

ELECTRON TRANSFER FROM THE HYDROXIDE ION
TO A CARBON-CARBON TRIPLE BOND

by

Janet E. Halliwell

B.Sc., Queen's University, 1967

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department of
Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

January, 1970

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study.

I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of CHEMISTRY

The University of British Columbia
Vancouver 8, Canada

Date January 21, 1969

ABSTRACT

Supervisor: Professor R. Stewart

A one-electron transfer from the hydroxide ion to the electron acceptor p-nitrotolan was studied in aqueous dimethylsulfoxide by means of visible spectroscopy and electron spin resonance techniques. The possibility of initial nucleophilic attack followed by electron transfer from the carbanion so formed was eliminated. The analogous reaction of methoxide with p-nitrotolan was briefly examined.

TABLE OF CONTENTS

	page
INTRODUCTION	1
A. The Formation of Radical-Anions in Organic Systems	1
B. Hydroxide Ion as an Electron Donor	4
C. Electron Transfer to a Carbon-Carbon Triple Bond	5
D. The Dimerization of the Tolan Radical-Anion	6
OBJECT OF THE PRESENT RESEARCH	7
EXPERIMENTAL	9
A. Purification of Solvents and Preparation of Solutions	9
B. Preparation of Compounds	11
C. Spectral Measurements	12
D. Electron Spin Resonance Measurements	13
RESULTS	14
A. Electron Spin Resonance Studies	14
B. Spectroscopic Studies	20
C. NMR Study	32
D. Further Reactions of p-Nitrotolan Radical-Anion	35

DISCUSSION	39
A. Electron Transfer as the Elementary Act of the Reaction	39
B. Further Reactions of the p-Nitrotolan Radical-Anion	41
SUGGESTIONS FOR FURTHER WORK	46
BIBLIOGRAPHY	48
APPENDIX	51

LIST OF FIGURES

	page
1. E.S.R. Spectrum (High Modulation) of p-Nitrotolan Radical-Anion Produced by Hydroxide Ion Reaction	15
2. p-Nitrotolan Radical-Anion: E.S.R. Spectrum	16
3. E.S.R. Spectrum of p-Nitrotolan Radical-Anion Produced Electrochemically	18
4. Calibration of Spectral Data for p-Nitrodeoxybenzoin Carbanion	22
5. U.V. - Visible Spectra of p-Nitrotolan and p-Nitrotolan Radical-Anion	24
6. Relative Rates of Radical-Anion Formation as a Function of Solvent	26
7. Rate of p-Nitrotolan Radical-Anion Formation	28
8. N.M.R. Spectrum of p-Nitrotolan in DMSO	33
9. N.M.R. Spectrum of Methoxide Addition Product of p-Nitrotolan	34
10. Rate of Formation of p-Nitrodeoxybenzoin Carbanion in the Presence of Oxygen	36
11. U.V. Absorption of Product	38

ACKNOWLEDGEMENT

I would like to thank Professor R. Stewart for his guidance throughout this work. My thanks are also extended to Mr D. Kennedy for his assistance with the E.S.R. work.

Grateful acknowledgement is made to the National Research Council for its financial assistance.

INTRODUCTION

A. The Formation of Radical-Anions in Organic Systems

It is only in the last 10 years that the existence of aromatic radical-anions as important reaction intermediates has been realized. Classifying reactions into "electrophilic" and "nucleophilic" attacks on a substrate disguise the possibility of heterolytic electron transfer as an initial step. As electron resonance spectroscopy became widely used in organic chemistry, large numbers of radical-anions were reported and their role in mechanism was more critically examined.

In 1963, G. A. Russell and E. J. Geels¹ published a summary of the standard methods of generating aromatic radical-anions², in addition to a number of newer methods:

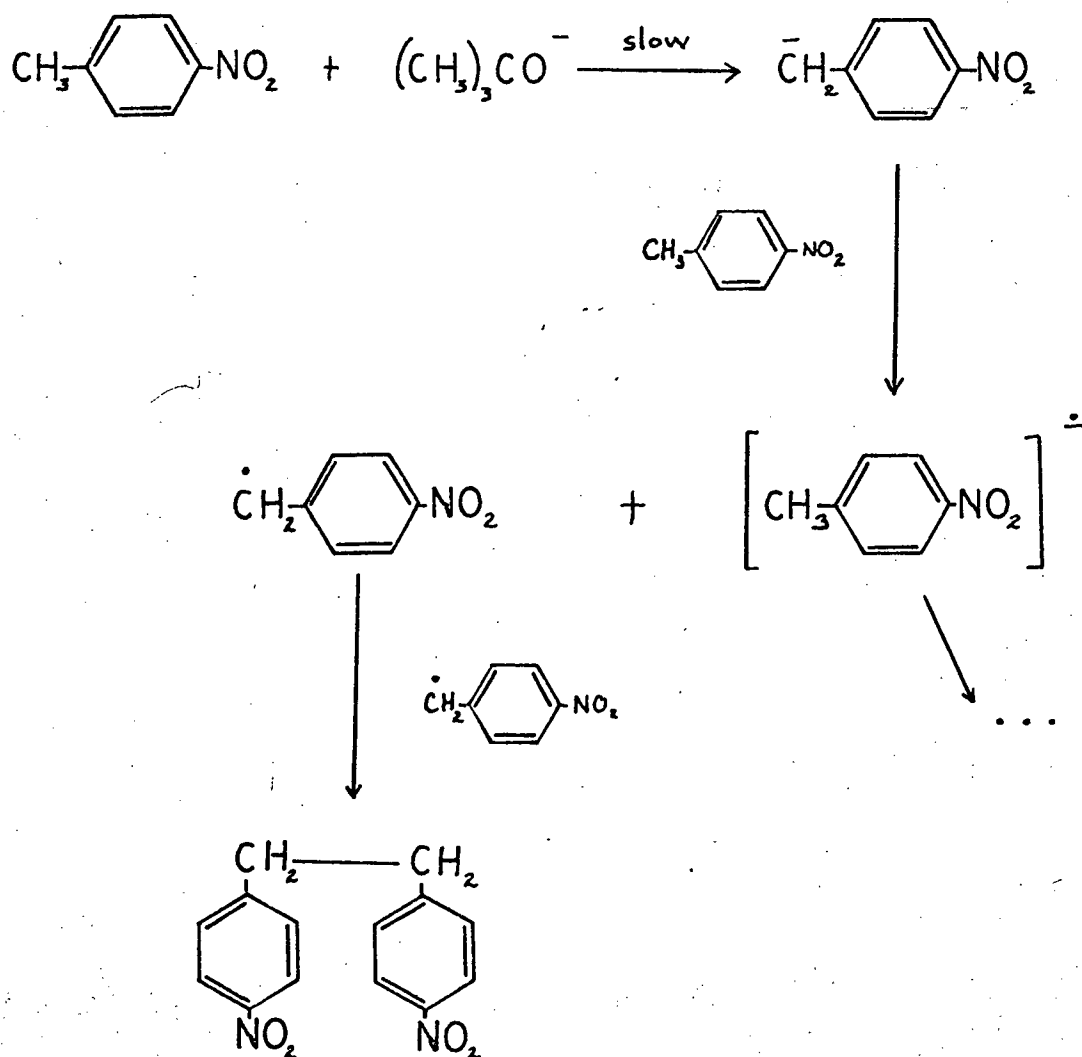
- 1) Reduction by an alkali metal
- 2) Electrochemical reduction
- 3) Zinc or glucose reduction in basic media
- 4) Photolytic generation
- 5) Electron transfer between anions and unsaturated systems
- 6) Homolytic dissociation of 1,4 dianions
- 7) Electron transfer between dianions and molecular oxygen
- 8) Formation of radical-anions in basic solution from hydroxide

addition products of unsaturated systems and electron acceptors

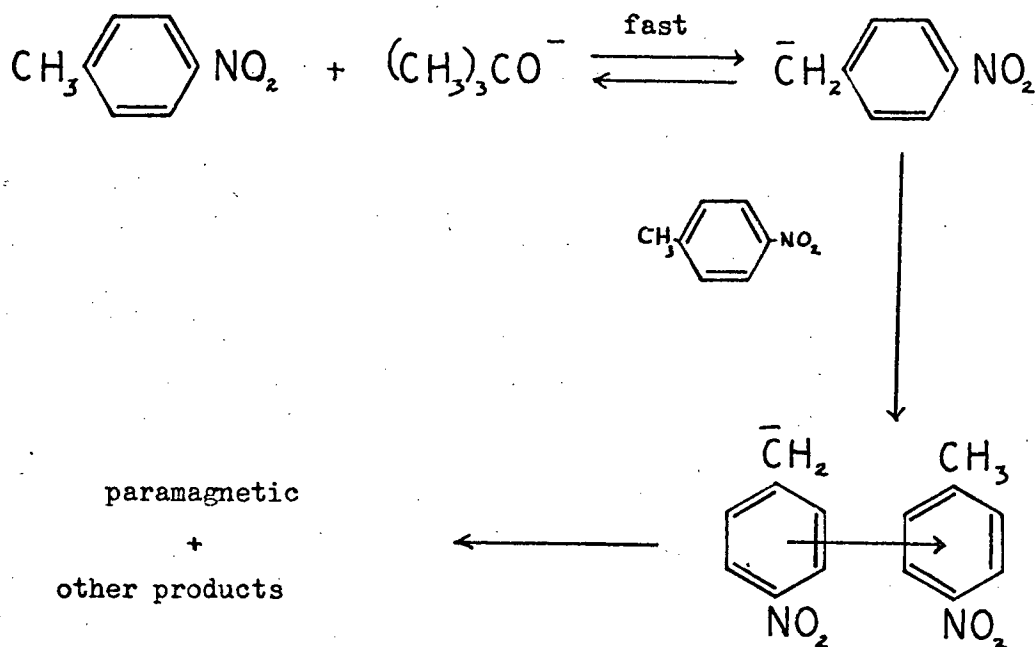
G. A. Russell and co-workers have carried out a great deal of work³⁻⁵

on radical-anion formation in aromatic nitro compounds in a t-butyl-alcohol or dimethylsulfoxide (DMSO) solution of potassium t-butoxide. For example, p-nitrotoluene yields a high concentration of radical-anion in either solvent system. The mechanisms postulated involve initial ionization of the benzylic protons, in both solvent systems, but a complex sequence of disproportionation reactions had to be invoked to rationalize the kinetics and products:

t-butyl alcohol:



DMSO:



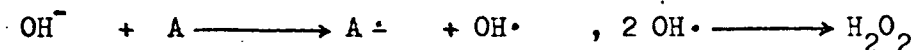
It was then concluded that the main difference in this disproportionation reaction of p-nitrotoluene in t-butyl alcohol and DMSO was merely a change in the rate determining step. In the first case, it was ionization of the benzylic proton, and in the second, the formation of the charge transfer complex or an electron transfer step. The authors then generalized that this "spontaneous disproportionation" reaction was to be expected whenever hydrogen atoms are α to an easily reducible group. Other work has been done by Russell et al on one-electron transfer to nitrobenzenes from strong bases⁶. Here the rate of radical-anion formation is solvent dependent. On the increase in concentration of a dipolar aprotic solvent in a mixture, the rate of production of the radical-anion is increased. These studies indicate the extreme probability of encountering radical-anion formation when

working with aromatic nitro compounds in highly basic media, and the different manners in which electron transfer can occur⁷.

Most radical-anions reported are very highly coloured, but visible absorption techniques have not been frequently employed in studies of these species. Chambers and Adams⁸ have reported a large solvent dependence of radical-anion absorptions in the visible region on studies of the nitrobenzene anion radical in a dimethylformamide: water solvent mixture. This effect was attributed to hydrogen bonding or solvation, and may be used as an indication that the absorption is due to a radical-anion species.

B. The Hydroxide Ion as an Electron Donor

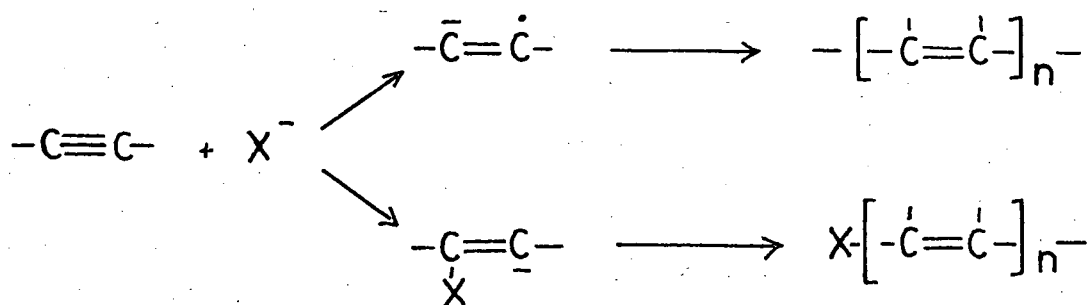
In the literature, there have been reports of a wide variety of anions acting as donors of an unpaired electron, as was indicated by Russell's summary¹. Alkoxide ions have, perhaps, received the most attention, whereas little work has been done on the hydroxide ion as donor. Some work has been done⁹ in this field on the well known electron acceptors: tetracyanoethylene, chloranil, p-benzoquinone, and duroquinone in an aqueous ethanol solution of potassium hydroxide. Here a direct one electron transfer from hydroxide was postulated:



and a qualitative correlation was observed between the yield of the radical anion and the electron affinity of the acceptor. Oxygen was observed to react rapidly with the radicals produced.

C. Electron Transfer to a Carbon-Carbon Triple Bond

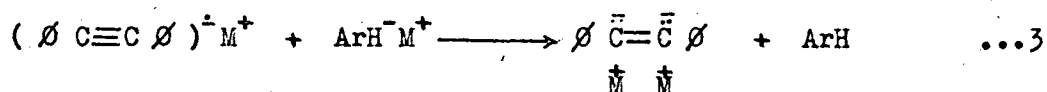
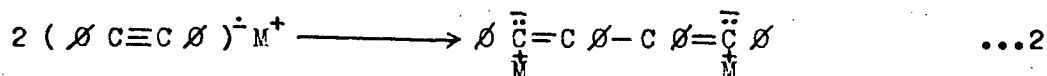
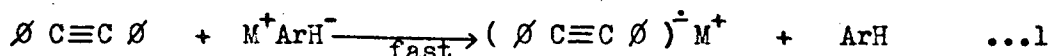
Recently, an investigation of electron transfer to a number of acetylenic compounds in DMF was reported by Dvorko and Shilov¹⁰; SCN^- and I^- both acted as donors to the substrates $\text{MeO}_2\text{C}\cdot\text{C}\equiv\text{C}\cdot\text{CO}_2\text{Me}$, $\text{H}\cdot\text{C}\equiv\text{C}\cdot\text{CO}_2\text{Me}$, and $\text{H}\cdot\text{C}\equiv\text{C}\cdot\text{CO}_2\text{OAc}$, and a one electron transfer was postulated to explain the observed E.S.R. signals. However, a competing nucleophilic attack was also proposed to rationalize the "inhibitory effects" of a proton donor on radical formation. By both mechanisms a polymeric product could be formed:



As previously indicated, a proton donor (acetic acid) decreased the concentration of radical observed, as did oxygen at temperatures above 40°C.

D. The Dimerization of the Tolan Radical-Anion

The dimerization of the tolan radical-anion produced by alkali metal anion reduction has been quite extensively studied^{11,12}, which is interesting in the light of the suggestion that the acetylenic compounds studied¹⁰ produced polymers of low molecular weight. Dadley and Evans looked at the reaction of an alkali metal-aromatic hydrocarbon with tolan in tetrahydrofuran (THF) . The following reaction sequence was postulated:

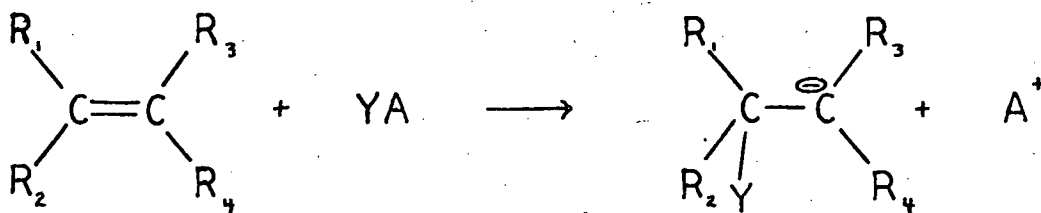


The relative rates of reactions (2) and (3) are dependent on the gegen-ion employed, i.e. K^+ , Na^+ , Li^+ , that is, there is a competition between the dimerization reaction and the second electron transfer. These reactions were followed by visible spectroscopy and by E.S.R. . An estimate of the electron affinity of tolan placed it between 2.70 eV and 2.96 eV . The influence of the alkali metal cation here is so strong that it is difficult to draw analogies with a strictly organic system.

OBJECT OF PRESENT RESEARCH

The initial purpose of this research was to examine the possibilities of forcing the hydration of an acetylenic triple bond by nucleophilic attack on the normally electron-rich centre. For this purpose, the acetylene bond must be sufficiently activated by electron withdrawing substituents, and contain no acidic protons. Thus, the substituted diphenylacetylene (tolan) system was chosen for study in highly basic DMSO : H₂O : OH⁻ medium.

This study was considered to be an extension of the work on nucleophilic attacks on carbon-carbon double bonds, which has received considerable attention over the past ten years^{13,14,15}. Here the primary nucleophilic attack was shown to be always on the positively polarized carbon atom of the double bond giving an unstable carbanion of the same general type. The further reaction of this carbanion was governed by a number of factors: 1) the nature of the nucleophile, 2) the substituent immediately adjacent to the double bond, and 3) the nature of the solvent system.



EXPERIMENTAL

A. Purification of Solvents and Preparation of Solutions

1. Purification of Dimethylsulfoxide (DMSO)

Baker analyzed grade DMSO was degassed with nitrogen and stirred over calcium hydride for 24 - 36 hours. It was then distilled under reduced pressure at 35 - 40°C. The first 15% of the distillate was discarded and subsequent fractions taken off under nitrogen by means of a Perkin triangle. Each flask was sealed with a ground glass stopper and waxed polyethylene film, and once opened was kept over molecular sieves. The DMSO obtained by this treatment contained no more than 0.01% water by titration with Karl Fischer reagent.

2. Preparation of DMSO : Water Stock Solutions

The water used for DMSO : water stock solutions was distilled and degassed by boiling and cooling with nitrogen bubbling through it.

The stock DMSO : water solutions were prepared in liquid reagent bottles and made up approximately by volume. The weights of DMSO and water added were recorded and then Karl Fischer titrations carried out on each solution to determine the exact mole % DMSO concentration. These solutions were sealed with a rubber serum stopper with a flap that bent over the lip and neck of the bottle. This

formed an airtight seal and it was possible to penetrate the serum cap many times without losing its seal.

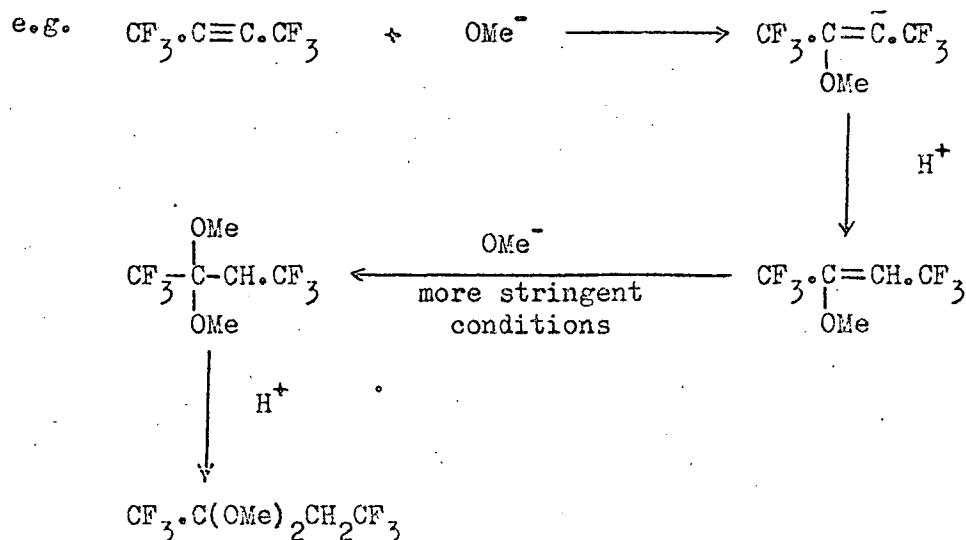
3. Hydroxide Ion Source

Tetramethylammonium hydroxide was employed as the hydroxide ion source using a constant concentration of approximately 0.01 mole/l. It was obtained as a 10% aqueous solution (Eastman Organic Chemicals). Before use it was transferred under nitrogen to a number of small vials sealed with rubber serum caps. In this manner, exposure of the base to air was minimized. The base was transferred to the reaction mixture by means of a calibrated micro syringe.

4. Preparation of Stock Solutions of Reactants

Knowing the concentration of substrate necessary to follow the reaction in the U.V. - visible, the required concentration of the stock solution was calculated for a ten fold dilution. The approximate amount of reactant was accurately weighed out in a 10 ml volumetric flask. To this was added DMSO to make the volume up to 10 ml, and the solution stored in a desiccator.

The only reported instance of such an attack on acetylenic substances was in 1952 by Haszeldine¹⁶, who studied the attack on hexafluorobut-2-yne by methoxide, ethoxide, and a secondary amine in ethanol solution yielding vinylic ethers:



The reaction occurred readily at less than 0°C, but it must be noted that CF₃ has such tremendous electron withdrawing properties that the electronic environment of the triple bond may be substantially altered from that of the tolan system.

In working with p-nitrotolan, it became obvious that some form of radical reaction was occurring, although there was also "evidence" of hydration of the substrate. Thus the system was examined by visible spectroscopy and E.S.R. to determine the mechanism(s) operative.

B. Preparation of Compounds

1. Diphenylacetylene (tolan)

Tolan was prepared from trans stilbene by bromination and subsequent double dehydrobromination of the dibromide in triethylene glycol and KOH¹⁸. The light brown crystals melted 60 - 61°C (Buchi mp), cf literature value of 60 - 61°C¹⁹, and the overall yield of purified tolan was 65% after three recrystallizations from 95% ethanol.

2. (p-Nitrophenyl)-phenylacetylene (p-nitrotolan)

p-Nitrotolan was synthesized from phenylacetylene and p-nitroiodobenzene by the method of Castro et al^{20,21}. Phenylacetylene was converted to the cuprous phenylacetylide by reaction with a Cu^I salt produced by the reaction of hydroxylamine hydrochloride with cupric sulphate. The product was extensively washed with water, ethanol, and ether, and then dried in a vacuum oven at 65°C for 12 hours. The purity of the cuprous phenylacetylide was essential for a reasonable yield of the disubstituted acetylene. The reaction of the acetylide was carried out in pyridine under nitrogen at 90°C for 9 hours. After extraction, the product was recrystallized twice from pet ether (30 - 60) and melted 119.7 - 120.1°C (Buchi); (literature value: 119 - 120°C²⁰).

Microanal. Calc. : C: 75.34 , H: 4.04 , N: 6.28

Expt. : C: 75.55 , H: 4.02 , N: 6.41

3. p-Nitrodeoxybenzoin

p-Nitrodeoxybenzoin was prepared from p-nitrophenylacetic acid by a Friedel Crafts acylation in the following manner. p-Nitrophenylacetic acid (5 gm) was suspended in benzene and anhydrous sodium hydride (0.7 gm) added in benzene, after washing it free of the storage oil. The mixture was stirred at room temperature for three hours. To the sodium salt of the p-nitrophenylacetic acid was added 5 drops of pyridine, followed by oxalyl chloride (4.7 ml)²² . After one hour of stirring at room temperature, the mixture was refluxed for one hour and filtered. This filtrate was concentrated to 50 ml, to which was added anhydrous AlCl_3 (3.8 gm) . After stirring for one hour, the dark reaction mixture was poured onto 25 gm of ice and 10 ml of concentrated HCl . The cream coloured precipitate was filtered, washed, and recrystallized from absolute ethanol to yield cream coloured crystals melting $144.0 - 145.2^\circ\text{C}$; (literature value: 145°C ²³).

C. Spectral Measurements

All U.V. - visible spectral studies were carried out using a Bausch and Lomb recording spectrophotometer, Model No. 502 , with 1 cm. quartz cells. This instrument was equipped with a constant temperature cell holder through which water was pumped from a thermostated bath.

Measurements were carried out in air, or under nitrogen at 25°C unless otherwise noted. The general procedure for measurements under nitrogen was as follows. The solutions were prepared in the quartz cells (which contain approximately 3.2 ml.) , fitted with neoprene stoppers which are easily punctured by syringe needles. The cell was flushed with dry nitrogen for a short time, and then 2.98 ml of the DMSO : water stock solution added by means of a syringe equipped with a Chaney adaptor. Twenty five μ l of the reactant stock solution was then added, and nitrogen bubbled through the solution for three minutes. The base solution was added after the cell had been allowed to equilibrate in the cell block of the spectrophotometer for at least 10 minutes.

The reference cells were handled in the same manner as described above, except for the addition of the 25 μ l of the substrate stock solution. These solutions were always prepared simultaneously with the sample to be studied.

Wavelength scans, or the change of absorption with time at one particular wavelength, were followed with the addition of hydroxide ion as zero time.

D. Electron Spin Resonance Measurements

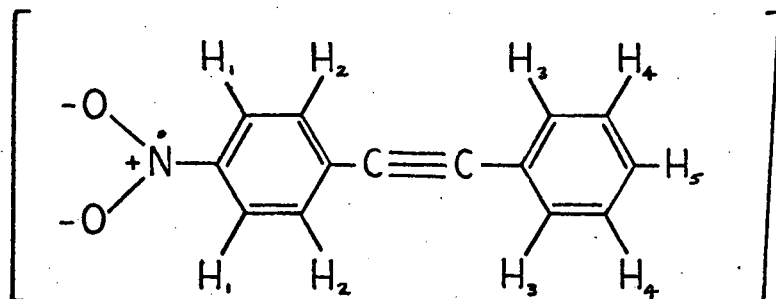
E.S.R. measurements were carried out on a Varian E - 3 spectrometer at room temperature. Care was taken to use degassed solutions and to not expose the reaction mixture to air.

RESULTS

A. Electron Spin Resonance Studies

1. Examination of p-Nitrotolan : Hydroxide Ion Reaction in DMSO

A thoroughly degassed DMSO solution, approximately 1.9×10^{-2} molar in p-nitrotolan, was treated with an excess of tetramethylammonium hydroxide. A very large E.S.R. signal was observed immediately from the deep green solution, and after a number of dilutions with degassed DMSO, a spectrum of high resolution was obtained. It consisted of seven major peaks when examined at high modulation (FIGURE 1 , p. 15), which were split into about 65 doublets or 120 distinct peaks in the high resolution spectrum (FIGURE 2 , p. 16). This spectrum did exhibit the unusual characteristic of being broader and less resolved at the high field end. The results are consistent with the formation of a p-nitrotolan radical-anion, produced by one-electron transfer to the neutral p-nitrotolan molecule from some donor anion or neutral species. The radical-anion may be pictures as:



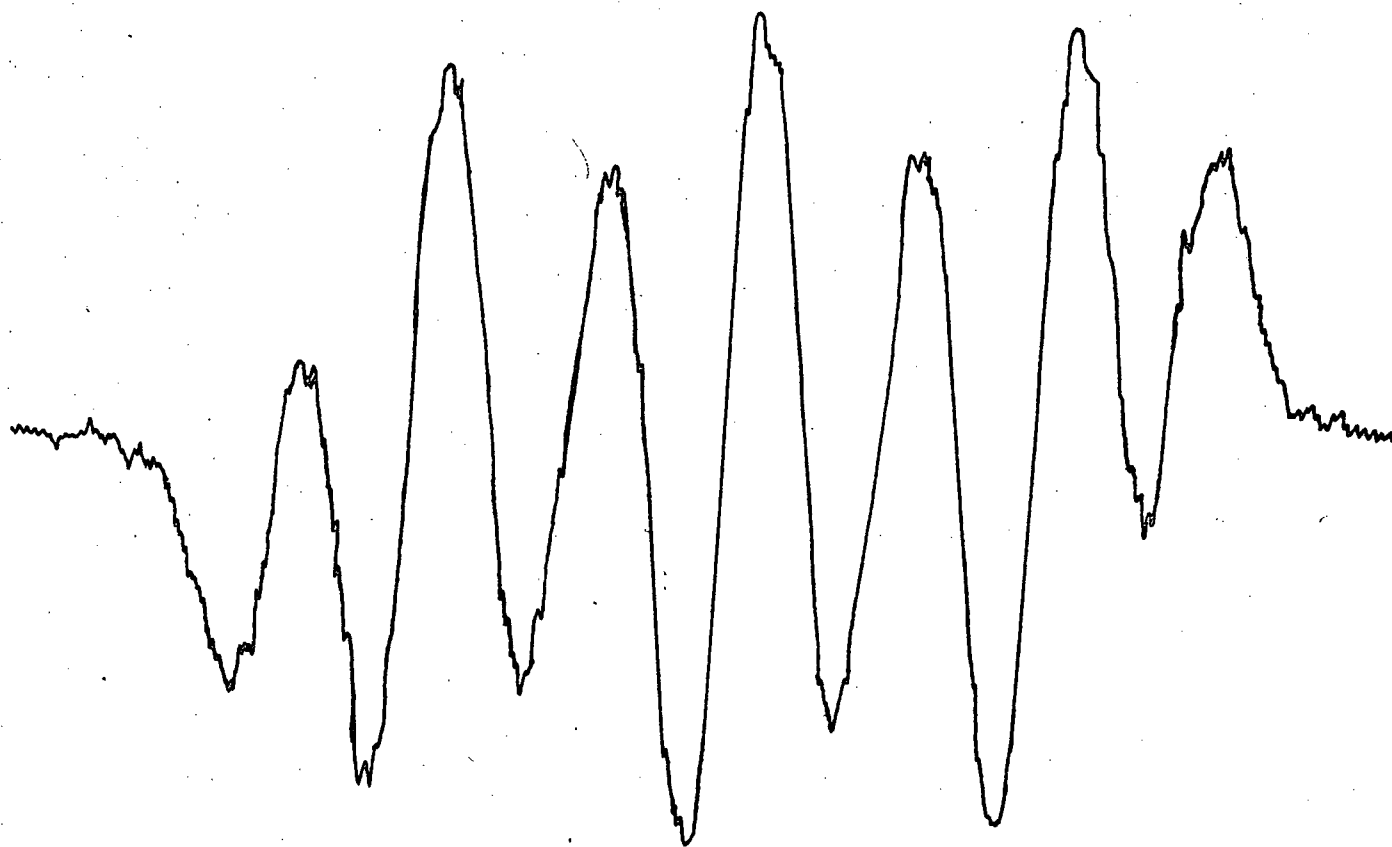
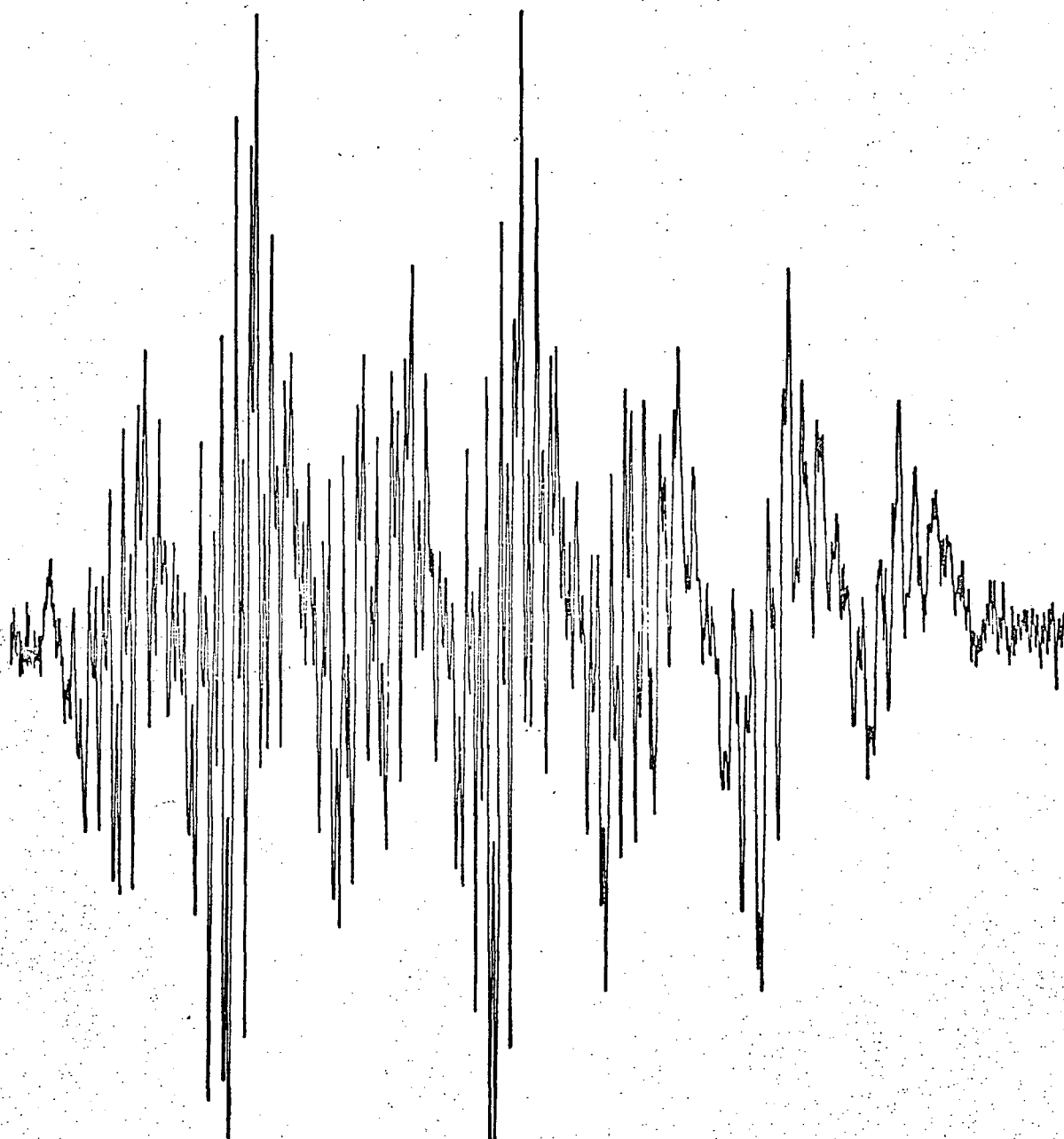


FIGURE I

E.S.R. Spectrum (High Modulation) of p-Nitrotolan Radical-Anion Produced by Hydroxide Ion Reaction



p-Nitrotolan Radical - Anion

FIGURE 2

Because of the interaction with the nitrogen nucleus, the free electron resonance is split into three components of equal intensity and with splitting a_N . A further interaction with the two equivalent H_1 's will further split each of these components into three of intensity 1 : 2 : 1, and with splitting a_{H_1} . But if $a_{H_1} \simeq \frac{1}{2}a_N$, a spectrum of seven components would be expected, as was actually obtained. Further analysis of the splitting due to more distant protons was consistent with those peaks observed.

2. Electrolytic Production of the p-Nitrotolan Radical-Anion

It was necessary to prove that the E.S.R. spectrum observed was actually due to the p-nitrotolan radical-anion, and not due to the radical of an addition product, which was a possibility analogous to some of the work of G. A. Russell et al. Hence, a radical was produced electrochemically from a solution of p-nitrotolan and TPAP (tetra-N-propylammonium perchlorate), used as charge carrier, in DMSO. A low current of about 1.5 volts was passed through the solution for a short time, and a greenish colour developed. A strong E.S.R. signal was recorded, which again consisted of seven major peaks. This is illustrated in FIGURE 3, p. 18. It was not possible to resolve this spectrum as completely as that of the previous case due to the high viscosity of the pure DMSO medium. In the first experiments, the

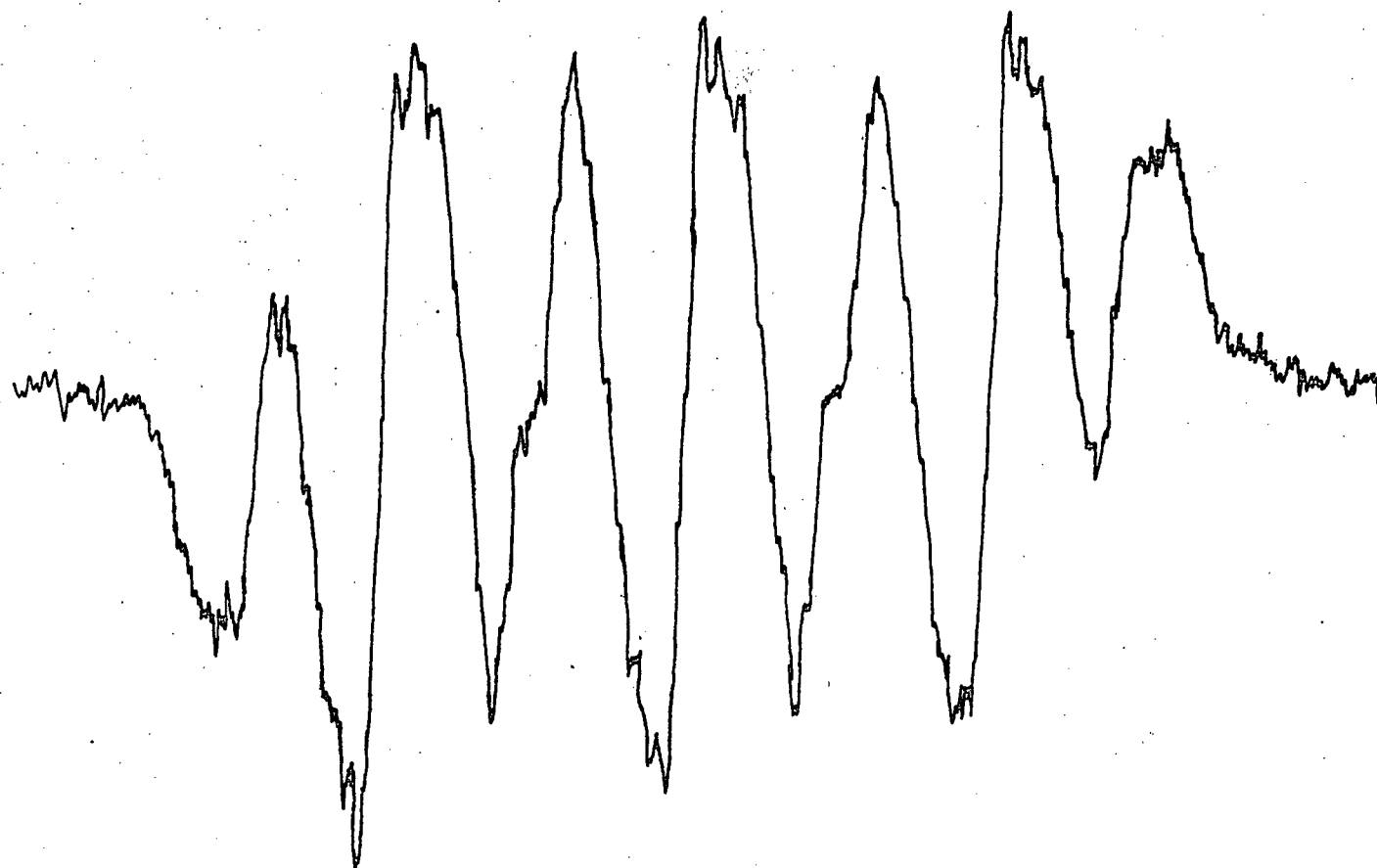


FIGURE 3

E.S.R. Spectrum of p-Nitrotolan Radical-Anion Produced
Electrochemically

hydroxide ion was added as an aqueous solution, and the resulting viscosity decrease allowed a much higher degree of resolution. However, this spectrum was seen to be superimposable on that produced by the reaction mixture and observed at high modulation.

3. Computer Analysis of Splitting Values

To obtain good approximations of the splitting constants from the spectrum a method of "best fit" was employed. The values of the splittings were estimated from the spectra, and were used in a computer programme which plotted the appropriate derivative E.S.R. signal. By comparison with the original spectrum, and by successive approximations, values for the splitting constants were obtained as follows:

$$a_N = 7.60 \text{ gauss}$$

$$a_{H_1} = 3.83 \text{ gauss} ; \quad a_{H_2} = 1.3 \text{ gauss} ; \quad a_{H_3} = 0.5 \text{ gauss} ;$$

$$a_{H_5} = 0.25 \text{ gauss} .$$

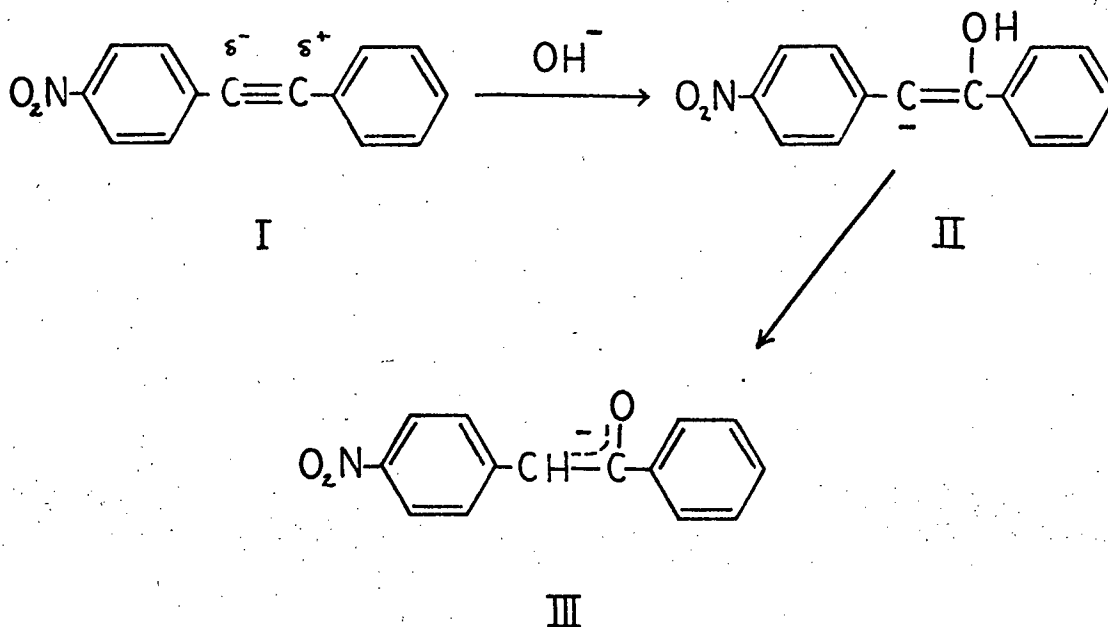
B. Spectroscopic Studies

1. Unsubstituted Diphenylacetylene

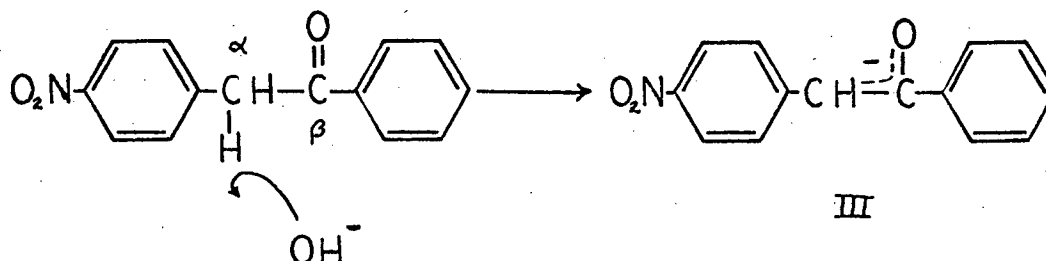
A tolan solution of concentration 4.55×10^{-5} molar was prepared in anhydrous DMSO. To this, at 25°C was added OH^- (0.01 molar) and the U.V. - visible spectrum observed as a function of time. No change was noted over 72 hours. This was repeated at 35°C , and again no change in spectrum was observed.

2. p-Nitrodeoxybenzoin

If a nucleophilic attack on p-nitrotolan were to occur, an unstable carbanion would be expected to form, which would then undergo rapid tautomerism to a more stable species according to the following scheme:



Thus, to absolutely identify intermediate III, it was prepared by the reaction of hydroxide ion on p-nitrodeoxybenzoin:



The α hydrogens of p-nitrodeoxybenzoin are weakly acidic, and a proton may be removed by KOH in ethanol. Thus it was assumed that OH^- in DMSO caused complete ionization, giving one a means of calculating the extinction coefficient.

On the addition of base (0.01 molar) to a p-nitrodeoxybenzoin solution of 1.8×10^{-5} mole/litre an intense blue colour develops, corresponding to a wide absorption peak at 584 $\text{m}\mu$. An extinction coefficient of 53,300 was calculated for this species at 584 $\text{m}\mu$ in 94.74 mole % DMSO.

A distinct solvent dependence of λ_{max} and O.D._{max} was observed for this carbanion (III) and hence these were calibrated against solvent molarity as indicated in TABLE 1, and FIGURE 4, p. 22.

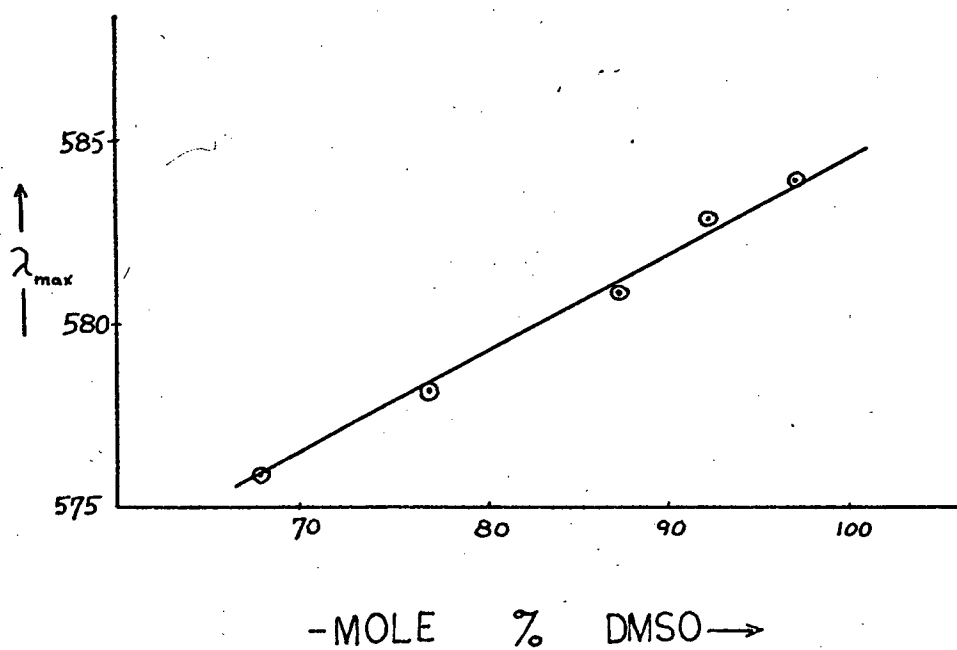
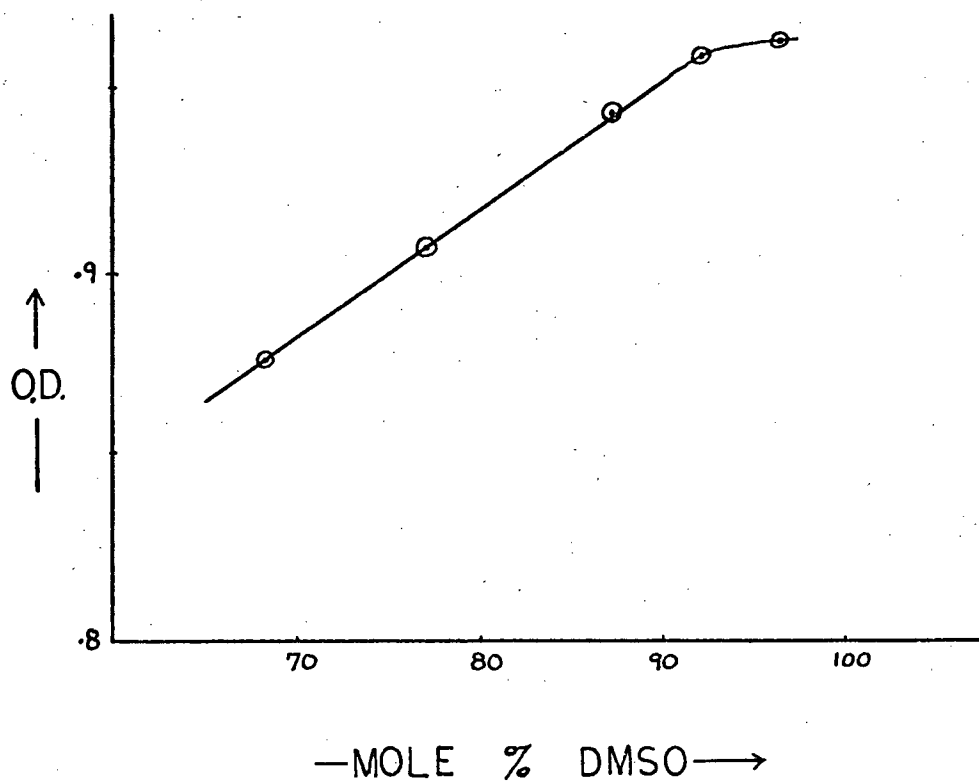


FIGURE 4

Calibration of Spectral Data for p-Nitrodeoxybenzoin Carbanion

TABLE 1

Mole % DMSO	O.D. _{max}	λ_{max} (m μ)
96.74	0.961	584
92.20	0.959	583
87.52	0.944	581
77.03	0.907	578
68.05	0.875	576

3. p-Nitrotolan and Hydroxide Ion

From a solution of p-nitrotolan (2.99×10^{-5} mole/litre) in DMSO, an extinction coefficient of 20,890 was calculated for the one major absorption peak, with no fine structure, at 332 m μ . (see FIGURE 5, p. 24).

The reaction of p-nitrotolan with hydroxide ion was first examined in the presence of oxygen, and a slow buildup of a blue species absorbing at 583 m μ was noted. The rate of production of this species increased with temperature, and with an increase of the DMSO content of the solvent. The rate of production of this species, identified as the p-nitrodeoxybenzoin carbanion, was reproducible, but after some time, the carbanion disappeared.

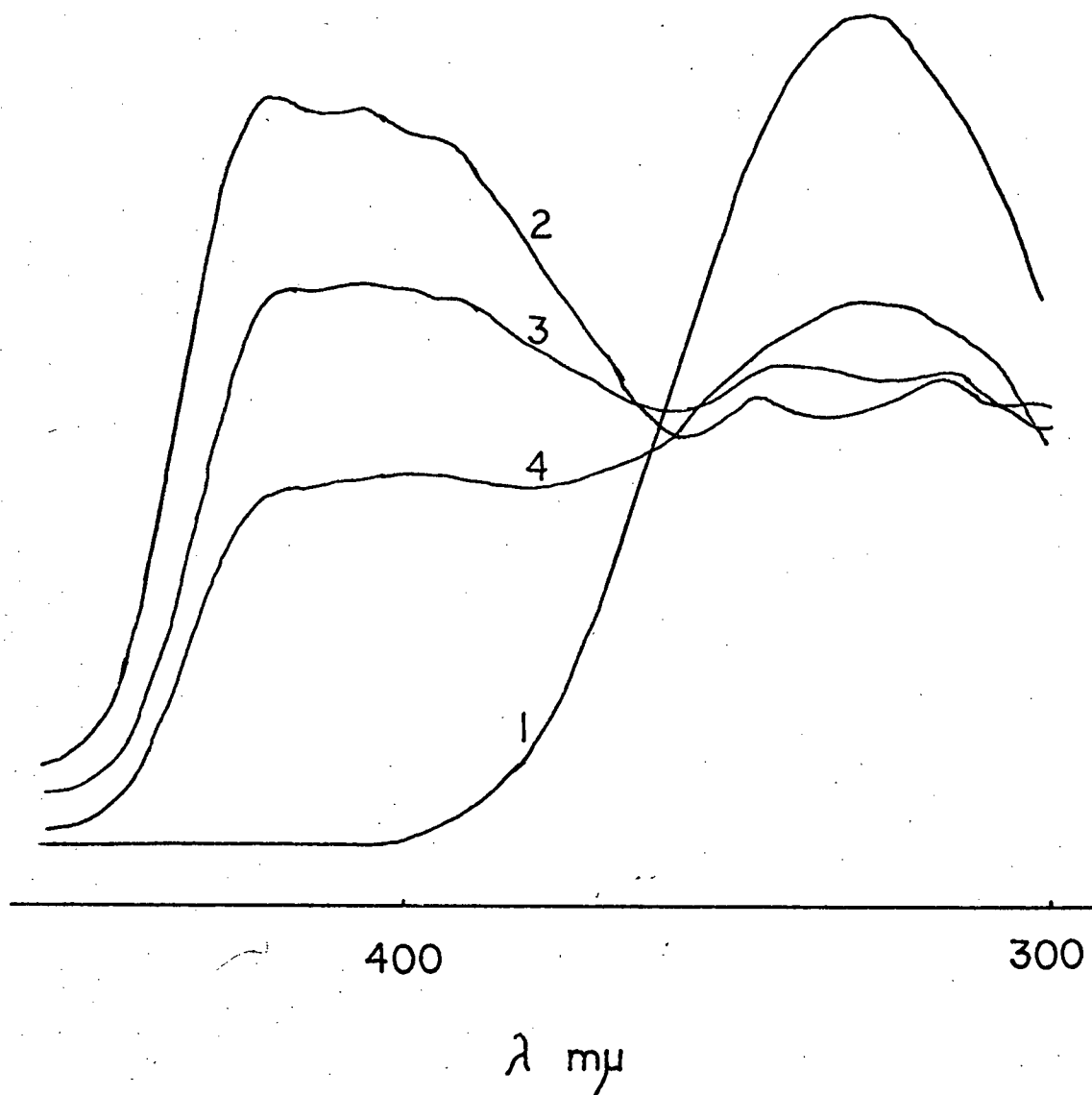


FIGURE 5

U.V. - Visible Spectra of p-Nitrotolan and p-Nitrotolan Radical-Anion

1. p-Nitrotolan (3×10^{-5} mole/litre)
2. p-Nitrotolan Radical-Anion produced in 96.74 mole % DMSO
3. p-Nitrotolan Radical-Anion produced in 94.04 mole % DMSO
4. p-Nitrotolan Radical-Anion produced in 92.20 mole % DMSO

The same reaction was then carried out in pure DMSO under nitrogen employing degassed solutions. On following the 300 - 600 μ region of the visible spectrum, a broad absorption band was observed to form in the 390 - 428 μ area with a maximum at 427 μ . This had some fine structure, and the absorption maximum seemed extremely sensitive to solvent composition, which is illustrated in FIGURE 5, p. 24. A small absorption peak was observed to form in the 583 μ region. These changes were accompanied by a rapid decrease in the p-nitrotolan peak (332 μ) and the creation of an absorption peak at slightly lower λ . On passing oxygen through the reaction mixture, the 390 - 428 μ peak disappeared immediately, and little change was initially observed in the 582 μ region. The wide absorption over 390 - 428 μ was thus attributed to a radical-anion.

The reaction of hydroxide ion with p-nitrotolan was then carried out in solvents of varying basicity (as measured by the H_- function), but always with a large excess of OH^- . The rate of increase of the radical-anion concentration was followed by monitoring the solution at the appropriate λ_{max} (see FIGURE 5, p. 24) and typical results are plotted in FIGURE 6, p. 26. Here values of O.D. vs time are plotted for DMSO : H_2O solvent systems: 1) 96.74 mole % DMSO at 427 μ ; 2) 94.04 mole % DMSO at 422 μ ; 3) 92.20 mole % DMSO at 410 μ . The absolute value of the extinction coefficient of the radical-anion is not known, and hence, only a relative picture can be

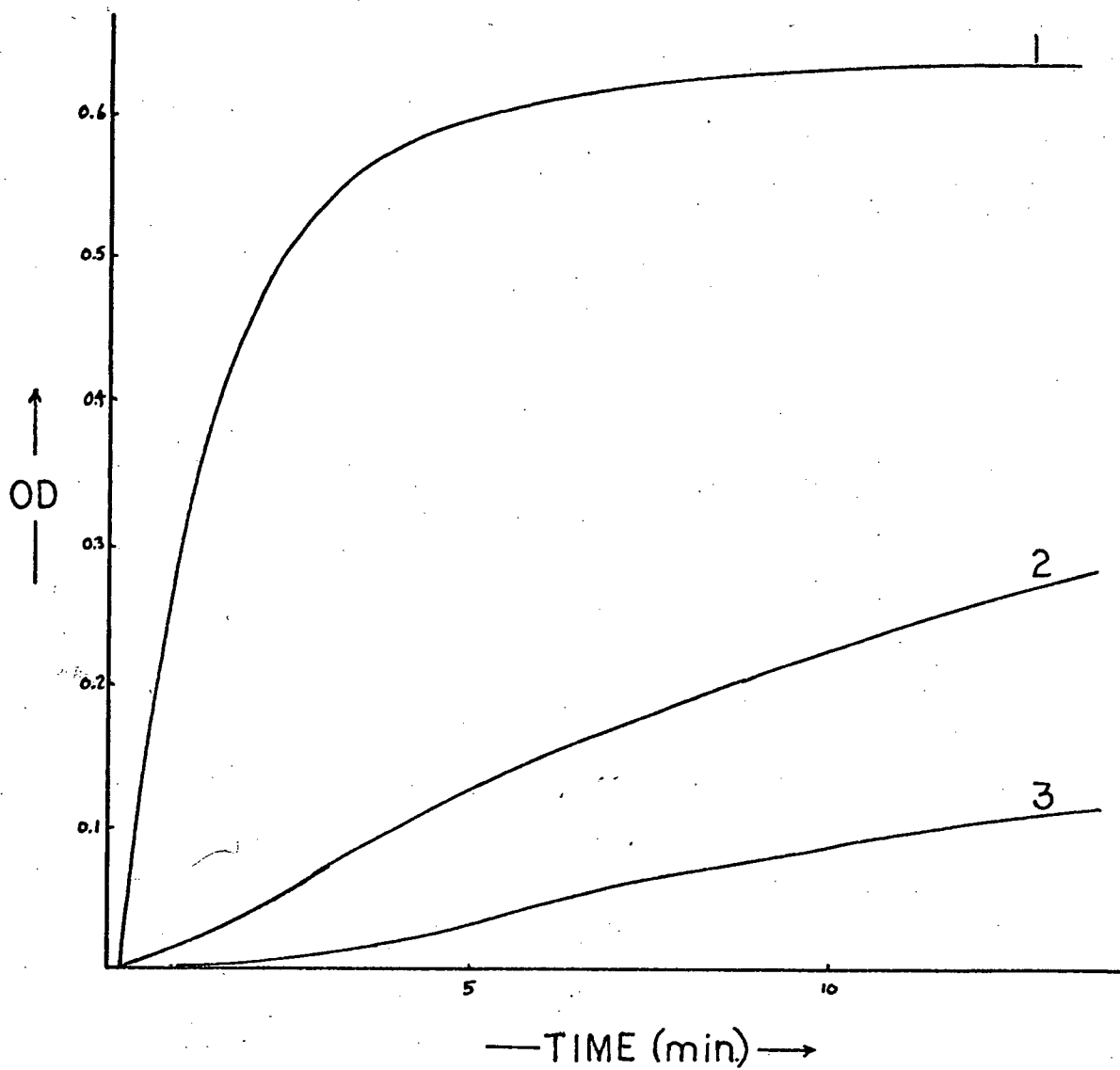


FIGURE 6

Relative Rates of Radical-Anion Formation as a Function of Solvent

- Composition:
- 1) in 96.74 mole % DMSO at 427 m μ .
 - 2) in 94.04 mole % DMSO at 422 m μ .
 - 3) in 92.20 mole % DMSO at 410 m μ .

obtained. The runs were carefully carried out in triplicate under nitrogen, but results were not completely reproducible, although runs for each solvent system fell in the same range. This was attributed to the action of oxygen as an electron scavenger. Due to the low concentration of substrate, 3×10^{-5} mole/litre, a very small amount of oxygen could have a relatively large effect on radicals in solution. Thus all solutions would have to be prepared and handled in an oxygen free atmosphere to obtain meaningful results.

The effect of a change in the initial concentration of the substrate, p-nitrotolan, was examined by using concentrations of 3×10^{-5} and 6×10^{-5} molar. Plots of O.D. at 427 m μ vs time for these reactions are shown in FIGURE 7, p. 28. The initial slopes of the curves give a relative measure of the rate of radical-anion production, and it was found that:

$$\frac{\text{Slope } 1_{\text{init.}}}{\text{Slope } 2_{\text{init.}}} = \frac{dc_1/dt}{dc_2/dt} = \frac{.665}{.342} = 1.95 \simeq \frac{[\text{p-nitrotolan}]_1}{[\text{p-nitrotolan}]_2}$$

Thus, assuming that the radical-anion is formed in the rate determining step of the reaction, or is a direct monitor of the rate determining step, this result indicates that the reaction of p-nitrotolan and OH^- in excess OH^- is pseudo first order in the p-nitrotolan.

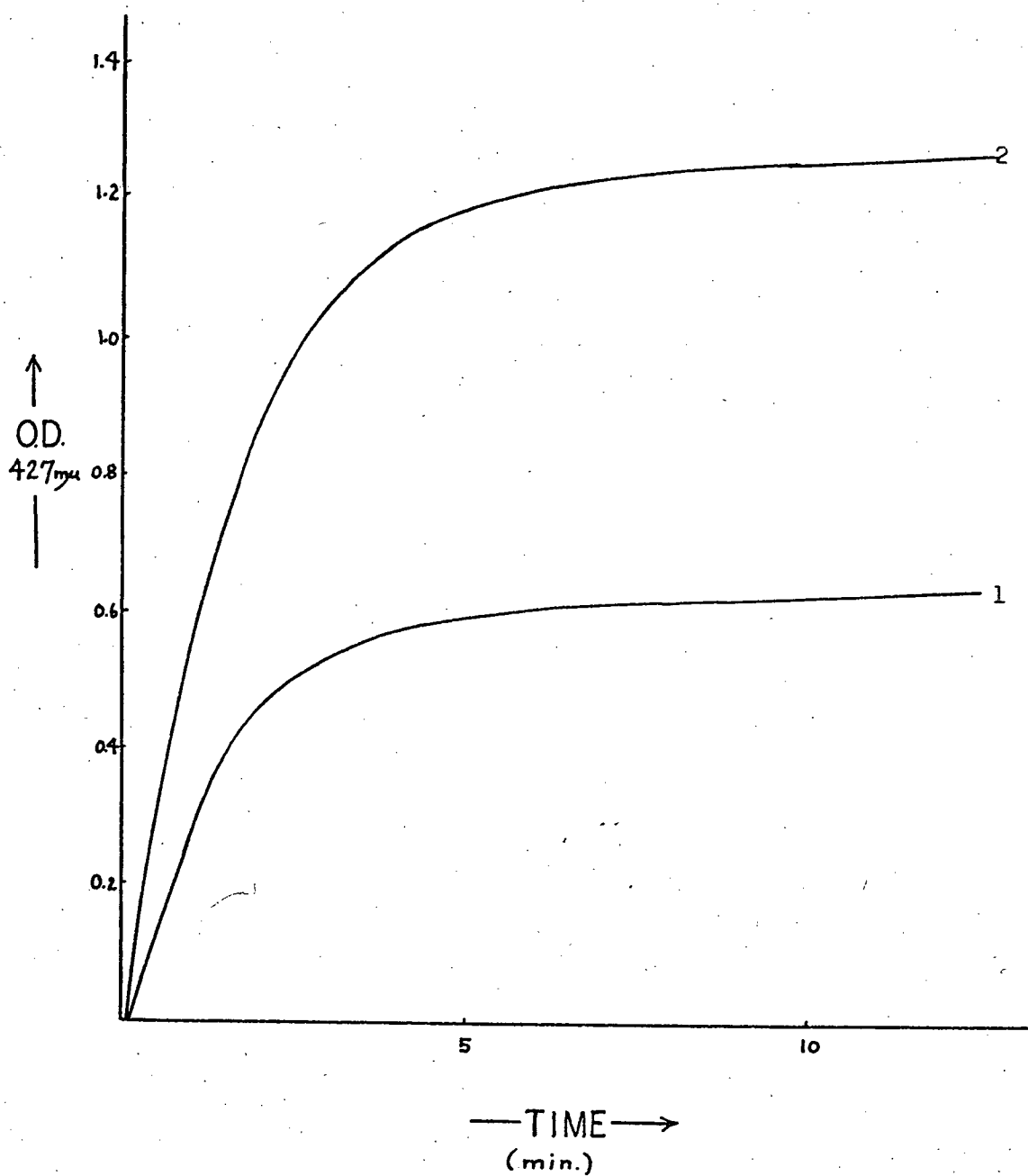


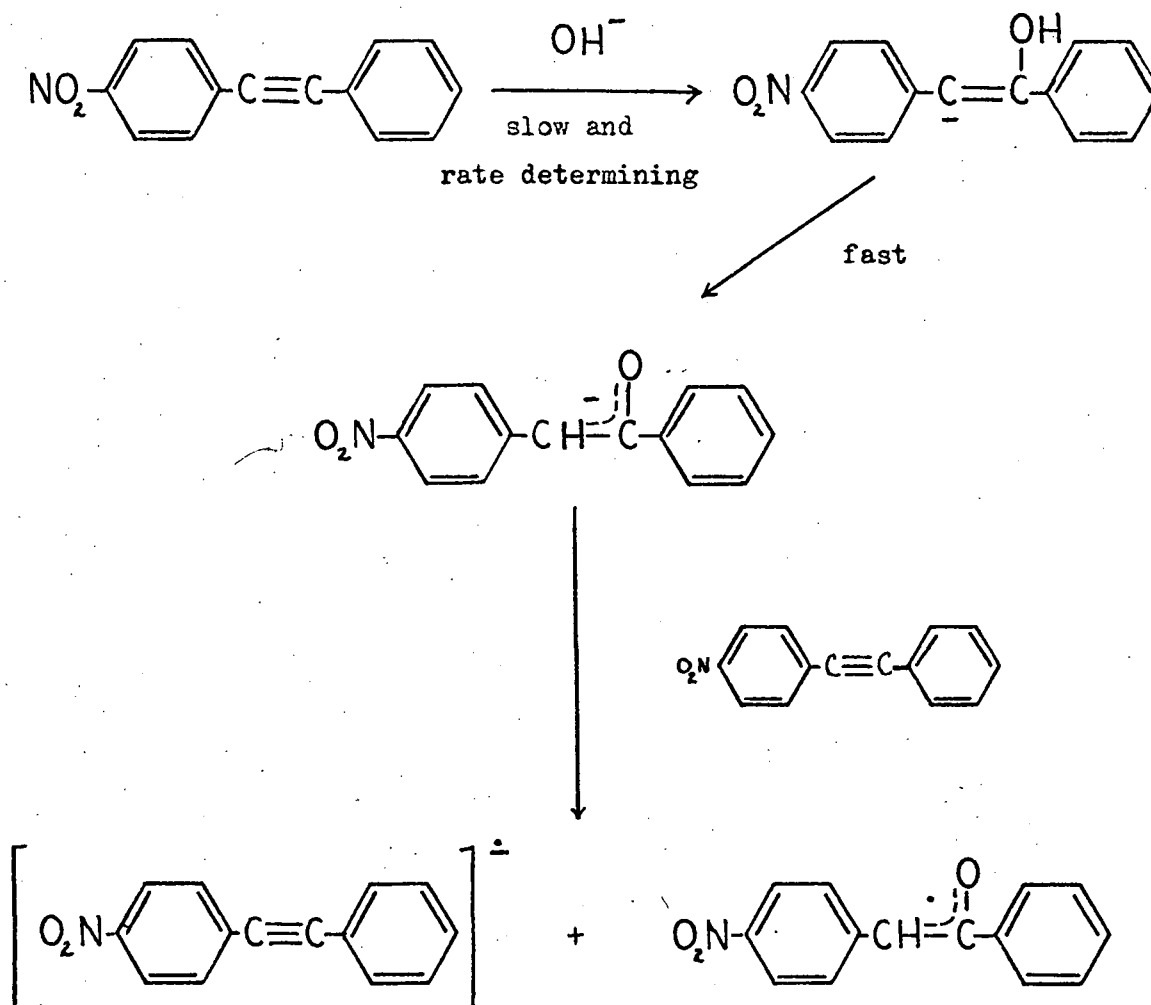
FIGURE 7

Rate of p-Nitrotolan Radical-Anion Formation

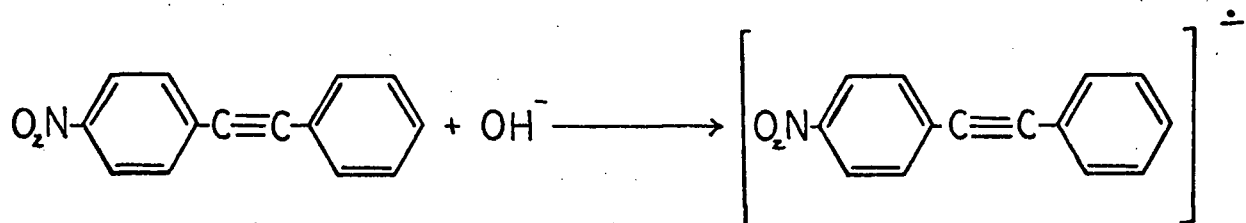
1) 3×10^{-5} molar	}	C_0
2) 6×10^{-5} molar		

An analysis of the results up to this point, taken in conjunction with the literature on radical-anion formation, allows one to postulate two plausible mechanisms to account for the formation of the p-nitrotolan radical-anion.

Mechanism 1: A nucleophilic attack followed by tautomerism and electron transfer from the carbanion so formed.



Mechanism 2: Single electron transfer from the hydroxide ion directly to p-nitrotolan.



Both mechanisms presented are consistent with the fact that the p-nitrotolan radical-anion is produced during the reaction and with the qualitative kinetic results.

To distinguish between the two mechanisms, a test reaction was prepared as follows. A 0.36×10^{-4} molar solution of p-nitrodeoxybenzoin was prepared in degassed DMSO, to which was added a very small amount of dilute OH^- solution. About one third of the p-nitrodeoxybenzoin was ionized to the carbanion as was seen from the O.D. of 0.7 at 584 mμ. Thus it was assumed that there was no excess base in the system, merely a source of carbanion as large or larger than could be present under reaction conditions. To this was added p-nitrotolan (to a concentration of 3×10^{-5} mole/litre) and the optical density at 427 mμ was monitored. No change was observed for about 30 minutes. Then, a large excess of base was added, whereupon the immediate formation of the radical-anion was observed. Thus mechanism 1 may be ruled out.

It has been shown that this reaction sequence is pseudo first order in p-nitrotolan, and in an analogous manner, an attempt was made to quantitatively examine the influence of hydroxide concentration. By employing a dilute base solution, it was found that the minimum amount of hydroxide required to observe any radical-anion formation was approximately a three fold excess over p-nitrotolan. Attempts to examine the rate of radical anion production as a function of $[\text{OH}^-]$ were unsuccessful due to an inability to keep the system free of oxygen. This will also vastly affect the minimum required hydroxide concentration to observe radical-anion production that was previously suggested.

4. Methoxide Ion as an Electron Donor

To further substantiate the idea of a rapid one-electron transfer from a small strongly nucleophilic reagent, the reaction of methoxide ion with p-nitrotolan was briefly studied.

To a solution of p-nitrotolan (3×10^{-5} molar) in anhydrous degassed DMSO was added a very small amount of solid sodium methoxide (Fisher chemical) . A fine stream of nitrogen gas was then passed through the mixture to further degass and agitate it . An immediate green colour developed and the characteristic U.V. - visible spectrum of the radical-anion was observed, with $\lambda_{\text{max}} = 428 \text{ m}\mu$.

C. NMR Study

To a fairly concentrated solution of p-nitrotolan (1.0 molar) in anhydrous DMSO was added a large excess of sodium methoxide (solid) in the presence of oxygen. An immediate deep red-green colour was observed, and the change in the NMR spectrum noted.

The NMR spectrum of the pure p-nitrotolan in DMSO clearly showed two sets of doublets downfield from the main aromatic resonance (at about 2.5τ) with the same coupling of ~ 8 cps. These doublets, due to the nitro-aromatic ring appear at $\tau = 1.8$ and $\tau = 2.3$ based on a reference of $\tau_{\text{DMSO}} = 7.5$. This spectrum is illustrated in FIGURE 8 , p. 33 . On the addition of methoxide, two effects were immediately evident: 1) the resonance intensity decreased markedly; and 2) the remaining signal shifted upfield. This is illustrated in FIGURE 9 , p. 34 . Here a clear doublet was observed at $\tau = 3.1$ with $J \sim 8$ cps as in the parent spectrum. The main aromatic resonance is centred on $\tau = 2.7$, a very slight upfield shift. Thus the nitro-aromatic ring has been shifted upfield relative to the unsubstituted ring, in that substance observed, and some other non resonating species seems to have been formed. This latter may be attributed to the radical-anion, as the green colour disappeared fairly rapidly, and a slight broadening of the spectrum was observed (although it was still reasonably

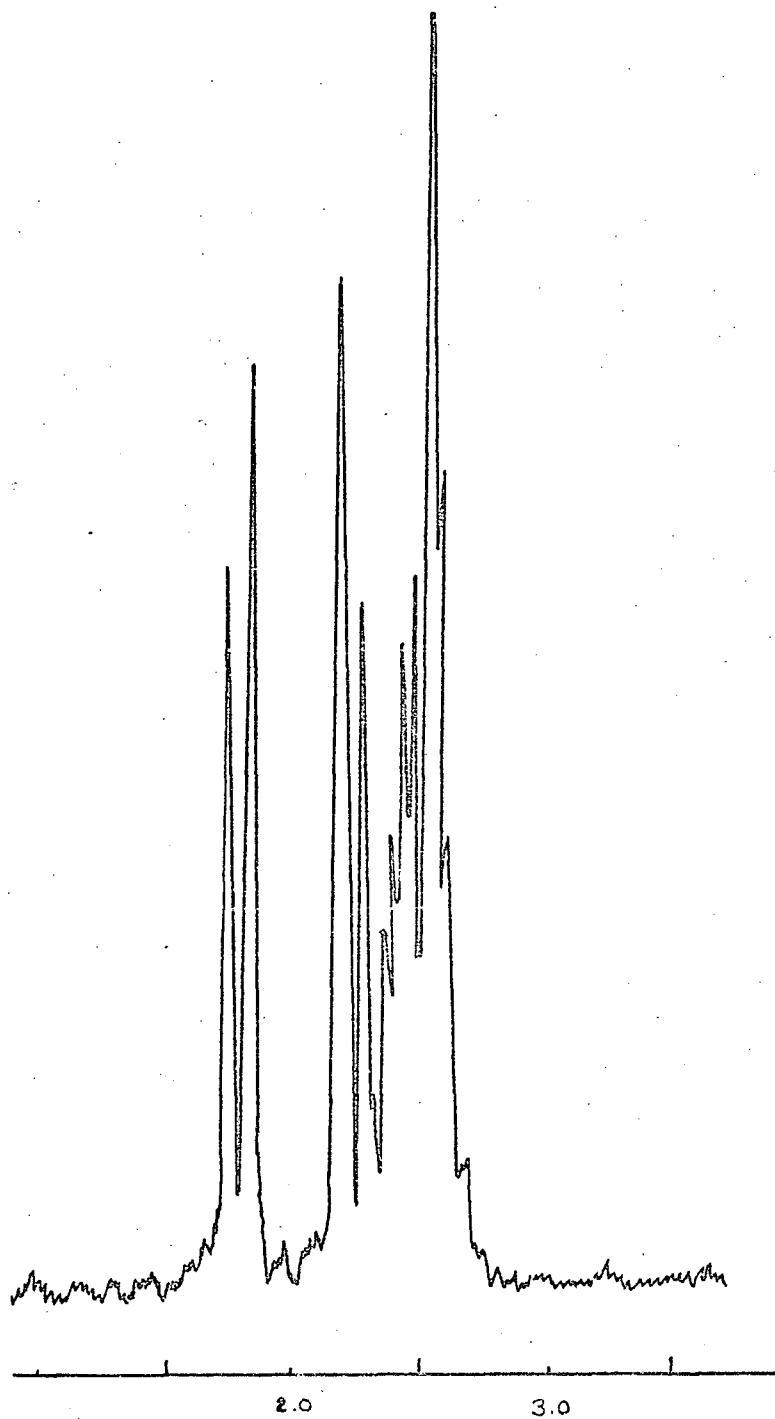


FIGURE 8

NMR Spectrum of p-Nitrotolan in DMSO

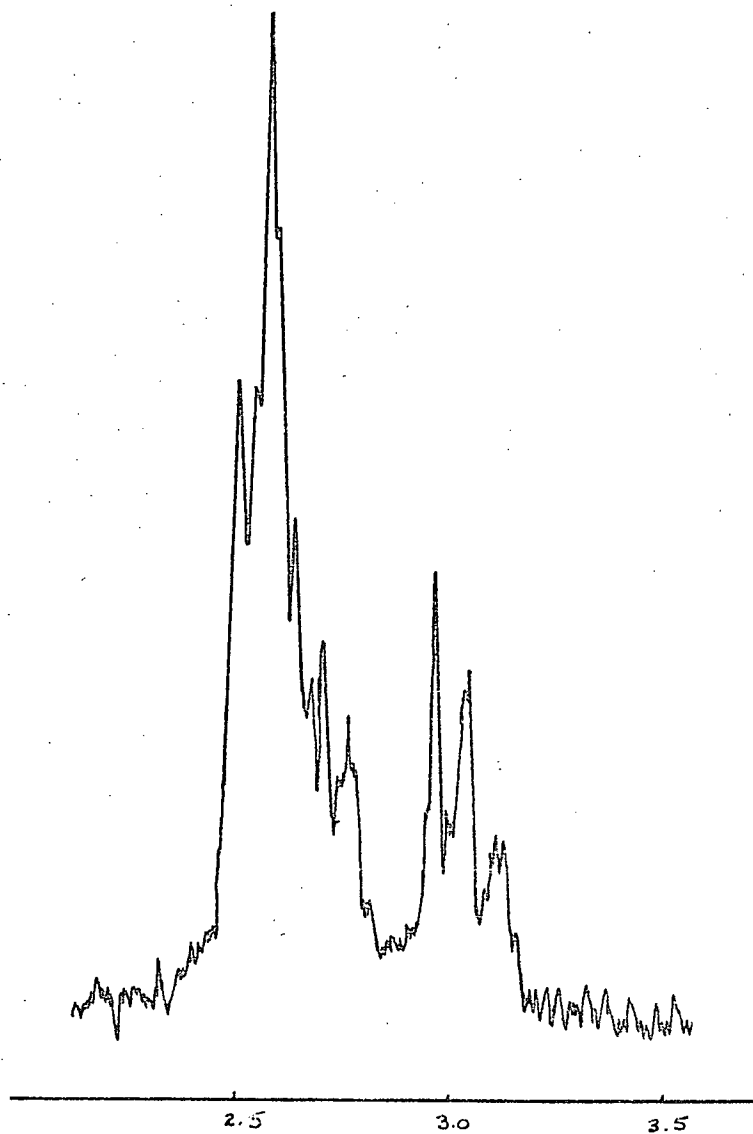
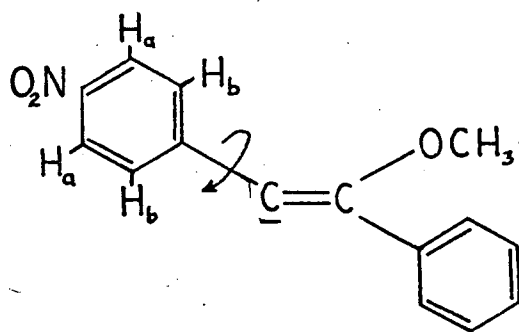


FIGURE 9

NMR Spectrum of Methoxide Addition Product of p-Nitrotolan

well resolved) . The NMR signal of the 'product' increased with time, and concurrent with this, better resolution was obtained.

The NMR spectrum, and probably the red colour observed may be attributed to a carbanion addition product of the form:



where there is free rotation around the bond indicated, as observed by the $(H_a)_2(H_b)_2$ system in the spectrum. The negative charge next to the aromatic ring has shifted the H_a and H_b resonances upfield.

D. Further Reaction of the p-Nitrotolan Radical-Anion

It has been mentioned previously, that in the reaction of p-nitrotolan with hydroxide in the presence of air, there is a reproducible build-up of p-nitrodeoxybenzoin carbanion. Typical plots of the carbanion concentration as a function of time in these systems are shown in FIGURE 10, p. 36 . It was also observed that a product

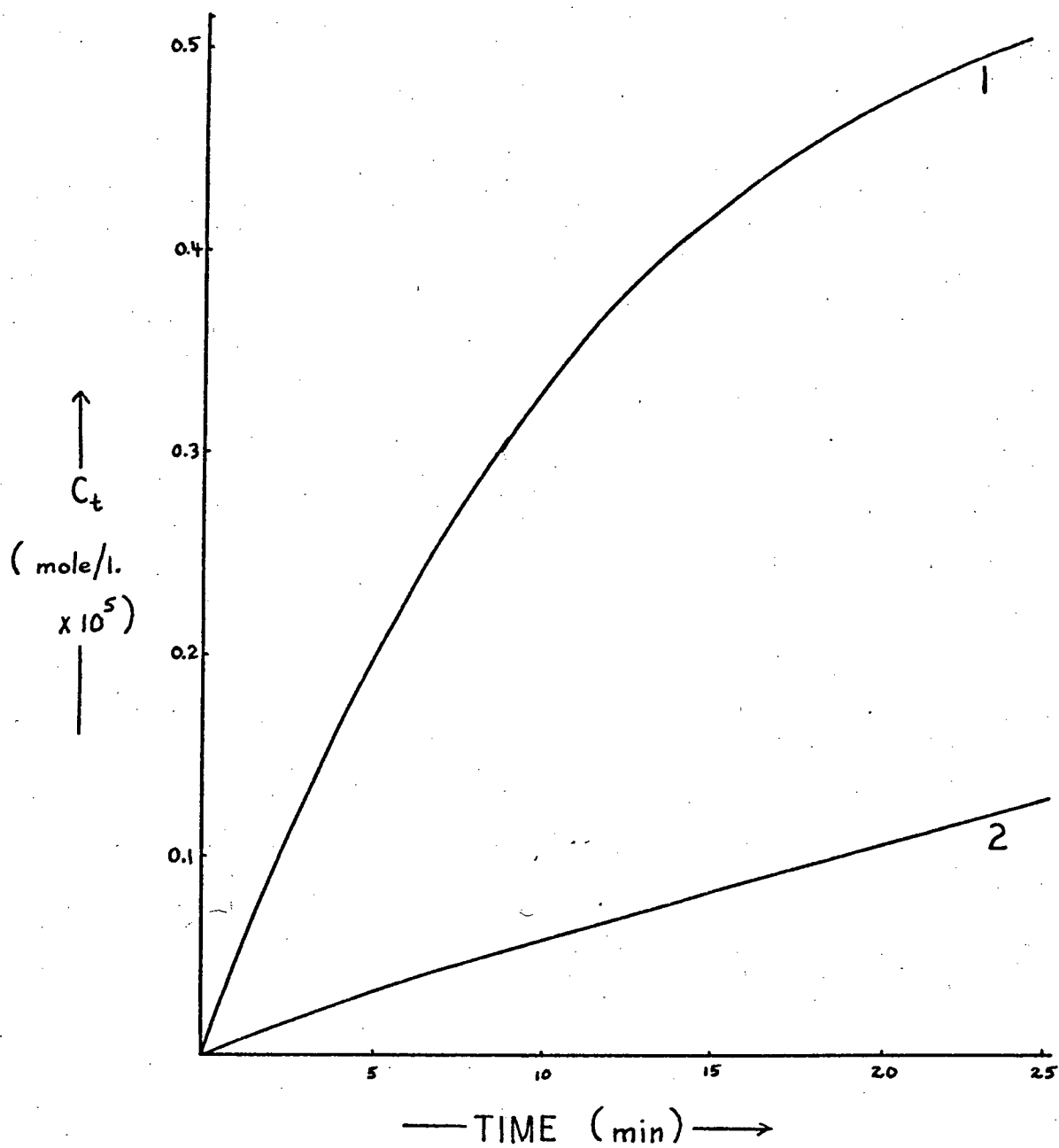


FIGURE 10

Rate of Formation of p-Nitrodeoxybenzoin Carbanion in the Presence of

- Oxygen:
- 1) in 96.74 mole % DMSO
 - 2) in 94.04 mole % DMSO.

absorbing in the 270 - 310 m μ range was formed slowly with time. The absorption was a broad band with maxima at 309 and 290 m μ , and is illustrated in FIGURE 11, p. 38 . Owing to the intense p-nitrotolan absorption at 290 - 340 m μ , no rate studies were carried out on the formation of this product. However, it was noted to form more rapidly in the better degassed systems, and its formation was independant of the nature of the electron donor.

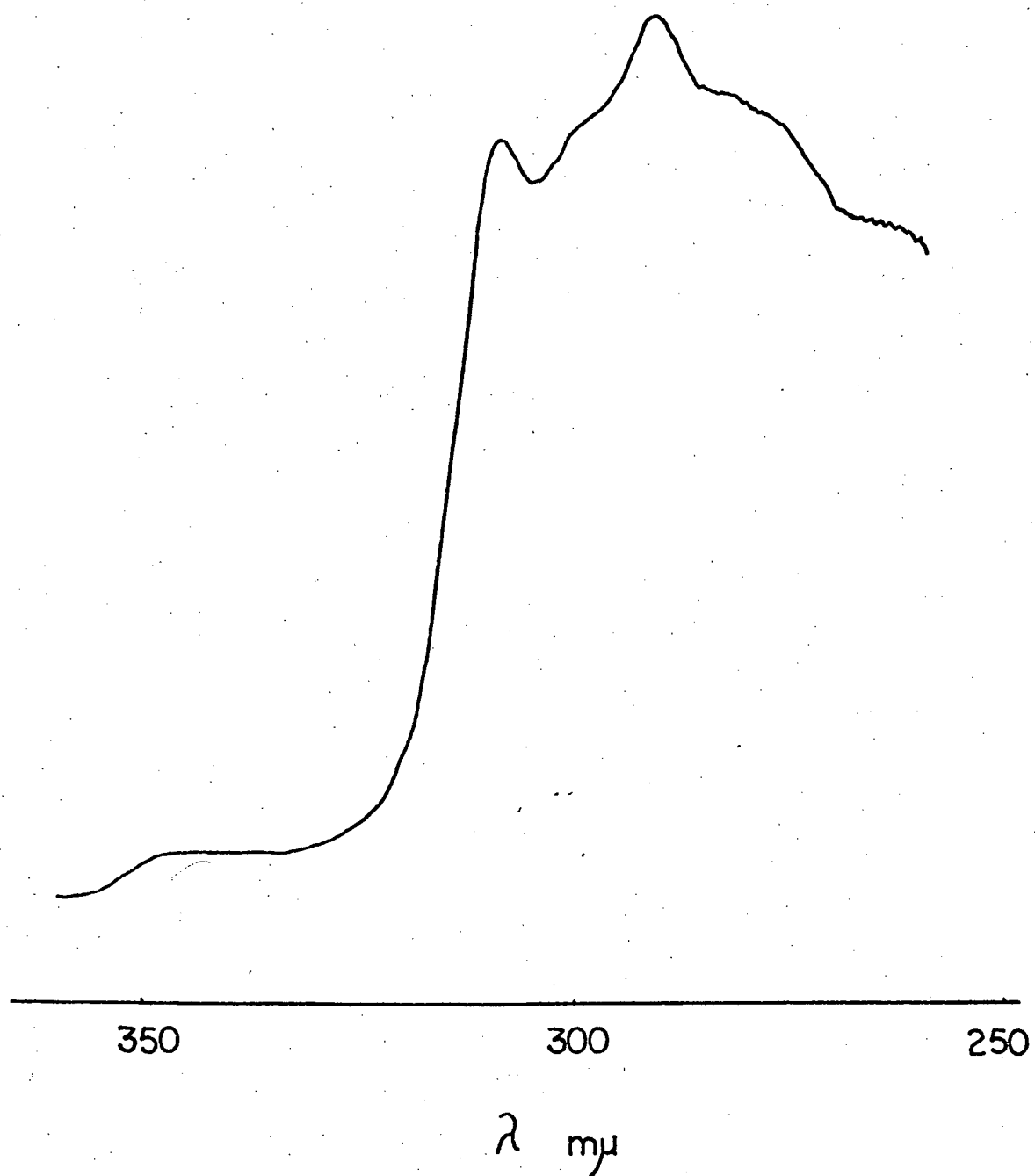


FIGURE II

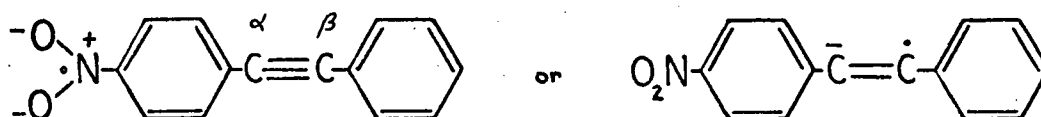
UV Absorption of Product

DISCUSSION

A. Electron Transfer as the Elementary Act of the Reaction

The necessary requirements for an electron transfer as the elementary act of any reaction are that an electron donor and an electron acceptor be present in the reaction medium. The capacity to receive one electron, and thus form a radical-anion, is exhibited by a number of classes of organic compounds; i.e. 1) aromatic compounds, 2) heterocyclic compounds, 3) compounds containing conjugated systems, and 4) those with strong electron withdrawing groups. p-Nitrotolan is a conjugated system with electron withdrawing groups, and hence is a potential electron acceptor. The actual ease of reduction of this system could, however, only be determined by studies with various electron donors and in relation to other acceptors. The hydroxide ion has previously been shown to be involved in electron transfer reactions as a donor. In the DMSO : water medium employed, the OH^- has a high enough activity that an electron transfer to even a relatively weak acceptor is feasible.

Any nucleophilic attack on the acetylenic bond has been ruled out by the U.V. - visible studies reported, and thus the electron transfer from hydroxide must be viewed as the elementary act, where the radical-anion may be simply pictured as either of the following species:



From an analysis of the splitting constants, it can be seen that approximately 0.3 of the total spin density is localized on the nitrogen atom, and at most 0.23 of the spin density on the β carbon (APPENDIX 1). This radical-anion is inherently a relatively stable organic radical, as coupling reactions between nitro groups (to form N-N compounds) are unfeasible, as are ring coupling reactions. Picturing the radical electron as being on the nitrogen, it is placed in a favourable position for delocalization into the benzene ring. The basic seven line E.S.R. spectrum, which can be resolved into more than 100 lines, is also consistent with this formulation.

The formation of the p-nitrotolan radical-anion is only possible because of the low reactivity of the substrate towards a nucleophile, and the fact that it contains no acidic protons. Thus the number of systems in which this electron transfer from OH^- may be expected to be seen is severely limited.

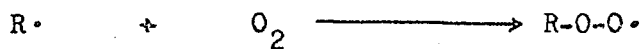
The influence of solvent on radical formation has not been extensively studied, although some work has been done on the effect of the medium on the behaviour of free radical intermediates (for a

review, see ref. 24). The solvent effects that have been noted for radical formation by decomposition of azo compounds are extremely small. They are attributed to differences in solvation of the ground state, the transition state being poorly solvated by both polar and non-polar solvents. But here the hydroxide ion is known to be poorly solvated and any transition state complex would be expected to be slightly better solvated, and hence reverse this situation. The addition of protic solvents almost always causes a rapid disappearance of the radical-anion, so the field of study is restricted to fairly aprotic solvents. For example, the hydrolysis of the radical-anion of an aromatic hydrocarbon yields the initial hydrocarbon and the corresponding dihydro derivative²⁵.

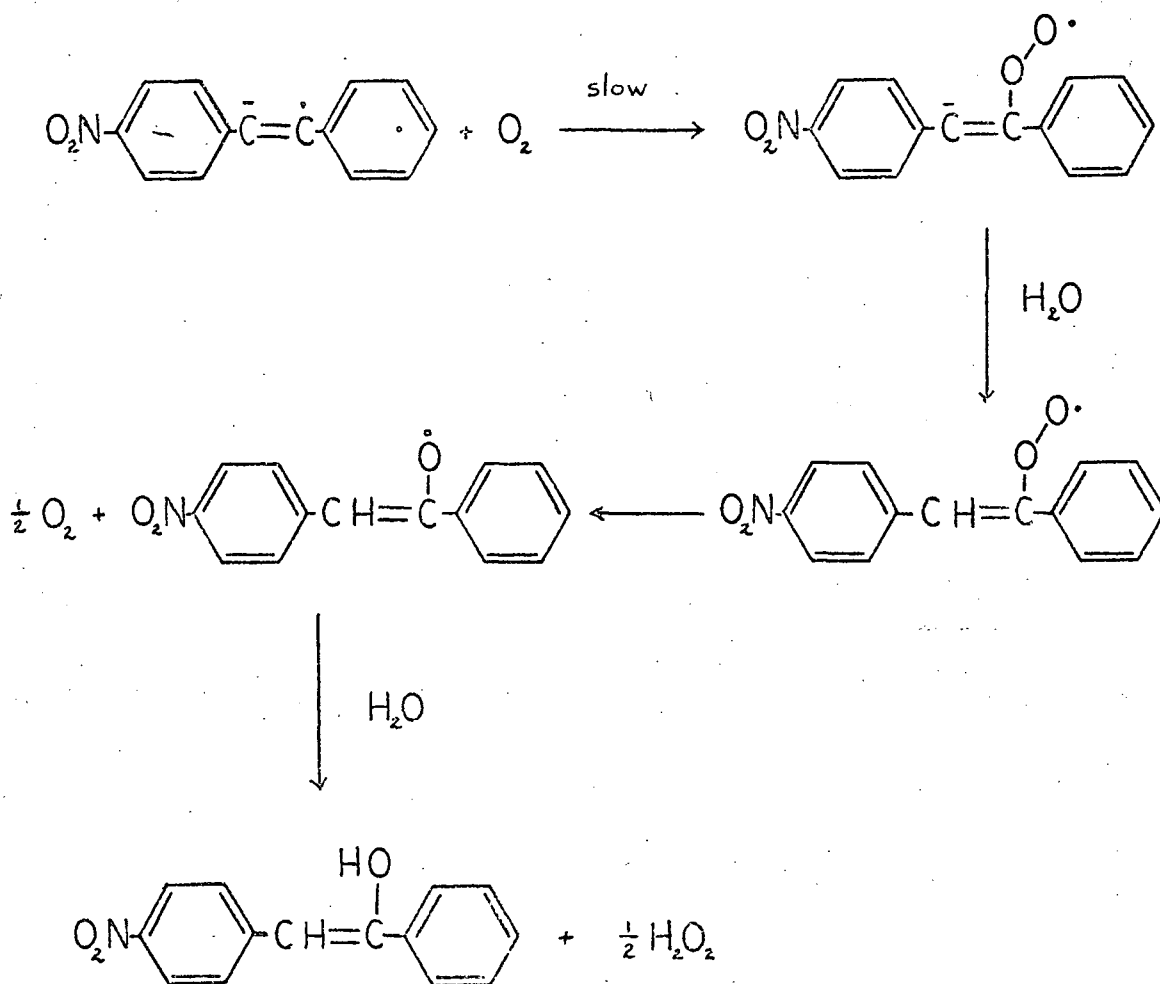
B. Further Reaction of the p-Nitrotolan Radical-Anion

The action of oxygen on the p-nitrotolan radical-anion appears to be rather anomolous. When exposed to a large excess of oxygen, the p-nitrotolan is immediately regenerated; however, in the presence of a small amount of oxygen, the deoxybenzoin carbanion is formed.

Carbon radicals are known to react very readily with molecular oxygen to form a peroxy radical:

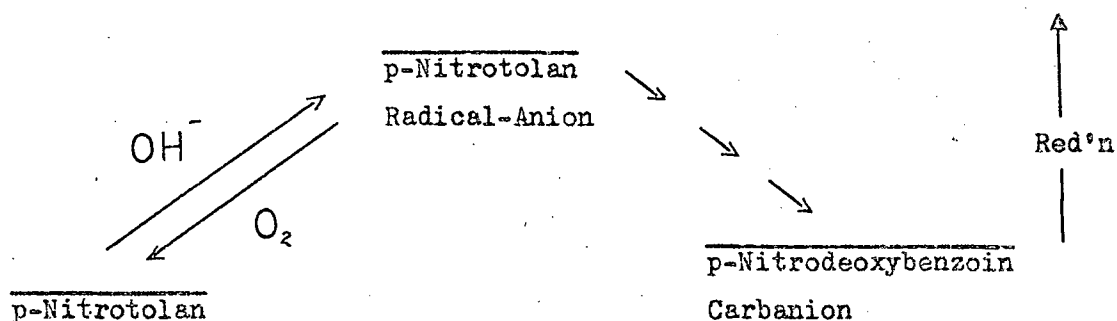


The resulting radical is unreactive relative to a carbon radical, and what actually happens to it depends on the particular system involved. It is reasonable to assume that this type of reaction is a step in the formation of the deoxybenzoin carbanion, followed by hydride abstraction and the decomposition of the hydroperoxy radical so formed to the keto radical:

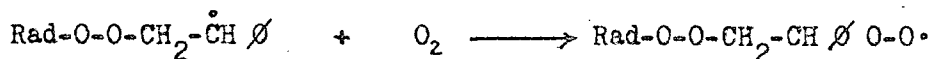
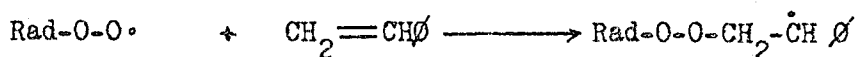
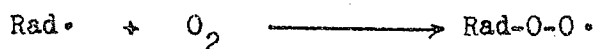


The decomposition of hydroperoxides is a relatively complex chain process^{27,28} and the scheme suggested may well be a vast oversimplification, as temperature, solvent, and the presence of other molecules in solution have considerable influence on the decomposition pathway.

The reaction of the p-nitrotolan radical-anion in the presence of excess oxygen may be simply pictured as an oxidation by electron transfer to the oxygen to produce neutral p-nitrotolan, which can again be reduced by hydroxide. The overall scheme can be pictured in terms of the relative oxidation levels of the various species:



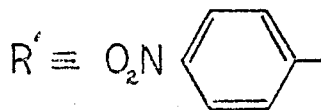
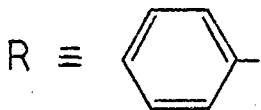
The possibility of the formation of the apparent copolymer of the peroxy radical $(-\text{O}-\text{O}-\text{RH}-)_n$ should not be overlooked, as this system could be considered analogous to the styrene polymerization where the following mechanism has been observed:

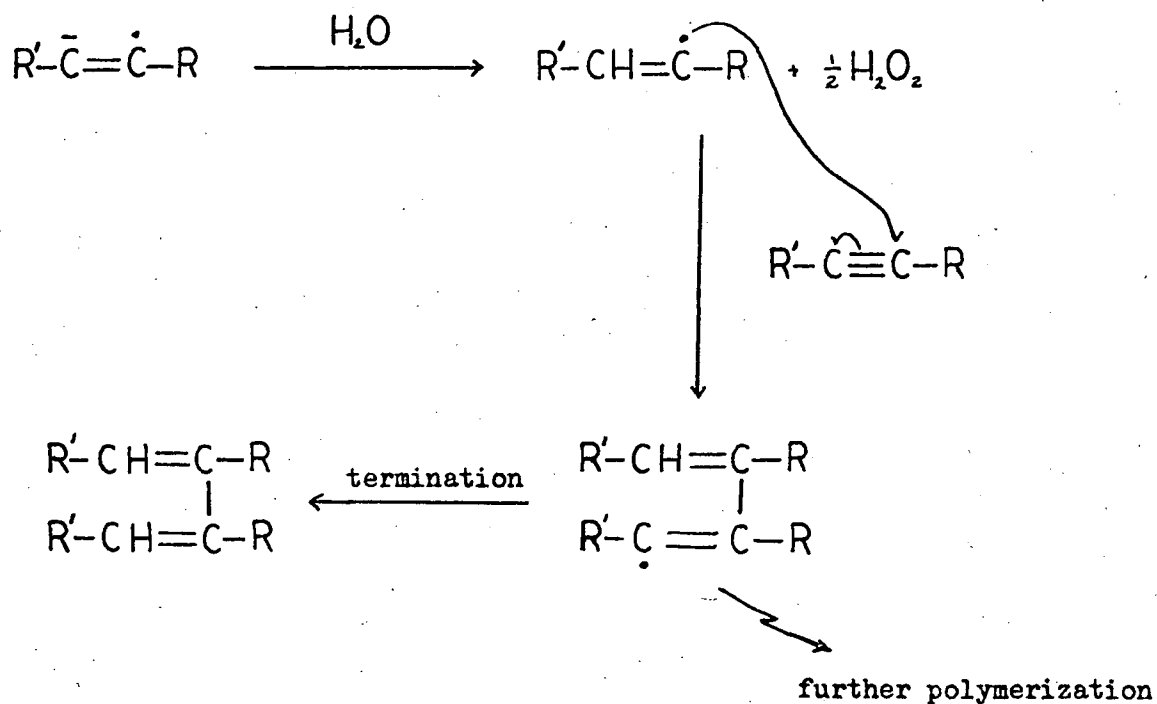


However, no evidence, other than that mentioned in the next paragraph, was seen to substantiate this product formation, and the regeneration of most of the p-nitrotolan from the radical-anion by oxygen indicated that no rapid polymerization was occurring.

The slow build up of the product showing the broad absorption band in the 290 - 340 μ region has still to be explained, and this can be done in two ways. The first is the formation of the copolymer of the peroxy radical that was previously discussed, and the second is a slow polymerization of the p-nitrotolan radical-anion itself by the following scheme:

where:

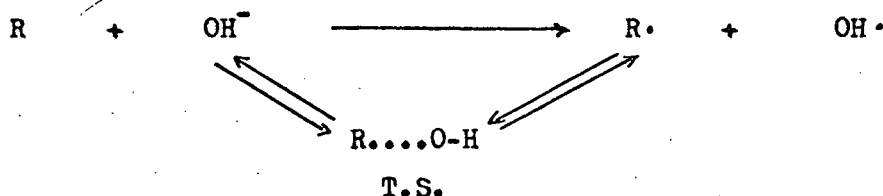




This mechanism of product formation is analogous to that suggested by Dvorko et al¹⁰ in the formation of polymeric products from acetylene radicals generated by electron transfer from negative ions. However, neither scheme has been definitely substantiated at present.

SUGGESTIONS FOR FURTHER WORK

In this thesis, it has been shown that the hydroxide ion can act as an electron donor towards p-nitrotolan in a highly basic DMSO : water medium. However, the effect of basicity on the formation of the p-nitrotolan radical-anion has not been thoroughly studied, and could lead to a further confirmation of the mechanistic picture involved. The correlation of kinetic behavior with acidity (basicity) has been examined by a number of authors for homolytic reactions^{29, 30, 31, 32} but there has not been complete agreement on the validity of this treatment. For example, Kresge³³ asserted in 1965 that kinetic acidity is a property of the substrate only, and hence provides insight into the structure of the transition state and not the mechanism. But this point of view has been widely disputed. For a reaction of the type:



$$\text{rate: } v = \frac{k (\text{OH}^-) (\text{R})}{f^\ddagger}$$

where f^\ddagger is the activity coefficient of the transition state. By using a number of assumptions, particularly with respect to the use of the H_- scale³⁴ a correlation of $\log k_{\text{obs}}$ and $H_- + \log a_{\text{H}_2\text{O}}$ can be predicted.

For this work it is necessary to prepare and handle all solutions in an inert atmosphere to obtain accurate data. As reported, in the present research considerable trouble was experienced with oxygen contamination.

The further reaction of the p-nitrotolan radical-anion again poses some experimental problems, particularly in the presence of oxygen. However, electrolytic generation of this radical-anion is a promising method of approach, as relatively concentrated solutions can be handled.

The fact that the corresponding electron transfer reaction with unsubstituted tolan did not proceed under the same conditions illustrates the necessity of the polarization of the acetylenic bond by a ring substituent. In the light of this, it would be interesting to examine a series of substituted tolans to see if rates and substituent constants may be correlated by the Hammett equation. Careful definition of the reaction taking place must be made due to the possibility of competing nucleophilic attack, especially in such compounds as p,p'-dinitrotolan. Here the effect of substituents is to remove electron density from the acetylenic bond rather than a polarization of charge.

Interesting extensions to the studies suggested would be a variation of both the nucleophile employed as electron donor and the dipolar aprotic solvent. Hexamethylphosphoramide has been reported³⁵ to have the lowest dielectric constant and the highest basicity of all dipolar aprotic solvents, and hence would be of particular interest in this system.

BIBLIOGRAPHY

1. G. A. Russell and E. J. Geels, Tet. Letters, 1333 (1963).
2. P. B. Ayscough and F. P. Sargent, Proc. Chem. Soc., (London) , 94 (1963).
3. G. A. Russell and E. G. Janzen, J. Am. Chem. Soc., 84 , 4153, 4154, 4155 (1962).
4. G. A. Russell and R. C. Williamson, J. Am. Chem. Soc., 86 , 2357, (1964).
5. G. A. Russell and E. G. Janzen, J. Am. Chem. Soc., 89 , 300 (1967).
6. G. A. Russell, E. G. Janzen and E. T. Strom, J. Am. Chem. Soc., 86 , 1807 (1964).
7. E. Buncel, A. R. Norris and K. E. Russell, Quart. Rev., 22 , 123 (1968).
8. J. Q. Chambers and R. N. Adams, Molec. Phys., 2 , 413 (1965).
9. G. V. Fomin, L. A. Blyumenfel'd and V. I. Sukhorukov, Dokl. Akad. Nauk., SSSR , 157 , 1199 (1964).
10. G. F. Dvorko and E. A. Shilov, Teor. Eksper. Khim., 3 , 606 (1967).
11. D. Dadley and A. G. Evans, J. Chem. Soc. (B) , 418 (1967).
12. D. Dadley and A. G. Evans, J. Chem. Soc. (B) , 107 (1968).
13. S. Patai and Z. Rappoport, J. Chem. Soc., 377, 383, 392 (1962).
14. S. Patai and Z. Rappoport, "The Chemistry of the Alkenes" Interscience, London (1964).
15. C. A. Fyfe, Can. J. Chem., 47 , 2331 (1969).
16. R. N. Haszeldine, J. Chem. Soc., 3490 (1952).

17. K. A. Bilevich and O. Yu Okhlobystin, Russ. Chem. Rev., 37 , 954 (1968).
18. "Organic Synthesis", Coll. Vol. 3 , 350, J. Wiley and Sons, N.Y., 1955.
19. Buttenberg, Ann., 279 , 327 (1894).
20. C. E. Castro, E. J. Gaughan and D. C. Owsley, J. Org. Chem., 31 , 4071 (1966).
21. R. D. Stevens and C. E. Castro, J. Org. Chem., 28 , 3313 (1963).
22. H. O. House, S. G. Boots and V. K. Jones, J. Org. Chem., 30 , 2522 (1965).
23. Petrenko-Kritschenko, B., 25 , 2242 .
24. "Advances in Free Radical Chemistry", 1 , 77 , Logos Press, 1965.
25. D. E. Paul, D. Lipkin and S. J. Weissman, J. Am. Chem. Soc., 78 , 116 (1956).
26. "Radical Ions" Ed. E. T. Kaiser and L. Kevan, Interscience, 1968.
27. C. Walling, "Free Radicals in Solution", J. Wiley and Sons Inc., 1957.
28. E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, 1959.
29. M. Anbar, M. Bobtelsky, D. Samuel, B. Silver and G. Yagil, J. Am. Chem. Soc., 85 , 2380 (1963).
30. R. Stewart, J. P. O'Donnell, D. J. Cram and B. Rickborn, Tetrahedron, 18 , 917 (1962).
31. G. Yagil and M. Anbar, J. Am. Chem. Soc., 84 , 1797 (1962).
32. W. D. Kollmeyer and D. J. Cram, J. Am. Chem. Soc., 90 , 1784 (1968).

33. A. J. Kresge, Chem. Comm., 46 (1965).
34. D. Dolman, PhD Thesis, University of British Columbia, 1966.
35. H. Normant, Angew. Chem. Int., 6 , 1046 (1967).

APPENDIX

The Calculation of Spin Density from Hyperfine Splitting Constants

The use of hyperfine splittings in E.S.R. spectra of radical-anions to determine the distribution of the unpaired electron over the molecule has been extensively reviewed²⁶. Thus, this appendix will serve merely as a description of the calculation used, and not the full derivation. It has been shown that:

$$a_i^H = Q^H \rho_i$$

where ρ is the spin density, 'a' is the hyperfine splitting, and 'Q' is a numerical factor (gauss/spin density). For the benzene negative ion Q_{CH}^H was found to be -22.5 G, and hence this value was used for both proton splitting and as an approximation to the nitrogen splitting. The distribution of the electron density over the molecule was required only to indicate if any of the electron density localized on the acetylenic carbons, so an accurate value was not essential. The splittings and spin densities calculated with this equation are tabulated below:

	'a' (splitting)	ρ (spin density)
N	7.72	0.305
H ₁	3.83	0.340
H ₂	1.00	0.090
H ₃	0.51	0.046
H ₄	0.12	0.005