethyl sulfoxide was added. Under these conditions, absorption of oxygen occurred smoothly and the color of the solution changed eventually to brown-green. After 3 hr at room temperature, during which time about 5 l. of oxygen was absorbed, the reaction mixture was poured into 2 l. of water, cooled in ice, and carefully neutralized with 4 N hydrochloric acid. A considerable amount of an orange solid separated from the aqueous solution even before the acid was added, and it did not dissolve upon acidification. The reaction mixture was filtered, and the insoluble solid was pulverized, washed thoroughly with water, and dried at 70° under reduced pressure (3 mm) to a constant weight of 20.8 g. The filtrate and washings were extracted repeatedly with ether. The combined ether layers were dried (anhydrous sodium sulfate) and evaporated to yield an orange-red, viscous liquid. Vacuum distillation of this material furnished 8.1 g (22.4%) of a yellow liquid, bp 137–139° (2.5 mm), $n^{27}D$ 1.5535, identified as p-nitrocumyl alcohol [lit.[25] bp 120.5–121.0° (2 mm), $n^{19.2}D$ 1.5552]. Infrared and nmr spectra were consistent with this structure. The solid product of the reaction was insoluble in 20% aqueous potassium hydroxide solution. It was found to consist of at least four components as judged by thin layer chromatography on silica gel (chloroform as developer); R_f values 0.92 (weak), 0.75, 0.092, and 0.00. The component R_f 0.092 is probably some residual p-nitrocumyl alcohol since the distilled p-nitrocumyl alcohol had the same R_f value, a conclusion supported by the infrared spectrum of a chloroform extract of the solid, which further indicated the absence of any carbonyl-containing compounds. The formation of a similar solid product was also noted in the small-scale experiment in dimethyl sulfoxide (50%)–t-butyl alcohol (50%).

The oxidation of the various nitro-substituted diphenylmethane derivatives yielded the corresponding ketones as the only identifiable products. p-Nitrodiphenylmethane gave p-nitrobenzophenone, mp 136° (lit.[26] mp 136–138°); bis(p-nitrophenyl)methane gave p,p'-dinitrobenzophenone, mp 187–188° (recrystallized) (lit.[27] mp 187–188°); bis(2,4-dinitrophenyl)-methane yielded traces of a solid material whose infrared spectrum was consistent with the tetranitrobenzophenone. Small amounts of p-nitrobenzophenone were also isolated from the oxidation of mono-p-nitrotriphenylmethane.

Reagents.—Potassium t-butoxide was prepared by the reaction of clean potassium metal with an excess of dry t-butyl alcohol at room temperature. In some experiments the commercially available potassium t-butoxide obtained from Mine Safety Appliance Corp. was used. A solution of lithium t-butoxide in t-butyl alcohol was prepared by the reaction of clean lithium wire with excess t-butyl alcohol at room temperature. Other solvents were commercially available grades and were dried and/or distilled prior to use.

p-Nitrotoluene (Eastman Kodak Co., practical grade) was twice recrystallized from alcohol, mp 52.8–53.6°. o-Nitrotoluene (Eastman Kodak Co., pure grade) was used as received. Phenylacetonitrile was distilled under vacuum through a 30-in.

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spinning-band column. A center fraction was collected for use, bp 60° (1 mm), n^{25}D 1.5211. *p*-Nitrophenylacetonitrile was recrystallized from a mixture of alcohol and water, mp 116–117°. *p*-Nitrocumene was prepared by the mixed acid nitration of freshly distilled cumene.[28] The compound was distilled through a 30-in. spinning-band column at a reflux ratio of 15:1. The fraction with bp 132° (13 mm), n^{25}D 1.5363, was collected and stored under nitrogen until used [lit.[29] bp 134° (13 mm), n^{20}D 1.5369]. 2,4-Dinitrocumene was prepared by the mixed acid nitration of pure cumene at 80° according to the method of Hansch and Helmkamp.[30] After a preliminary distillation the material was carefully fractionated under vacuum through a 30-in. spinning-band column at a reflux ratio of 15:1. Physical constants were bp 134–136° (0.5 mm), n^{20}D 1.5548 [lit.[31] bp 169–171° (11 mm), n^{25}D 1.5523]. 2,4-Dinitrotoluene (Eastman Kodak Co., pure grade) was used as received. *meso*-2,3-Diphenylbutane was prepared by the method of Conant and Blatt[32] by treatment of the Grignard reagent from α-phenethyl bromide with anhydrous cuprous chloride. The solid *meso* isomer obtained in 20% yield was recrystallized from ethanol, mp 126–127°. This compound was nitrated with nitric acid in acetic anhydride to yield *meso*-2,3-bis(*p*-nitrophenyl)butane,[33] mp 254–256° (recrystallized from acetic acid). *p*-Nitroethylbenzene was prepared by the mixed acid nitration of ethylbenzene.[28] After vacuum distillation through a spinning-band column the fraction of bp 125–125.4° (13 mm), n^{20}D 1.5458, was collected and stored under nitrogen until used [lit.[25] bp 126° (13 mm), n^{20}D 1.5459]. *p*-Nitrodiphenylmethane was prepared by the condensation of *p*-nitrobenzyl alcohol with benzene in the presence of sufuric acid.[34] The compound was recrystallized from ethanol, mp 31–32°. Bis(*p*-nitrophenyl)methane was prepared by the method of Parkes and Morley.[35] After several recrystallizations from acetic acid, pale orange needles were obtained, mp 186–187°. Bis(2,4-dinitrophenyl)methane was prepared by the nitration of diphenylmethane yielding yellow platelets from acetic acid, mp 173.5–175°, using potassium nitrate as the nitrating agent.[36] Mono-*p*-nitrotriphenylmethane was prepared as described by Curtin and Kauer,[37] mp 92–93° (recrystallized from hexane). Tris-*p*-nitrophenylmethane was prepared by the mixed-acid nitration of triphenylmethane at 0°.[38] The compound was recrystallized from a mixture of chloroform and ether, mp 212.5–214°. 2,4,6-Trinitrotoluene (Eastman Kodak Co., practical grade) was recrystallized five times from ethanol, mp 81–81.7°. *sym*-Trinitrobenzene (Eastman Kodak Co., pure grade) was recrystallized from acetic acid, mp 122–123°.

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Thermal Decomposition of *t*-Butylperoxy 6-Bromohexanoate. Lack of Evidence for Radical Displacement on Carbon and 1,5-Bridged Bromine Radicals[1a]

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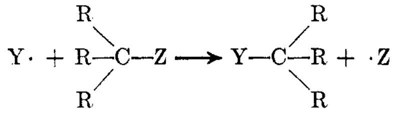
The products and rates of the thermal decomposition of *t*-butylperoxy 6-bromohexanoate (**2**) and *t*-butylperoxy hexanoate (**3**) in various solvents and the gas phase were studied. Cyclopentane was not produced under any conditions, which means that the 5-bromopentyl radical (**1**) does not undergo an intramolecular radical displacement reaction on carbon. Since the main products of the bromo per ester and the unsubstituted per ester are very similar, there is no evidence that the 5-bromopentyl radical forms a 1,5-bridged bromine radical (**4**). The similar rates of decomposition of the two per esters are also consistent with no 1,5-bromine participation.

A type of radical reaction that has been observed in only a few special cases is radical displacement on carbon as illustrated by eq 1. Ogg and Polanyi[2] called



(1)

this bimolecular homolytic substitution reaction an "SH2" reaction. The similarities between SH2 and SN2 reactions are obvious.

Early attempts to characterize the SH2 reaction by studying the racemization of optically active *sec*-butyl iodide in the presence of iodine were unsuccessful.[2,3] The study merely pointed out the enormous difficulties one encounters with free-radical reactions of this type.[3b]

Opening of cyclopropane rings by free-radical processes has been presented as an example of a homolytic displacement reaction.[4] However, because of the considerable "unsaturated" character of the cyclopropane ring,[5] the evidence obtained could be interpreted as the addition of a free radical into the cyclopropane ring followed by ring opening. Even if radical displacement on carbon is occurring, the carbon is part of a strained system and is consequently a special type of carbon.

Applequist has recently presented evidence for a radical substitution reaction on carbon by demonstrating the free-radical nature of the bromination of 9,10-dehydrodianthracene.[6] Again, the radical displacement is on a special type of carbon that is involved in a highly strained ring system. Friswell and Gowenlock have recently reported that the heptyl radical cyclizes to form cyclohexane by the displacement of a methyl radical.[7] However, the identity of cyclohexane was based on gas–liquid partition chromatography (glpc)

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[1] (a) Based on work by M. P. Doyle in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University; (b) U. S. Public Health Service Fellow, 1966.

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