

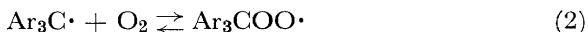
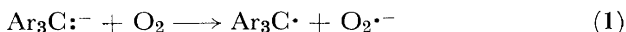
DETECTION OF PARAMAGNETIC INTERMEDIATES IN THE OXIDATION OF CARBANIONS†

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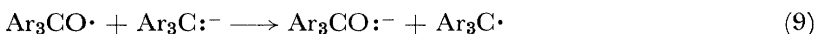
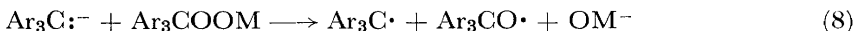
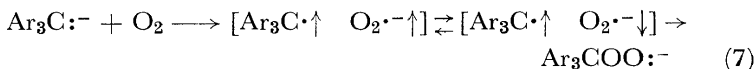
INTRODUCTION

Gomberg demonstrated the rapid formation of trityl peroxide by the reaction of oxygen with the triphenylmethyl radical in the presence of hexaphenylethane¹. The rapid reaction of oxygen with triphenylmethylsodium or triphenylmethyl Grignard reagents produces mainly the hydroperoxide but significant amounts of trityl peroxide are also produced²⁻⁵. This suggests the intermediacy of the triphenylmethyl radical. The major products are consistent with the reaction sequence outlined in reactions 1-6.



The occurrence of reaction (5) in the presence of oxygen is reasonable since reaction (2) occurs rather slowly⁶, and is readily reversible⁷, for the triphenylmethyl radical.

However, the products observed can be rationalized in other ways; for example, reactions (7)-(9) followed by (5) and/or (6). Moreover, the effect of the metal ion (sodium, magnesium) in non-polar ethereal solvents is a complicating factor⁸.



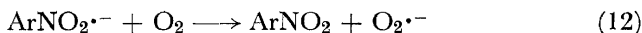
† This paper may be considered part XXVIII in the series, *Reactions of Resonance Stabilized Anions*, and to be co-authored with Alan G. Bemis, Edward G. Janzen, and Wayne C. Danen. This work was supported by a grant (1760-C) from the Petroleum Research Fund administered by the American Chemical Society.

OXIDATION OF TRIPHENYLMETHYL ANION

We have investigated the oxidation of the triphenylmethyl anion, generated by ionization of triphenylmethane, in polar solvents such as dimethyl sulphoxide (DMSO) or hexamethylphosphoramide (HMPA)⁹. In DMSO an additional important reaction occurs, namely the reduction of the hydroperoxide to the alcohol by the solvent.



Reaction of triphenylmethane with potassium *t*-butoxide in HMPA or DMSO (80 volume per cent)-*t*-butyl alcohol (20 volume per cent) in the presence of oxygen at a partial pressure of about 1 atm leads to the consumption of one mole of oxygen and the formation of triphenylmethyl hydroperoxide in HMPA and triphenylcarbinol in DMSO. Neither oxidation displays induction or inhibition periods characteristic of a free radical process. Moreover, the rates of oxidation are unaffected by electron transfer agents, such as the nitroaromatics, which should catalyze a radical-chain oxidation by reactions (11)-(13)^{10, 11}.



α -Deuteriotriphenylmethane is oxidized about 10-times as slowly as triphenylmethane itself [DMSO (80)-*t*-BuOH (20)] suggesting that the rate of oxygen absorption may be limited by the rate of ionization of the hydrocarbon¹². In fact the rate of oxidation of deuterated triphenylmethane and the rate of deuterium exchange in DMSO (80)-*t*-BuOH (20) are nearly equivalent⁹. The overall reaction sequence is apparently given by equations (14)-(16).



The kinetics of the oxidation are easily measured because of the simple stoichiometry which allows the instantaneous concentration of triphenylmethane to be equated to $[[\text{R}_3\text{CH}]_0 - \text{O}_2 (\text{absorbed})]$ (see *Figure 1*). In DMSO (80)-*t*-BuOH (20) the rate of oxygen absorption is first order in triphenylmethane and first order in potassium *t*-butoxide. Moreover, the rate of oxidation is independent of the oxygen pressure above 400 mm. The value of k_1 for reaction (14) is 0.134 l./mole-sec at 24.5°, $\Delta H^\ddagger = 9.8$ kcal/mole, $\Delta S^\ddagger = +29.4$ e.s.u.

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Similar observation and conclusions were reached in a study of the oxidation of diphenyl- α -naphthylmethane and 1,1-diphenylethane. A mechanism similar to that of reaction (7) is suggested.

In pyridine solution the reaction of triphenylmethane with potassium *t*-butoxide and oxygen (heterogeneous) yields mainly the hydroperoxide but

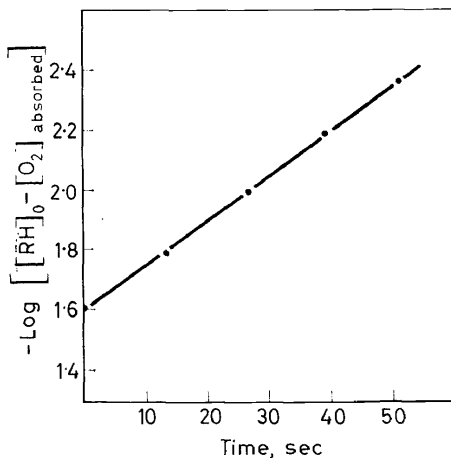
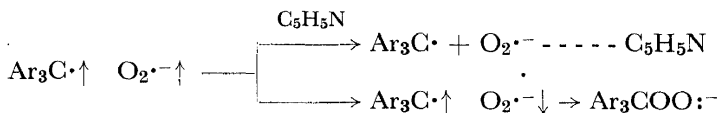


Figure 1. Pseudo first-order kinetic relationship observed in the autoxidation of triphenylmethane at 24.5° in dimethyl sulphoxide (80 volume %)-*t*-butyl alcohol (20%); solution 0.2 M in potassium *t*-butoxide, $[R_3CH]_0 = 0.025$ M, 750 mm saturation pressure of oxygen.

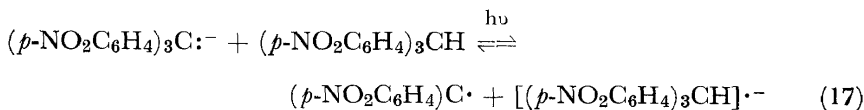
about 10 per cent of trityl peroxide is observed. Pyridine is recognized to form a specific complex with the superoxide ion¹³ and perhaps in this solvent reactions (1) and (7) compete.



Triphenylmethane derivatives that are much more acidic, such as tris(*p*-nitrophenyl)methane or 9-phenylfluorene, show a rather different oxidation behaviour. The rates of oxidation are now much slower than the rates of ionization. Catalysis by added nitroaromatics is readily detected and in the presence of such catalysts a reaction scheme involving reactions (11), (12), (13), (1) and (2) followed by reaction (4) [or in the presence of DMSO, reaction (16)] is envisioned¹¹. However, the mechanism of the uncatalyzed reaction may proceed by a different course, more similar to reaction (7). The major difference between triphenylmethane and these derivatives is the relative rates of reactions (14) and (7) or (1).

The oxidation of tris(*p*-nitrophenyl)methane shows some characteristics not consistent with reactions (1) or (7) that illustrate rather general phenomena as far as nitro-substituted carbanions are concerned. The oxidation in a given solvent is slower in excess base than in the presence of deficient

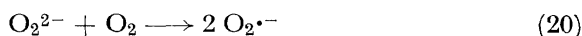
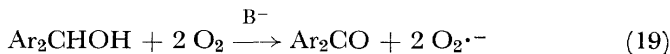
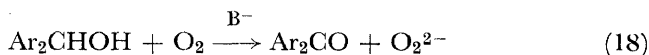
quantities of base, particularly in the presence of light. This suggests a spontaneous initiation process of the type shown in equation (17).



In the presence of traces of oxygen significant quantities of the tris(*p*-nitrophenyl)methyl radical can be detected from the reaction of tris(*p*-nitrophenyl)methane and base in *t*-butyl alcohol. However, this observation may be due to the occurrence of reaction (8) rather than reaction (1).

OXIDATION OF DIPHENYLMETHANE

The oxidation of diphenylmethane in the presence of base in HMPA or DMSO (80)-*t*-BuOH (20) is similar to the oxidation of triphenylmethane and is a process limited by the rate of ionization of the hydrocarbon. In DMSO (80)-*t*-BuOH (20) the reaction involves two steps, the formation of the alcohol via reactions (14)-(16) (one mole of oxygen absorbed per mole of diphenylmethane), $k_1 = 0.085 \pm 0.015$ litre/mole-sec at 24.5°, followed by a slower oxidation of benzhydrol to benzophenone¹⁴⁻¹⁶. The stoichiometry of this conversion is complex because of the occurrence of at least three reactions (18)-(20) of which reaction (20) can be observed in the absence of the carbinol.

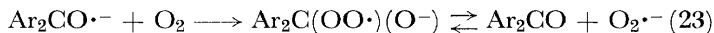
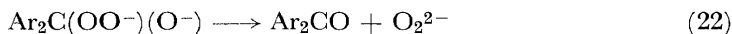
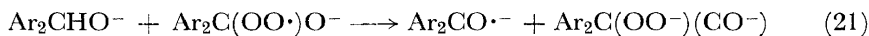


OXIDATION OF BENZHYDROL

The oxidation of benzhydrol in basic solution shows a large isotope effect when an alpha deuterium atom is substituted [$k_{\text{H}}/k_{\text{D}} \approx 10$ in DMSO (80)-*t*-BuOH (20)]. Recovered benzhydrol from this experiment did not show any hydrogen-deuterium exchange. The oxidation shows an induction period that is greatly extended by arsenic trioxide or ferric chloride in catalytic amounts, and is removed by cupric ion (experiments in *t*-butyl alcohol) (see Figure 2). There is no effect of nitroaromatics on the oxidation. Of special interest is the fact that the rate of oxidation of benzhydrol is independent of the concentration of excess base and independent of the solvent. The observed rates of oxidation in *t*-butyl alcohol, pyridine, and DMSO (80)-*t*-BuOH (20) solutions are nearly the same, whereas for di- or triphenylmethane there is a rate difference (potassium *t*-butoxide as base) of more than 100-fold between *t*-butyl alcohol and DMSO (80)-*t*-BuOH (20).

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These results suggest the radical chain mechanism depicted in reactions (21)–(23).



Some additional chain-branching step, presumably involving the superoxide ion, must occur since the reaction can be nearly completely inhibited by arsenic trioxide.

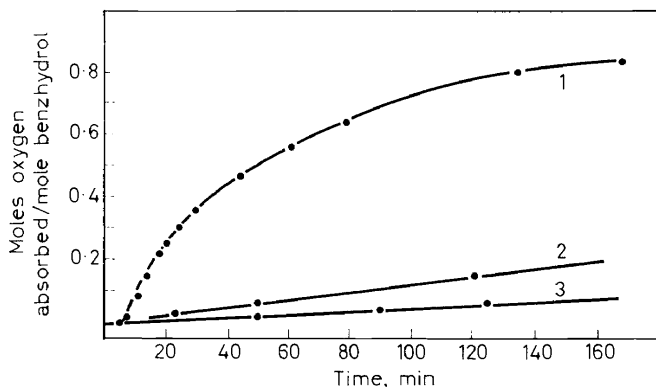
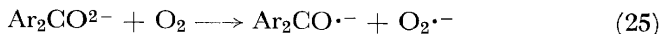
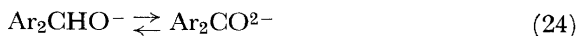


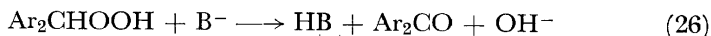
Figure 2. Oxidation of 0.12 M benzhydrol in *t*-butyl alcohol containing 0.36 M potassium *t*-butoxide at 25°, 750 mm oxygen pressure: (1) no additive; (2) 0.002 M ferric chloride; (3) 0.01 M arsenic trioxide (As_2O_3).

OXIDATION OF 9-FLOURENOL AND 9-XANTHENOL

With the more acidic (as a carbon acid) 9-fluorenol and 9-xanthenol an effect of solvent and base upon the rate of oxidation is observed, no deuterium isotope effect is observed in DMSO (80)–*t*-BuOH (20), catalysis by nitroaromatics is observed, and the metal superoxide is the major reactions product with potassium or rubidium alkoxides as the base. Here a dianion is apparently involved [reactions (24), (25), and (23)].



The oxidation of fluorene in *t*-butyl alcohol containing potassium *t*-butoxide yields fluorenone in high yield with the absorption of one mole of oxygen¹⁷. The initially formed hydroperoxide apparently undergoes a base-catalyzed decomposition¹⁸. The stoichiometry observed



excludes the intervention of 9-fluoreno1. The reaction shows little isotope effect consistent with the finding that 9,9-dideuteriofluorene undergoes hydrogen-deuterium exchange in basic solution much more rapidly than the fluorene is oxidized. Pronounced catalysis by the nitroaromatics is observed (see *Figure 3*) and the reaction proceeds faster in solvents such as DMSO or HMPA than in *t*-butyl alcohol (see *Figure 4*). The catalyzed

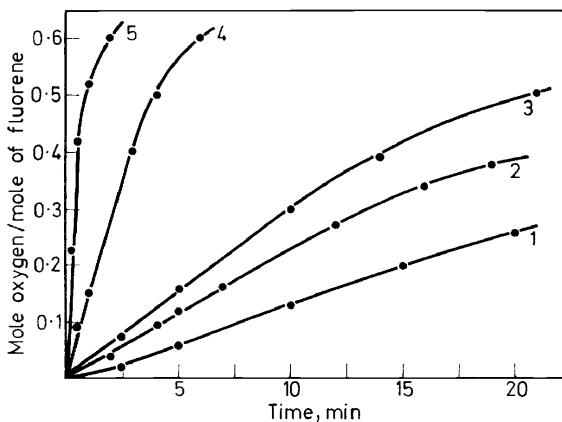


Figure 3. Catalyzed oxidation of 0.10 M fluorene in *t*-butyl alcohol containing 0.2 M potassium *t*-butoxide at 25°; 750 mm saturation oxygen pressure: (1) uncatalyzed; (2) 0.005 M *m*-nitrotoluene; (3) 0.005 M nitrobenzene; (4) 0.005 M *p*-chloronitrobenzene; (5) 0.005 M *p*-cyanonitrobenzene.

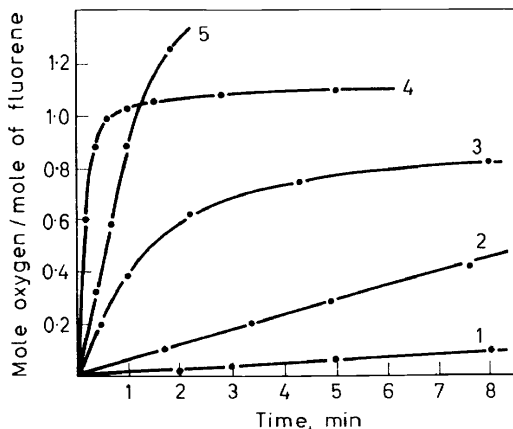
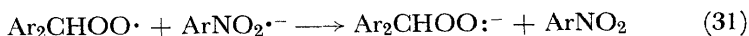
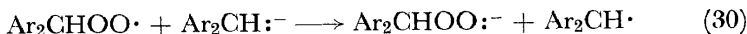
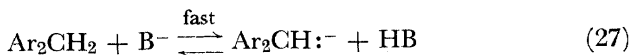


Figure 4. Oxidation of 0.1 M fluorene in the presence of 0.2 M potassium *t*-butoxide at 25°, 750 mm saturation oxygen pressure: (1) *t*-butyl alcohol; (2) benzene (80 volume %)-*t*-butyl alcohol (20%); (3) dioxane (80 volume %)-*t*-butyl alcohol (20%); (4) dimethyl sulphoxide (80 volume %)-*t*-butyl alcohol (20%); (5) piperidine (80 volume %)-*t*-butyl alcohol (20%).

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reaction apparently involves the steps shown in equations (27)–(31) followed by reaction (26).



Strong support for this interpretation is furnished by the correlation between the rate of reaction (28) observed by e.s.r. techniques in the absence of oxygen (see Figure 5) and the rates of oxygen absorption observed in the presence of oxygen and the nitroaromatics (see Figure 6)¹¹. Since the rates of oxidation

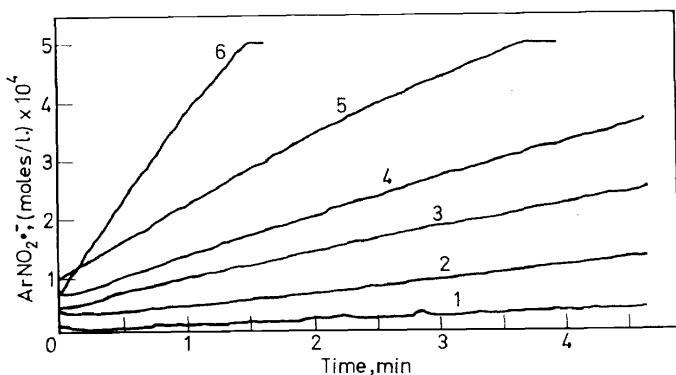


Figure 5. Initial rates of formation of nitroaromatic radical anions in *t*-butyl alcohol at 25° from the reaction of 0.10 M fluorene, 0.20 M potassium *t*-butoxide and 0.0048 M nitroaromatic: (1) *m*-nitroaniline; (2) *m*-nitrotoluene; (3) nitrobenzene; (4) *m*-nitroanisole; (5) *p*-chloro-nitrobenzene; (6) *m*-nitrobenzotrifluoride. Radical anion concentrations at zero time reflect reaction occurring during the filling of the e.s.r. cell. Signal deflections were observed at constant field for overmodulated e.s.r. signals. Concentrations were calculated by comparison with signal intensity of overmodulated diphenylpicrylhydrazyl solution under exactly the same experimental conditions.

are about 35 times faster than the rates of electron transfer (0.1 M fluorene, 0.2 M potassium *t*-butoxide, 0.0048 M nitrobenzene) a short but appreciable kinetic chain length for reactions (28)–(31) is indicated.

Although the mechanism of the catalyzed oxidation of fluorene seems to be well documented the question still remains as to the mechanism that occurs in the absence of an added catalyst. Either the reaction can be a "one-step" process [reaction (7)] not involving a chain process¹⁴ or reaction (1) can initiate a free radical chain process. If the triphenylmethyl radical cannot escape from the reaction cage for reaction (7), it seems unlikely that the less stable fluorenyl radical would escape. There is little, if any, auto-catalysis in the oxidation of fluorene which indicates that either reaction (32) is unimportant



or else the concentration of $R_2\text{CHOOH}$ rapidly reaches a low, steady state value [possibly due to the rapidity of reaction (26)]. The rate of oxidation of fluorene in the absence of added catalysts in *t*-butyl alcohol containing potassium *t*-butoxide varies linearly with the oxygen pressure as required by reaction (7) (see Figure 7).

The rate of ionization of fluorene by potassium *t*-butoxide in *t*-butyl alcohol can be estimated by the rate of oxidation observed at high concentrations of the nitroaromatic catalyst. Under conditions of constant

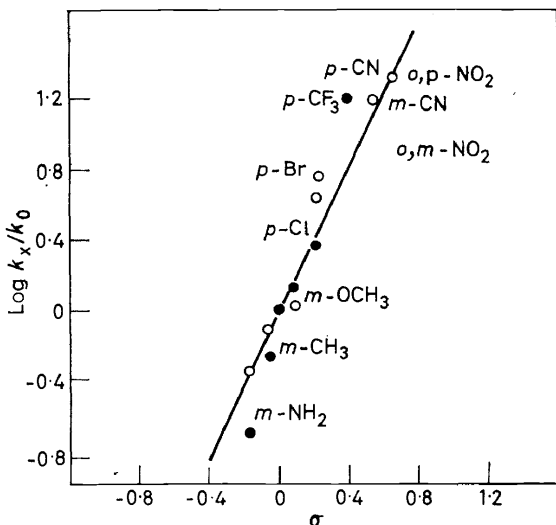


Figure 6. Hammett correlation between substituent constants, the rate of electron transfer from the fluorene anion to substituted nitrobenzenes (\circ) and the catalyzed oxidation rate observed with substituted nitrobenzenes (\bullet). All experiments performed in *t*-butyl alcohol at 25°, 0.1 M in fluorene, 0.2 M in potassium *t*-butoxide, and 0.00048 M in nitroaromatic. For all experiments the ordinate is log initial rate with substituted nitrobenzene-log initial rate with nitrobenzene.

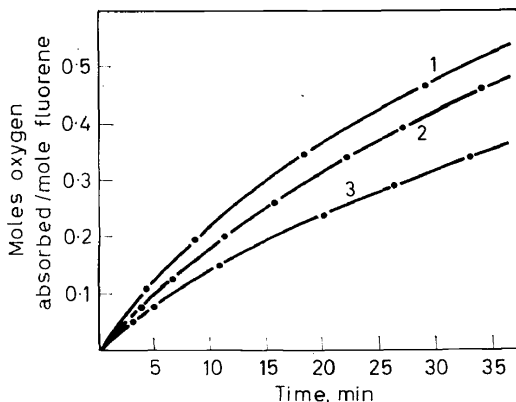


Figure 7. Effect of oxygen pressure on rate of oxidation of 0.1 M fluorene in *t*-butyl alcohol containing 0.2 M potassium *t*-butoxide; (1) 800 mm saturation pressure; (2) 600 mm saturation pressure; (3) 400 mm saturation pressure.

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concentration of base and fluorene the oxidation rate increases linearly with nitrobenzene concentrations up to at least 0.1 M. The rate then asymptotically approaches a maximum value with a second order ionization rate constant (k_i) of ≈ 0.8 litre/mole-sec at 3 M nitrobenzene.

However, some rate increase is still observed at 3 M nitrobenzene. With *m*-trifluoronitrobenzene the rate maximum is reached at a lower concentration of nitroaromatic (see *Figure 8*) and little increase in the rate of

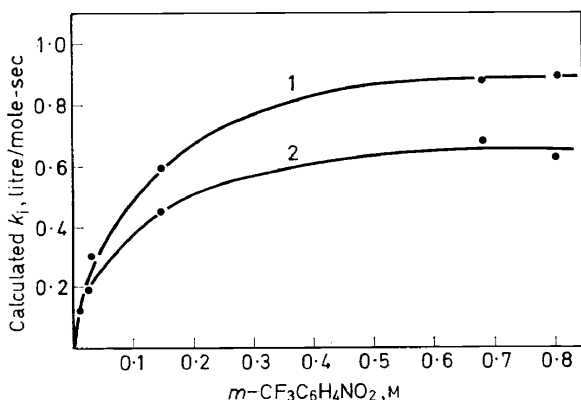
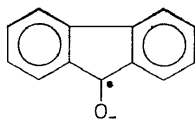


Figure 8. Initial rate of oxidation of fluorene/[fluorene]₀[KOC(CH₃)₃]₀ at 29.5° in *t*-butyl alcohol (curve 1) and initial rate of electron transfer from fluorene to *m*-nitrobenzotrifluoride under the same conditions (curve 2) at 25°. Initial concentration of fluorene and base were approximately 0.02 M.

oxidation is observed above a concentration of *m*-trifluoronitrobenzene of 0.7 M. The value of k_i (litre/mole-sec) indicated for *m*-trifluorobenzene concentrations between 0.7 and 1.3 M is 0.88 ± 0.05 . This can be compared to a rate of hydrogen-deuterium exchange for 9,9-dideuteriofluorene in *t*-butyl alcohol (potassium *t*-butoxide) in accord with $k_i = 0.12 \pm 0.01$ litre/mole-sec. The rate of radical anion formation from the reaction of fluorene, potassium *t*-butoxide and *m*-trifluoromethylnitrobenzene also approaches a limiting value as the nitroaromatic concentration exceeds 0.7 M whence the observed rate of electron transfer is about 0.8 that of oxidation. In view of experimental uncertainties in absolute concentration measurements by e.s.r. spectroscopy (± 30 per cent) it appears that both techniques are consistent with an ionization rate constant of fluorene (*t*-butyl alcohol, potassium *t*-butoxide) of about 0.9 litre/mole-sec, $k_H/k_D \approx 8$.

Oxidation of fluorene in DMSO (80)-*t*-BuOH (20) containing potassium *t*-butoxide occurs quite readily. Interrupted oxidations were shown by e.s.r. spectroscopy to contain significant quantities of fluorenone ketyl (I) (*Figure 9*). However, the formation of (I) is probably not pertinent



(I)

to the oxidation mechanism since (I) can be readily formed and detected in this solvent system by (a) the reaction of deficient quantities of oxygen with 9-fluorenone and base¹¹, (b) electron transfer between 9-fluorenone and

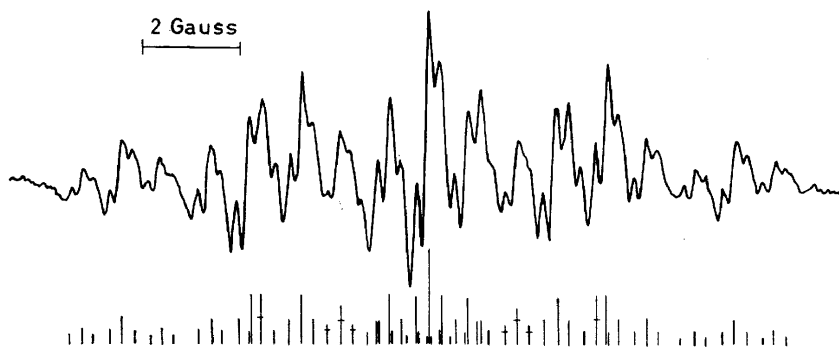
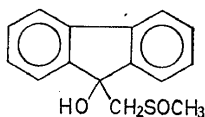


Figure 9. E.s.r. spectrum of fluorenone ketyl detected by the exposure of a solution of fluorenone (0.1 M) in *t*-butyl alcohol (80 volume %)-dimethyl sulphoxide (20%) containing 0.2 M potassium *t*-butoxide to 10 mole % (based on fluorenone) of oxygen at 25°. The correlation diagram is based on the hyperfine splitting constants $a^H = 3.65, 3.65, 2.61, 2.61, 0.81, 0.81, 0.24, \text{ and } 0.24$ gauss.

9-fluorenone in the presence of base¹⁰, or (c) electron transfer between the fluorenyl anion and the ketone¹⁰.

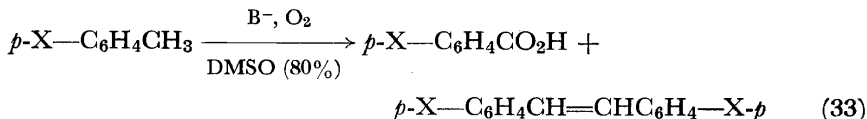
In DMSO (80)-*t*-BuOH (20) the final oxidation product is the fluorenone dimethylsulphoxide adduct (II).



(II)

OXIDATION OF TOLUENE AND *p*-NITROTOLUENE

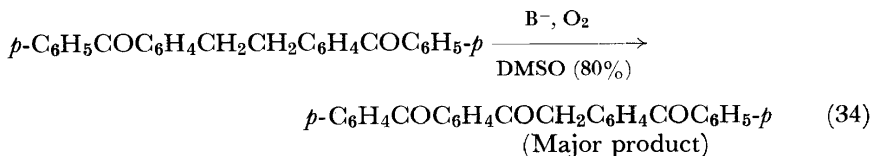
Toluene can be oxidized very slowly to benzoic acid in HMPA solution of potassium *t*-butoxide²⁰. Since the α, α, α -trideuterio derivative is oxidized much more slowly, it appears that ionization rate limited process is involved. More acidic toluene derivatives, such as the *p*-cyano, *p*-carboxy, *p*-phenylazo, *p*-phenylsulphonyl and *p*-benzoyl derivatives give rise to a mixture of the acid and stilbene derivative⁹. No trace of the bibenzyl dimer is detected.



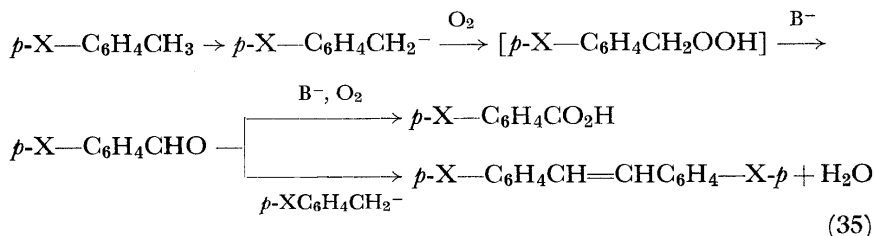
Moreover, in several instances the bibenzyl dimer oxidizes in basic solution

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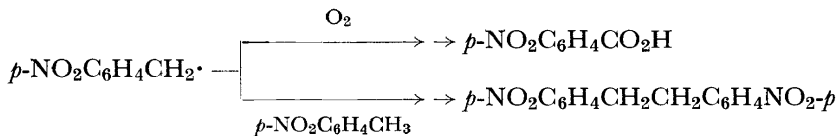
to give products other than the stilbene dimer [see equation (34)]²¹. The addition of radioactive *p*-phenylsulphonylbenzaldehyde to oxidizing



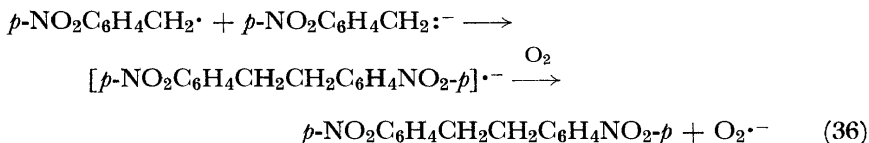
p-phenylsulphonyltoluene showed that the aldehyde and toluene were distributed into the two products to the same degree. Therefore, the oxidation of these aforementioned toluene derivatives apparently involves the initial formation of the aldehyde¹¹



The oxidation of *p*-nitrotoluene in basic solution yields *p*-nitrobenzoic acid and *p,p'*-dinitrobenzyl. The bibenzyl can be slowly oxidized to the stilbene and in solvent systems such as DMSO (80)-*t*-BuOH (20) the stilbene can be converted to the acid in the presence of base and oxygen. The percent conversion to the bibenzyl increases as the initial *p*-nitrotoluene concentration is increased and decreases as the oxygen pressure is increased. The results are qualitatively in agreement with a process involving the *p*-nitrobenzyl radical which can either be trapped to yield the acid or converted to the dimer by some reaction involving additional molecules (or intermediates derived therefrom) of *p*-nitrotoluene.



Elementary considerations exclude the coupling of *p*-nitrobenzyl radicals to yield the bibenzyl from occurring in the presence of oxygen²². A possible pathway involves the trapping of the *p*-nitrobenzyl radical by the *p*-nitrobenzyl anion followed by loss of one electron.



In the absence of oxygen *p*-nitrotoluene spontaneously disproportionates in *t*-butyl alcohol solutions containing potassium *t*-butoxide to yield *p*-nitrotoluene radical anion (2 moles, see Figure 10) and *p,p'*-dinitrobibenzyl

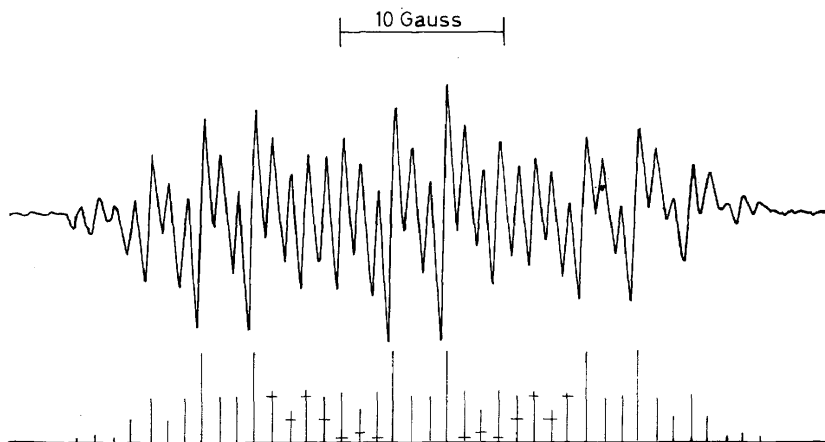


Figure 10. E.s.r. spectrum of *p*-nitrotoluene radical anion formed spontaneously from 0.0025 M *p*-nitrotoluene in *t*-butyl alcohol containing 0.05 M potassium *t*-butoxide. The correlation diagram is based on the hyperfine splitting constants, $a_0^{\text{H}} = a_p^{\text{H}} = a_{\text{CH}_3}^{\text{H}} \approx 3.4$ gauss, $a_m^{\text{H}} = 1.1$ gauss, $a^{\text{N}} = 12.7$ gauss.

(1 mole)²³. The reaction may be driven to completion by the insolubility of the bibenzyl. The rate of formation of the *p*-nitrotoluene radical anion (from initial rate measurements) is first order in *p*-nitrotoluene (Figure 11) and first order in potassium *t*-butoxide (Figure 12). This suggests a process

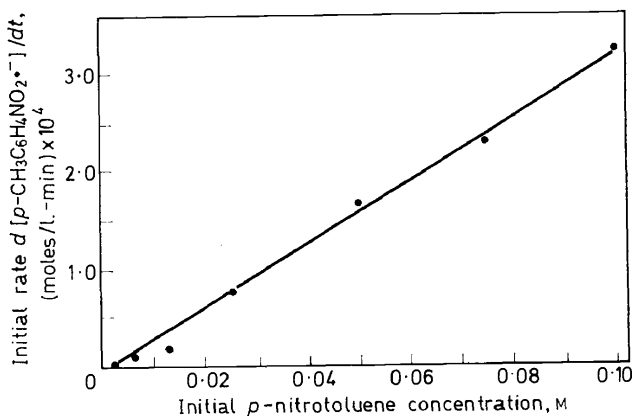
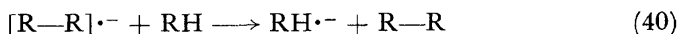
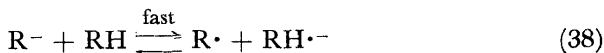
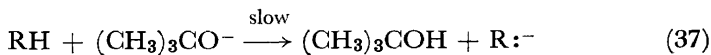


Figure 11. Initial rate of formation of *p*-nitrotoluene radical anion from solutions of *p*-nitrotoluene in *t*-butyl alcohol containing 0.2 M potassium *t*-butoxide at 25°. The concentrations were measured by e.s.r. spectroscopy by comparison of peak heights of the overmodulated signals obtained at constant field with standard solutions of diphenylpicrylhydrazyl under identical instrumental conditions.

DETECTION OF PARAMAGNETIC INTERMEDIATES

limited by the rate of ionization of *p*-nitrotoluene (RH) as described in reactions (37)–(40).



In the presence of oxygen some of the *p*-nitrobenzyl radicals can be trapped to eventually yield *p*-nitrobenzoic acid. However, the high yields of *p,p'*-dinitrobenzyl isolated from reaction mixtures saturated with oxygen at one atmosphere pressure requires that reaction (39) is an exceedingly

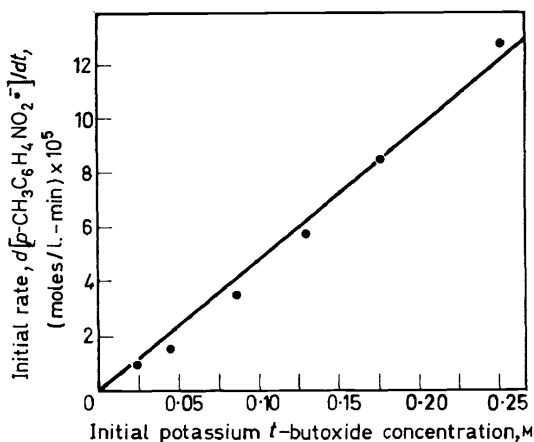


Figure 12. Initial rates of formation of *p*-nitrotoluene radical anion from 0.025 M *p*-nitrotoluene in *t*-butyl alcohol containing potassium *t*-butoxide at 25°.

facile one. The presence of oxygen will reconvert the *p*-nitrotoluene radical anion to *p*-nitrotoluene and superoxide ion [reaction (12)] thus allowing a higher yield of dimer to be achieved in the presence of oxygen than in the absence. The ionization rate constant of *p*-nitrotoluene in *t*-butyl alcohol (potassium *t*-butoxide) is estimated to be 3×10^{-4} litre/mole-sec (experimental uncertainty ± 30 per cent) from the rate of the spontaneous disproportionation reaction as measured by e.s.r. spectroscopy.

In DMSO (80)–*t*-BuOH (20) solutions the spontaneous disproportionation reaction is much faster. Moreover the kinetics of the formation of *p*-nitrotoluene radical anion (Figures 13, 14) take a different form (see kinetic equation).

$$\frac{d[\text{RH}\cdot^-]}{dt} = k[\text{RH}]^2[\text{B}^-]/(k' + [\text{B}^-])$$

This result is consistent with a rapid ionization of *p*-nitrotoluene followed by a slow and rate determining electron transfer step from the carbanion to the unionized *p*-nitrotoluene.

It is concluded that the absorption of oxygen by *p*-nitrotoluene in basic solution is a process not really connected with carbanion oxidation but

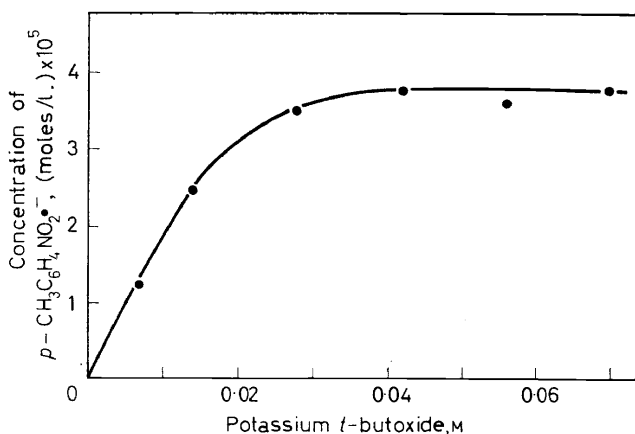


Figure 13. *p*-Nitrotoluene radical anion formed in 2.5 sec by reaction of 0.005 M *p*-nitrotoluene with potassium *t*-butoxide in dimethyl sulfoxide (80 volume %)-*t*-butyl alcohol (20%) at 25°. Each point represents the average of 2-4 experiments.

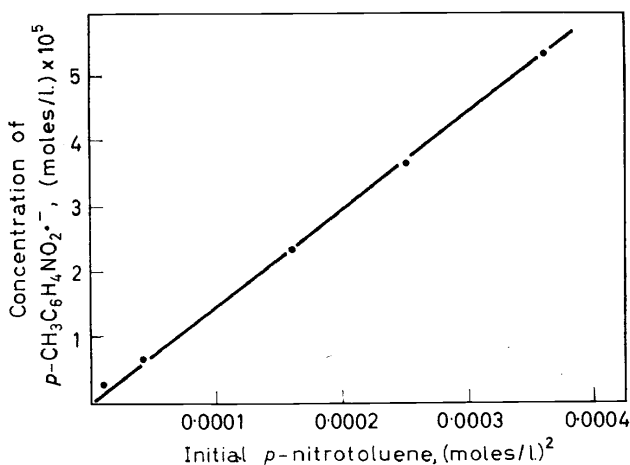


Figure 14. Formation of *p*-nitrotoluene radical anion in 2.5 sec in dimethyl sulfoxide (80 volume %)-*t*-butyl alcohol (20%) containing 0.35 M potassium *t*-butoxide.

simply a side reaction that follows the spontaneous disproportionation reaction (38). Similar disproportionations are noted for many derivatives of *p*-nitrotoluene²³ as well as members of the generalized class of compounds,

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π -CH₃, wherein π is an acid strengthening group that is easily reduced, such as the *p*-nitrophenyl, quinone nucleus, tetrazine nucleus, the isoalloxazines nucleus, or the α -diketone moiety.

OXIDATION OF ALIPHATIC KETONES AND ESTERS

Aliphatic ketones and esters containing ionizable *alpha* hydrogen atoms are readily oxidized in basic solution to yield final products consistent with the formation of an intermediate hydroperoxide. Evidence has been presented that the oxidation of certain unsaturated esters in basic solution does not involve the free radical, i.e., a one-step process similar to reaction (7). The oxidation of acetophenone is catalyzed by nitroaromatics in *t*-butyl alcohol solutions containing potassium *t*-butoxide and there is a correlation between the magnitude of the catalysis and the rate of the electron transfer reaction observed between the enolate anion and the nitroaromatic in the absence of oxygen¹¹.

The reaction of ketones containing an alpha methylene group with deficient quantities of oxygen in basic solution yields only a single type of paramagnetic intermediate identified as the semidione, RC(O[•])=C(O⁻)R' (see Figure 15)²⁴. The formation of semidione radical anions is undoubtedly

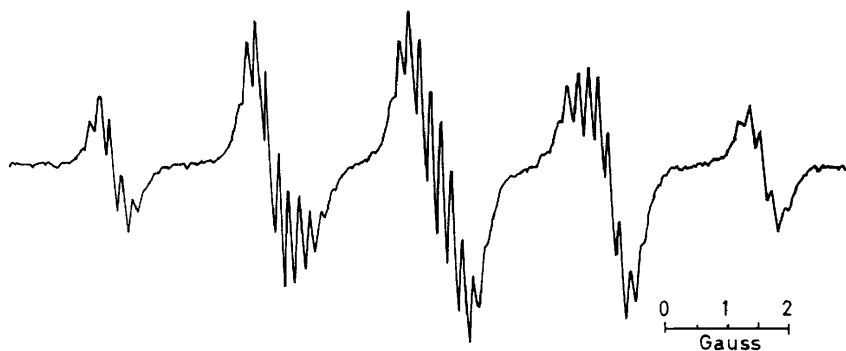
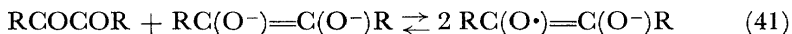
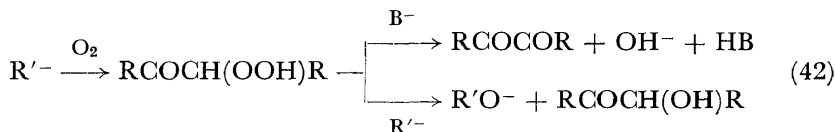


Figure 15. Semidione formed by oxidation of 1-methyl-*syn*-7-methylbicyclo[2.2.1]heptan-2-one (β -santenone) in dimethyl sulphoxide solution containing potassium *t*-butoxide. Long range hyperfine splittings are observed for the 7-*anti* hydrogen atom and the *exo*-5,6-hydrogen atoms [G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.* **87**, 4381 (1965)]. The observed hyperfine splitting constants for hydrogen atoms are: *anti* C-7, 3.05 gauss; C-4, *exo* C-5, *exo* C-6, 2.55 gauss; *syn*-7-methyl, 1-methyl, 0.18 gauss.

a secondary process in the oxidation of a monoketone since both α -diketones and α -hydroxyketones spontaneously yield semidione radical anions in basic solution. Particularly high yields of semidiones are obtained from mixtures of the α -diketone and α -hydroxyketone, presumably via the electronic disproportionation [shown in equation (41)]²⁵.



The formation of both the diketone and hydroxyketone from an initial α -hydroxyperoxy ketone are readily envisioned, reaction (42) with $R'^- = RC(O^-)=CHR$.



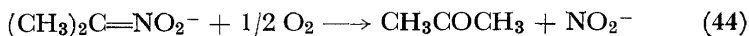
β -Diketones such as cyclohexane-1,3-dione, acetylacetone or malonic esters, are not oxidized by base and oxygen. This is true of many other extremely stable carbanions such as those conjugated with several nitro or cyano groups. In these cases apparently too much resonance energy is lost for the carbanion to participate in reaction (1) or (7)²⁶.

OXIDATION OF 2-NITROPROPANE

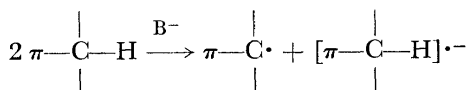
The oxidation of 2-nitropropane in basic solution is a clean cut example of a carbanion oxidation proceeding via a radical chain mechanism²⁷. In the presence of a large excess of hydroxide ion in aqueous solution or a very slight excess of ethoxide ion in ethanol solution, the alkali metal salts of 2-nitropropane are stable to molecular oxygen. Neither reactions (1) nor (7) occurs readily. Under these conditions the reaction can be initiated by nitroaromatics and light, presumably via reaction (43). In the presence of deficient quantities of ethoxide ion or when the hydroxide ion is



not in a large excess, oxidation will occur in an autocatalytic manner in alcohol or water solution. The overall process involves the consumption of one-half mole of oxygen per mole of 2-nitropropane with the production of acetone and nitrite ion in high yield.



In aqueous solution the reaction can be inhibited for extremely long periods of time by arsenic trioxide, a known reducing agent for hydroperoxides. The inhibition periods observed in water can also be removed, by the addition of metal ion, such as the ferrous-feric couple (see *Figure 16*). These results seem to be explainable by a reaction similar to (2)-(4) with a spontaneous initiation step of the type



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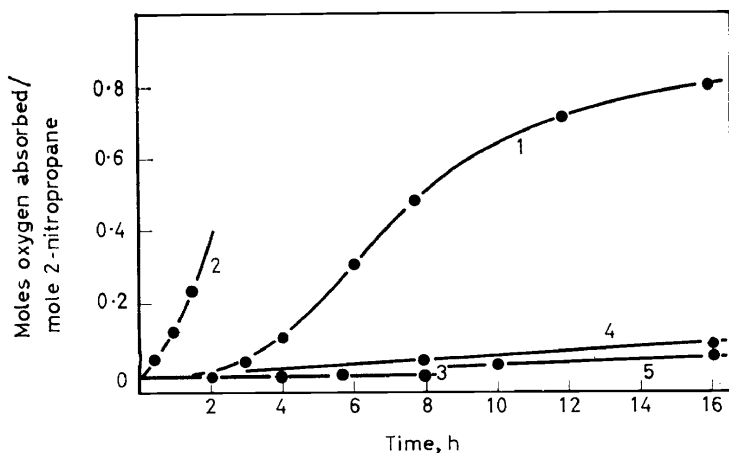
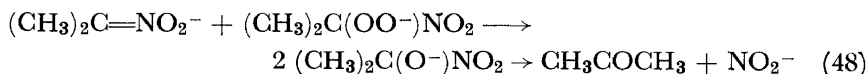
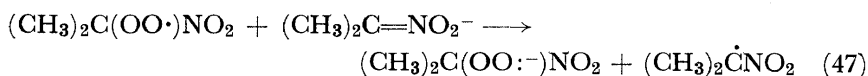
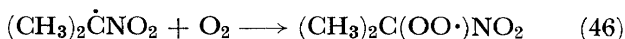
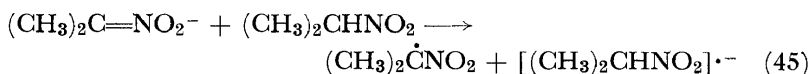
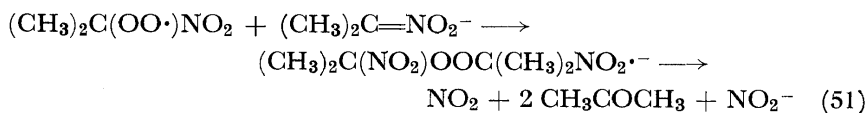
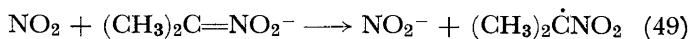


Figure 16. Oxidation of 1.0 M 2-nitropropane in aqueous solution; (1) 2.0 M sodium hydroxide, at this concentration of base the initially formed acetone undergoes extensive further oxidation; (2) 2.0 M sodium hydroxide and 0.01 M Fe^{III}; (3) 2.0 M sodium hydroxide and 0.01 M arsenic trioxide (As₂O₃); (4) 10 M sodium hydroxide; (5) 1.0 M sodium hydroxide, in 16 h 6 per cent of the 2-nitropropane was converted to 2,3-dinitro-2,3-dimethylbutane.

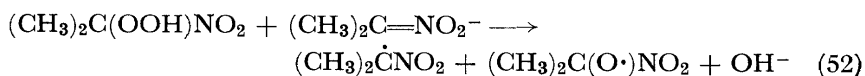
The oxidation sequence can be described by reactions (45)–(48).



However, an alternative chain process involving nitrogen dioxide as an intermediate has not been eliminated [reactions (49)–(51)].

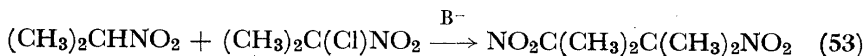


Chain branching (autocatalysis) can be readily explained in terms of a hydroperoxide mechanism by reaction (52).



Since in the presence of excess base the 2-nitro-2-propyl anion does not react with oxygen, whereas the 2-nitro-2-propyl radical is readily oxygenated, a potentially valuable technique for detecting the 2-nitro-2-propyl radical in reactions of the 2-nitro-2-propyl anion is suggested.

This technique has been applied to the coupling reaction of 2-nitropropane and 2-halo-2-nitropropanes in basic solution [reaction (53)].



The coupling reaction occurs readily in ethanol solution in the presence of light to give yields of the dimer in excess of 85 per cent. In the presence of oxygen and light no dimer is formed, the halonitropropane is not consumed, and the 2-nitropropane is converted to acetone and nitrite in high yield. The oxidation will occur under conditions wherein 2-nitropropane is not oxidized in the absence of the halonitropropane. In the dark no oxygen absorption is observed and in the absence of oxygen no dimer is formed (*Figure 17*). The light reaction (coupling) can be inhibited by *p*-dinitrobenzene

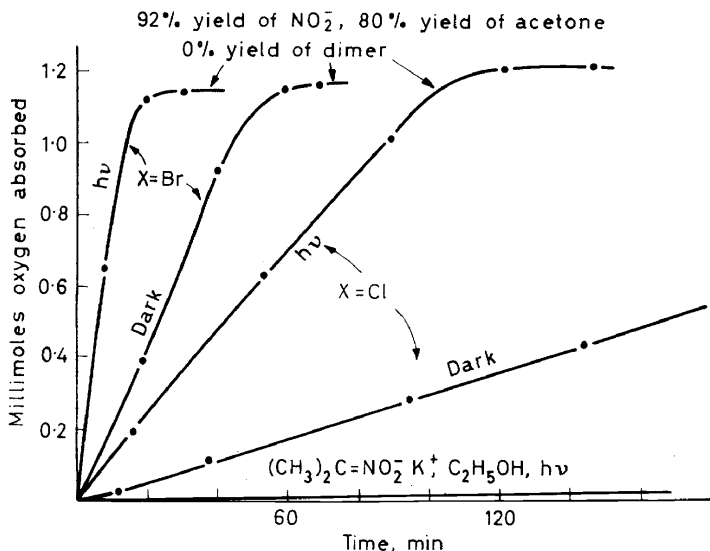
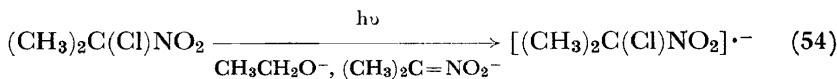


Figure 17. Reaction of molecular oxygen with 10 ml of 0.256 M solutions of 2-X-2-nitropropane, 2-nitropropane and potassium *t*-butoxide at 29°.

with the formation of *p*-dinitrobenzene radical anion. The photochemical coupling reaction is also completely inhibited by Gomberg's radical until the radical has been destroyed whence the coupling occurs at the normal rate (see *Figure 18*).

These results appear to demand the reaction scheme given in equations (54)–(57)²⁹.



DETECTION OF PARAMAGNETIC INTERMEDIATES

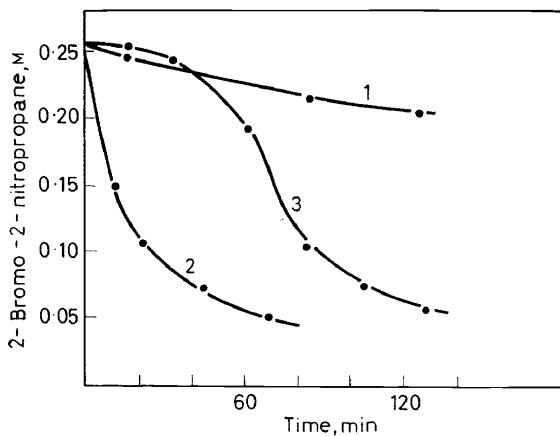
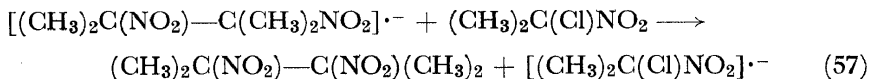
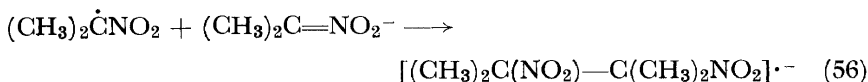
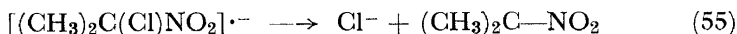


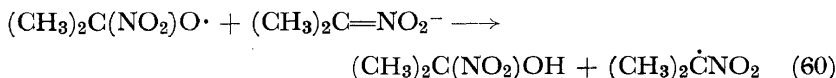
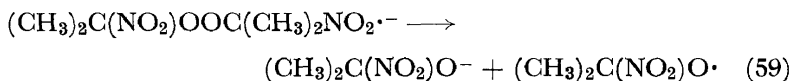
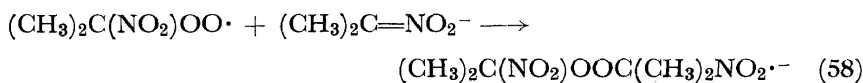
Figure 18. Reaction of 2-nitropropane (0.256 M) with 2-bromo-2-nitropropane (0.256 M) in ethanol containing 0.256 M potassium ethoxide at 13°: (1) the dark reaction; (2) the reaction illuminated with a 275 watt General Electric "ultraviolet" Sunlamp in a water jacketed Pyrex reaction flask, an ultimate yield of 86 per cent of 2,3-dinitro-2,3-dimethylbutane was observed; (3) illumination as in experiment 2 in the presence of 0.002 M-hexaphenylethane.



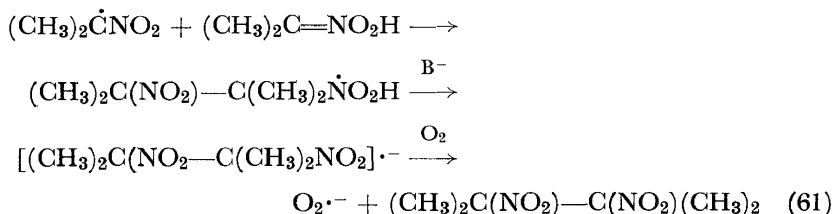
Oxygen, *p*-dinitrobenzene, or triphenylmethyl radical can interrupt the chain reaction by either destroying the 2-nitro-2-halopropene radical anion or the 2-nitro-2-propyl radical.

TRAPPING OF RADICALS BY CARBANIONS IN OXIDATIVE COUPLING

The trapping of a radical by a carbanion which can yield a relatively stable radical anion may be a very important step in oxidative coupling reactions. In the case of *p*-nitrobenzyl radicals reacting with *p*-nitrobenzyl anions we concluded that this reaction could compete with the trapping of the *p*-nitrobenzyl radical by oxygen. In the case of the reaction of 2-nitropropyl radicals with the 2-nitro-2-propyl anion oxygen can completely trap the radical. The conclusions drawn in regard to the coupling reaction suggest another possible radical chain mechanism for the oxidation of 2-nitropropane in basic solution, namely a mechanism involving interaction of the peroxy radical with the anion [reactions (58)-(60)].

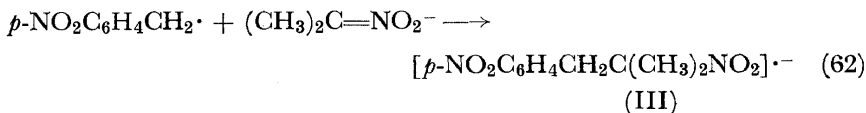


It is of interest that in aqueous solution containing deficient hydroxide ion that a free radical chain oxidation of 2-nitropropane can not be sustained. Instead the dimer is formed very slowly. A possible explanation is that the 2-nitro-2-propyl radical [formed slowly by reaction (45)] is readily trapped by the *aci*-form of 2-nitropropane to yield an intermediate readily destroyed by oxygen to give a product that cannot propagate a chain reaction [reaction (61)].



By the same techniques employed in the investigation of the coupling of the 2-nitro-2-propyl anion with 2-halo-2-nitropropanes it can be shown that the coupling of acetylacetone and malonic esters by iodine in basic solution does not involve free radical intermediates but must involve a $\text{S}_{\text{N}}2$ displacement reaction on the initially formed halo compound.

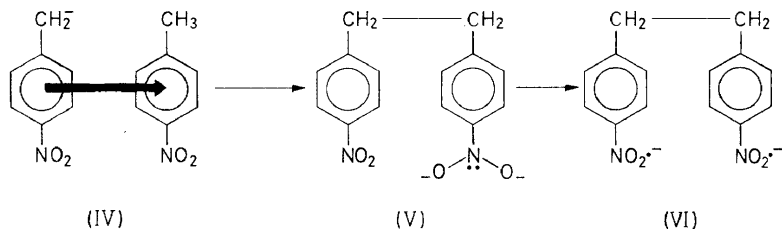
The reaction of *p*-nitrobenzyl chloride with the anion of 2-nitropropane²⁸ also proceeds via a chain process that is readily photochemically initiated and retarded by oxygen, *p*-dinitrobenzene, or hexaphenylethane. The free radical process involves reaction (62) as a key step. In fact (III) is readily



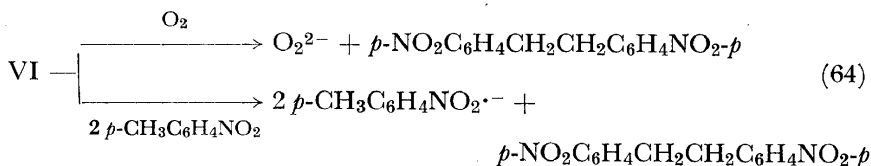
detected under the reaction conditions by e.s.r. spectroscopy. Since reaction (62) occurs readily it follows that if the mechanism suggested previously for the coupling of *p*-nitrotoluene is correct then the coupled product, *p*-NO₂C₆H₄CH₂C(CH₃)₂NO₂, should be formed by the spontaneous disproportionation of *p*-nitrotoluene in the presence of the 2-nitro-2-propyl anion. However, we find only a few per cent of such coupled products³⁰, or the corresponding cross reaction products between the *p*-nitrobenzyl radical and numerous other nitro-substituted carbanions.

DETECTION OF PARAMAGNETIC INTERMEDIATES

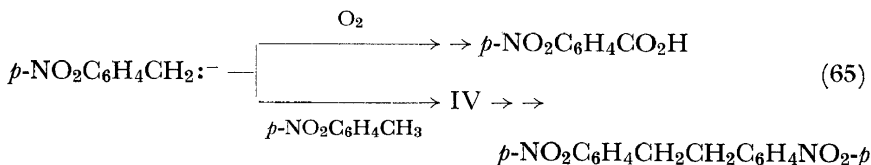
An alternative mechanism for the dimerization of *p*-nitrotoluene in basic solution can be formulated involving a charge transfer complex (IV) between the *p*-nitrobenzyl anion and *p*-nitrotoluene.



Ionization of (IV) would yield intermediate (V) which is formally a dimer of *p*-nitrobenzyl anion³⁰. Intermediate (V) would be expected to rapidly undergo intramolecular electron transfer to yield (VI) which could be readily oxidized to the observed products [reaction (64)]



The oxidation of *p*-nitrotoluene in basic solution to form a mixture of the bibenzyl and *p*-nitrobenzoic acid can be formulated to involve the competition shown in equation (65)³¹.



References

- ¹ M. Gomberg. *Ber. dt chem. Ges.* **33**, 3150 (1900).
- ² W. Schlenk and E. Marcus. *Ber. dt chem. Ges.* **47**, 1964 (1914).
- ³ C. A. Kraus and R. Rosen. *J. Am. Chem. Soc.* **47**, 2739 (1925).
- ⁴ W. E. Backman and F. Y. Wiselogle. *J. Am. Chem. Soc.* **58**, 1943 (1936).
- ⁵ J. Schmidlin. *Ber. dt chem. Ges.* **39**, 628, 4183 (1906).
- ⁶ D. G. Hendry and G. A. Russell. *J. Am. Chem. Soc.* **86**, 2371 (1964).
- ⁷ C. L. Ayers, E. G. Janzen, and F. J. Johnston. *J. Am. Chem. Soc.* **88**, 2610 (1966).
- ⁸ C. Walling and S. A. Buckler. *J. Am. Chem. Soc.* **77**, 6032 (1955).
- ⁹ G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski. *J. Am. Chem. Soc.* **84**, 2652 (1962).
- ¹⁰ G. A. Russell, E. G. Janzen, and E. T. Strom. *J. Am. Chem. Soc.* **87**, 1807 (1964).
- ¹¹ 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* (American Chemical Society), **51**, 112 (1965).
- ¹² G. A. Russell and A. G. Bemis. *Chem. and Ind.* 1261 (1965).
- ¹³ W. Slough. *Chem. Commun.* 184 (1965).
- ¹⁴ A. LeBerre. *Bull. soc. chim. France* 1198 (1961).
- ¹⁵ A. E'ttiene and A. LeBerre. *C.R. Acad. Sci., Paris* **252**, 1166 (1961).
- ¹⁶ A. LeBerre. *C.R. Acad. Sci., Paris* **252**, 1341 (1961); *Bull. soc. chim. France* 1543 (1961), 1682 (1962).

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- 17 Y. Sprinzak. *J. Am. Chem. Soc.* **80**, 5449 (1958).
- 18 N. Kornblum and H. E. DeLaMare. *J. Am. Chem. Soc.* **73**, 880 (1951).
- 19 H. R. Gersmann, H. J. W. Nieuwenhuis, and A. F. Bickel. *Tetrahedron Letters* 1383 (1963).
- 20 J. E. Hofmann, A. Schriesheim, and D. D. Rosenfield. *J. Am. Chem. Soc.* **87**, 2523 (1965).
- 21 Unpublished results with Mr. Y. Suzuki.
- 22 G. A. Russell and R. C. Williamson. *J. Am. Chem. Soc.* **86**, 2364 (1964).
- 23 G. A. Russell and E. G. Janzen. *J. Am. Chem. Soc.* **84**, 4153 (1962).
- 24 G. A. Russell and E. T. Strom. *J. Am. Chem. Soc.* **86**, 744 (1964).
- 25 G. A. Russell, E. G. Janzen, and E. T. Strom. *J. Am. Chem. Soc.* **84**, 4155 (1962).
- 26 G. A. Russell, A. J. Moye, and K. L. Nagpal. *J. Am. Chem. Soc.* **84**, 4154 (1962).
- 27 G. A. Russell. *J. Am. Chem. Soc.* **76**, 1595 (1954).
- 28 R. C. Kerber, G. W. Urry, and N. Kornblum. *J. Am. Chem. Soc.* **87**, 4520 (1965).
- 29 G. A. Russell and W. C. Danen. *J. Am. Chem. Soc.* **88**, 5663 (1966).
- 30 G. A. Russell and E. G. Janzen. *J. Am. Chem. Soc.* **89**, 300 (1967).
- 31 G. A. Russell, A. J. Moye, E. G. Janzen, S. Mak and E. R. Talaty. *J. Org. Chem.* **32**, 137 (1967).