Flow Nuclear Magnetic Resonance Investigation of the Transient and Stable Species Formed by the Attack of Alkoxide Ions on 2,4,6-Trinitrotoluene[1]

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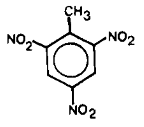
Abstract: High-resolution nuclear magnetic resonance spectroscopy in both flowing and static systems has been used to investigate the reaction of 2,4,6-trinitrotoluene with methoxide ion in various Me_2SO–methanol solvent mixtures. In solutions of high Me_2SO content and a 1:1 ratio of TNT–methoxide ion, a Meisenheimer complex is formed which then decays with the formation of the carbanion formed by proton removal from the methyl group, while a 1:2 or lower ratio of TNT–methoxide yields a dianion in which there has been both addition of base to the ring and proton abstraction from the methyl group. The uv-visible spectral characteristics of these species have been determined and the dependence of the reaction on solvent composition investigated by both uv-visible and NMR and the present work related to the results of previous studies. It is found that formation of the dianion in the presence of excess base is favored for concentrated solutions of substrates in solvents of high Me_2SO content. Large concentrations of radicals have been found in the reaction mixtures and a preliminary investigation carried out.

The interaction of bases with nitroaromatic compounds can give rise to a variety of products, including charge-transfer complexes, σ-complexes by base addition, radical ions by electron transfer, and, in cases where there is a substituent alkyl group, carbanions by proton abstraction.[4-10] The system of 2,4,6-trinitrotoluene (**1**) with alkoxide ions is one where all of these products are possible and have been postulated. However, although a considerable amount of work has been done by a number of groups, the species involved have not been unambiguously identified.

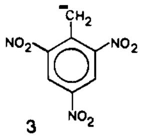
As first observed by Caldin and co-workers[11,12] and subsequently confirmed by other workers, the reaction at low temperatures is characterized by the fast appearance of a brown color, which is replaced by a purple color in a relatively slow reaction. Caldin and co-workers assigned the brown color to the charge-transfer complex **2** and the purple color to the anion **3**. The assignment of structure **2** to the species initially produced was made by analogy to the structure suggested by those authors for the species initially produced in the trinitroanisole–ethoxide ion system.



1

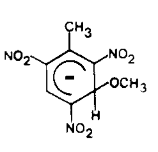
$TNT \leftarrow {}^{-}OCH_3$

2



3

More recent kinetic investigations[13-15] on these systems have indicated the essential correctness of Caldin's early work, although the Meisenheimer complex structure **4** has been assigned to the brown colored species. One very significant additional feature from these studies was the observation of a large primary isotope $k_H/k_D = 7.0 \pm 0.5$ in the rate of the formation of the purple species, in agreement with it being the anion **3**.[13] Recently, Bernasconi has investigated the reaction under conditions of excess TNT using temperature-jump techniques.[16] He found evidence for the formation of a Janovsky complex (**5a** or **5b**) from uv-visible spectral measurements.



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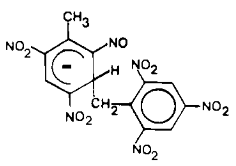
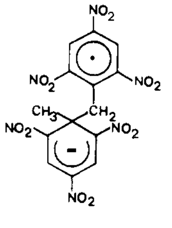


5a



5b

One point of note is that, while high resolution NMR has proven a very successful technique in the determination of the structures of complexes formed by attack of bases on many nitroaromatic substrates,[4-10] there have been no successful NMR investigations reported of those formed by attack of alkoxides on TNT, although attempts have been made by several authors.[17,18] (This point will be discussed subsequently.)

Significant concentrations of anion radicals were found to be produced by the action of base on *o*- and *p*-nitrotoluenes and their subsequent reaction, well documented bv Russell and Janzen.[19,20] They reported that radicals could be produced by the action of base on TNT, but only in small quantities.

High-resolution nuclear magnetic resonance spectroscopy in flowing, chemically reacting systems has proven a useful technique for the identification of transient species[21-23] and effects[24] in chemical reactions, and the necessary equipment has been described.[25,26] The purpose of the present work was to apply these techniques to the TNT–alkoxide ion system in an attempt to identify which, if any, of the species **1** → **5** were in fact produced in the reaction, and their relationships to each other.

Experimental Section

NMR spectra were recorded using a Varian HA 100 spectrometer. The equipment used for the flow NMR and flow uv-visible studies was as previously described.[22,25,26] Uv spectra were measured using Unicam SP800 and Cary 118 spectrophotometers. Flow ESR spectra were recorded on a Varian E. 12 spectrometer utilizing the same mixing chamber as the NMR and uv studies and a quartz flow ESR cell.

2,4,6-Trinitrotoluene (Aldrich) was recrystallized from ethanol, mp 80 °C. The solvents used were purified by standard techniques. TNT-d_3 was prepared by the method of Buncel, Norris, Russell, and Tucker.[13]

The carbanion **3** was isolated as the potassium and tetraphenylarsonium salts by the following procedures. (a) **Tetraphenylarsonium Salt.** 0.1561 g of TNT was dissolved with warming in a solvent mixture of 24 ml of 2-propanol and 3 ml of heptane and the solution cooled to 0 °C. To this cooled solution was added slowly a solution containing 0.20 ml of a 4.23 M solution of $NaOCH_3$ in MeOH dissolved in 3 ml of 2-propanol. The solution turned orange-brown initially, then more slowly a deep purple-red color. When the second color change was complete, a solution of 0.71 g of tetraphenylarsonium chloride dissolved in 3 ml of 2-propanol was added to the cooled solution. A precipitate formed immediately. The solution was cooled for 30 min at 193 K and the precipitate collected by filtration at low temperature. The precipitate was washed twice with cold 2-propanol and twice with cold ether and the cold solid dried by passing a stream of cold, dry nitrogen gas over it. The tetraphenylarsonium salt of the anion (**3**) (0.350 g) was thus obtained as a brown-black solid and stored at low temperature under nitrogen. The salt readily dissolves in a variety of organic solvents at room temperature to yield deep purple-colored solutions.

(b) **Potassium Salt.** TNT (0.1893 g) was dissolved at room temperature in a solvent mixture of 7 ml of *n*-heptane and 24 ml of 2-propanol. This solution was added slowly to a cooled (193 K) solution of base containing 1.5 ml of 0.60 M potassium 2-propoxide in 5 ml of 2-propanol. The initial color of the solution is brown, but this changes to purple and a precipitate slowly developed. The solution was cooled at 193 K for 30 min and then filtered at low temperature under nitrogen. The precipitate was washed twice with cold 2-propanol and twice with cold ether and dried at low temperature under a stream of nitrogen gas. The potassium salt of **3** (0.21 g) was obtained as a brown-black solid. This salt is soluble in most organic solvents only with the addition of a crown ether e.g., 18-crown-6. These solutions are a deep purple color.

Both salts were stable when kept at low temperatures, but decomposed both in solution and as solids at ambient temperatures and could not be analyzed. They yielded identical uv and NMR spectra (except for the tetraphenylarsonium NMR signals) and these are presented in Table I together with those for **3** generated in situ.

Results and Discussion

The reaction has been investigated using several different techniques and under several sets of different conditions. As will be shown, the reaction is dependent on both the relative concentrations of the two components and also the solvent composition, and for clarity of presentation, the different sets of results will be presented separately. The NMR and uv-visible spectral parameters of the different species identified are collected in Table I.

(a) **TNT (0.5 M in Me_2SO) Plus Methoxide Ion (0.5 M in 87.5% Me_2SO–12.5% MeOH) at 30 °C.** Spectra of the ring proton absorptions as a function of time during the reaction are shown in Figure 1. The top spectrum shows the single absorption at δ 8.92 due to the two equivalent ring hydrogens of TNT (0.5 M in Me_2SO). The second spectrum is of the same spectral region of the reaction mixture under flowing conditions at a flow rate of 60 ml/min (0.5 s after mixing). The apparatus used to make this measurement was that described previously.[25,26] There is a loss of signal intensity due to both the liquid flow and the twofold dilution. There are two single peaks of relative areas 1:1 at δ 6.18 and 8.45. The intensities and chemical shifts of these are consistent with the Meisenheimer complex (**4**). There is no variation in this spectrum when the time between mixing and observation is changed from 0.3 to 1.0 s, so the complex is formed very quickly, and its subsequent disappearance is relatively slow. Two single peaks of relative ratios 1:1 at δ 6.3 and 8.45 are also observed when TNT-d_3 is used in place of TNT in the above experiments, again consistent with the formation of **4**.

The flow was then stopped and the spectrum quickly and repeatedly scanned. The spectrum of **4** is gradually replaced by a second spectrum consisting of two single peaks at δ 5.53 and 8.18 (relative ratio 1:1). In about 80 s the conversion is complete and the third spectrum in Figure 1 is obtained.[27] In this case, the use of TNT-d_3 completely removes the signal at higher field. This and the values of the chemical shifts are consistent with this species being the carbanion formed by proton abstraction (**3**). There are subsequent, much slower, decomposition reactions giving a mixture of products.

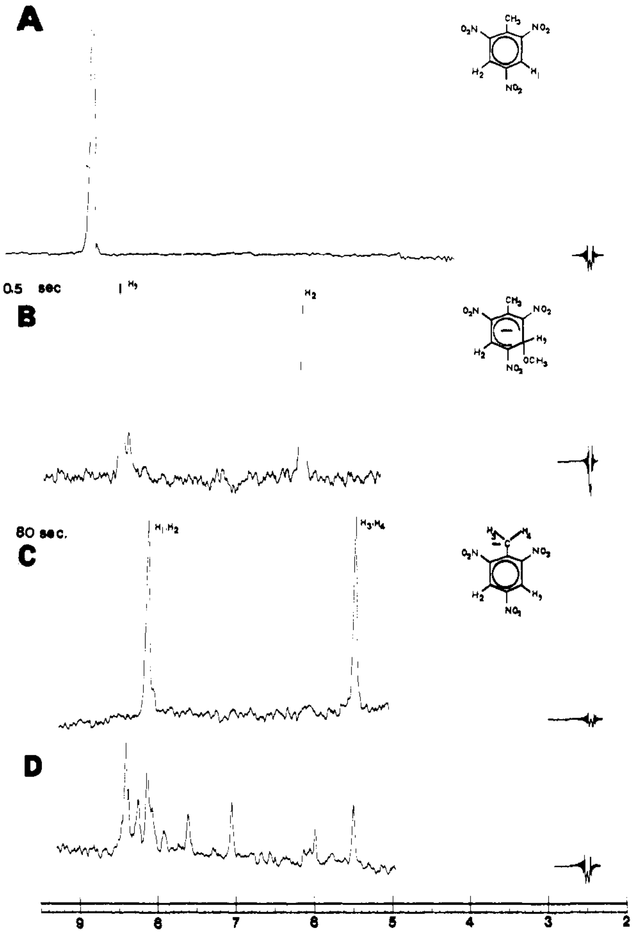
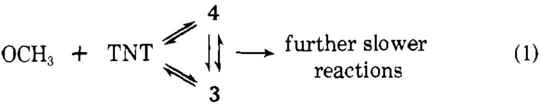


Figure 1. Static and flow 100-MHz proton NMR spectra of the absorptions of trinitrotoluene (0.5 M in Me_2SO) during its reaction with methoxide ion (0.5 M in 87.5% Me_2SO–12.5% methanol) at 30 °C: A, static spectrum of TNT (0.5 M in Me_2SO) before mixing; B, flow spectrum 0.5 s after mixing, flow rate 60 ml/min; C, static spectrum 80 s after stopping flow; D, static spectrum 500 s after stopping flow.

The anion **3** can be isolated as described in the Experimental Section as either the potassium or tetraphenylarsonium salts. When redissolved it has identical uv-visible and NMR spectra to the species generated in situ. This data is presented in Table I. It is stable in solid or solution at temperatures below 0 °C, but decomposes in either state at room temperature.

Thus, under these specified conditions, the reaction is thought to involve the fast formation of **4** and the subsequent slow formation of **3**. It cannot be deduced from these measurements whether **3** is formed directly from **4** or via TNT.

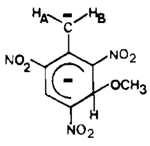


$$\begin{tikzcd} & 4 \arrow[dl, shift left] \arrow[dd, shift left] & \\ {}^{-}OCH_3 + TNT \arrow[ur, shift left] \arrow[dr, shift left] & \arrow[r] & \text{further slower reactions} \\ & 3 \arrow[ul, shift left] \arrow[uu, shift left] & \end{tikzcd} \qquad (1)$$

However, there are indications that the reaction is somewhat more complex. The efficiency of the conversion of the different species was measured by adding benzene, which does not take part in the reaction, to the TNT solution and relating the concentrations to this fixed concentration. The efficiency of conversion of TNT to **4** was 95%, but the conversion to the anion **3** was only 50%. Furthermore, the time dependence of the concentrations of **4** and **3** could not be fitted to any simple kinetic expression. The latter observation may, in part, be due to the high concentrations of reactants used, and the kinetic investigations should be made using uv-visible spectroscopy in much more dilute and ideal solutions, but when the formation of the anion **3** is complete, there are *no* other peaks in this region of the spectrum. This apparent anomaly may be explained if neutral species and anion radicals are both produced in the reaction. Since the anion radicals will undergo electron exchange reactions with the neutral species (including TNT), the NMR spectra of any neutral species will be broadened and may well not be observed. This will not affect the spectrum of either the Meisenheimer complex or the anion, as they already bear negative charges and will not be involved in such exchange reactions. It does, however, imply the existence in these solutions of substantial concentrations of radicals. This has been investigated and confirmed (see on).

At least a partial answer may be given from these studies as to why previous attempts to investigate this system using conventional NMR techniques have been unsuccessful. If less than 1 equiv of base is used, there is a much greater degree of decomposition of the anion and much larger concentrations of radicals formed. If there is more than 1 equiv of base present (see below), another species is produced. In the present work, there is very efficient mixing and the reaction is very clean. Using conventional techniques, i.e., adding the base solution to an NMR tube containing the substrate and shaking, the efficiency of mixing is low and a mixture of different species, including substantial amounts of decomposition products from irreversible reactions, will be produced as well as large concentrations of radicals. These effects, together with the relatively short lifetime of the anion at probe temperatures of about 30 °C, make the observation of this species difficult using conventional techniques, although it is now possible to detect its presence in such mixtures at 25 °C from the chemical shift values presented in Table I.

(b) TNT (0.25 M in Me_2SO) Plus Methoxide Ion (0.5 and 0.6 M in 87.5% Me_2SO–12.5% MeOH) at 30 °C. The spectra of the ring proton absorptions of the resultant solution are shown in Figure 2. The top spectrum was recorded on a flowing system and the second spectrum after the flow was stopped. A single species is formed in a very fast reaction and is very stable, showing no decomposition after 60 min. The spectrum consists of three absorptions at δ 6.18 (rel intensity 1), 6.48 (multiplet center, rel intensity 2), and 8.45 (rel intensity 1). The chemical shifts and relative intensities of the signals are consistent with the formation of a dianion of structure **6**. The two methylene hydrogens give rise to an AB multiplet (Figure 2), indicating that there is restricted rotation about the ring carbon–methylene carbon bond. This might be due to delocalization of the charge into the ring, as the ring is now unsymmetrically substituted, but could also be due to the methylene group being rotated due to steric interactions with the two adjacent nitro groups, since one of the hydrogens would then be on the same side of the ring as the methoxy group and one on the same side as the hydrogen on the sp^3 carbon. The use of TNT-d_3 causes the complete disappearance of this multiplet as expected (Figure 2, bottom spectrum). The NMR experiments thus indicate the presence of a new and stable species in the reaction mixture, which is formed at ratios of base–TNT of 2:1 or larger in this solvent mixture.



6

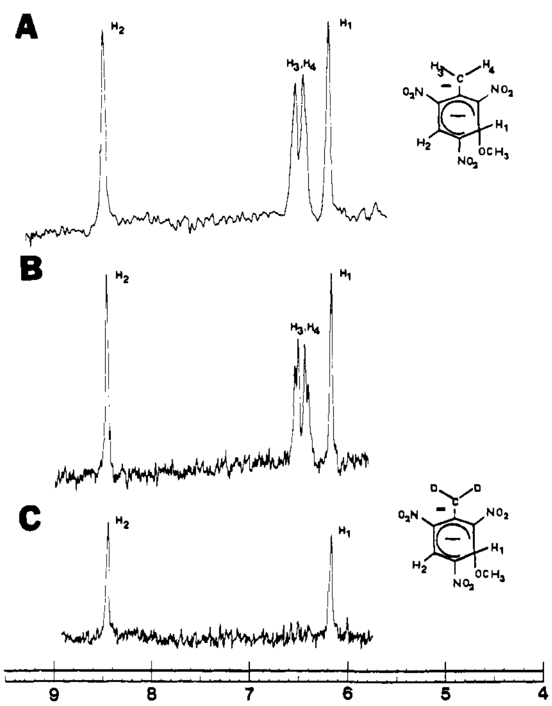


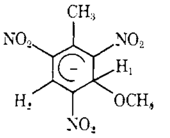
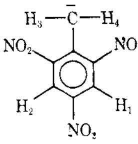
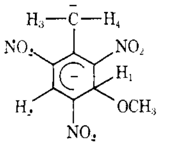
Figure 2. Static and flow 100-MHz proton NMR spectra of the absorptions of trinitrotoluene (0.25 M in Me_2SO) after reaction with methoxide ion (0.5 M in 87.5% Me_2SO–12.5% MeOH) at 30 °C: A, flow spectrum 0.5 s after mixing (flow rate 60 ml/min); B, static spectrum 3 min after stopping the flow; C, conditions as B except that TNT-d_3 was used as reactant.

(c) The Uv-Visible Spectral Changes during the Reaction. Because of its relative insensitivity, NMR will not, as has been pointed out previously,[22] be the best technique for the quantitative investigation of kinetic processes. The best use of the flow NMR technique will be in the identification and characterization of transient species and, subsequently, in the unambiguous assignment of their uv-visible spectra. In the present work, the very short path length cell described previously[22] was used and uv-visible spectra recorded under static and flowing conditions on the reaction mixtures described in sections a and b. It was not possible to use identical substrate concentrations in the uv experiments because of the very large extinction coefficients of the species formed, but it was possible to use reactant solutions which were 0.02 M in TNT. For the stable dianion species **6**, the proton NMR spectra were recorded using FT techniques on the more dilute solution used in the optical work and identical NMR spectra with those described above in section b were obtained.

(i) 0.02 M TNT in Me_2SO Plus Methoxide Ion (0.02 M in 98% Me_2SO–2% MeOH and 0.02 M in 60% Me_2SO–40% MeOH). Under flowing conditions, the uv-visible spectrum observed under both sets of conditions (Figure 3A) showed two absorptions ($\lambda_{1,\max}$ 433, $\lambda_{2,\max}$ 505 mμ), which from the NMR measurements are assigned to the Meisenheimer complex (**4**). Upon stopping the flow a new spectrum appeared, having absorptions ($\lambda_{1,\max}$ ~520, $\lambda_{2,\max}$ ~640 mμ) indentical with that reported by other workers and assigned to anion **3**. The present NMR measurements confirm this assignment.

(ii) 0.02 M TNT in Me_2SO Plus Methoxide Ion (0.04 M in 98% Me_2SO–2% MeOH). When the ratio of methoxide–TNT is increased to 2:1 or greater, a different spectrum ($\lambda_{\max}$ 550 mμ) is observed under both flowing and static conditions (Figure 3C). This spectrum is assigned to the dianion **6** characterized by the NMR studies (section b). The spectrum is quite stable and accurate extinction coefficients can be obtained for it in dilute solution. These are presented in Table I. The absorption maximum of this species is relatively close to that observed for the anion and, since the production of **6** could also give a primary isotope effect as observed in earlier kinetic

Table I. NMR and uv Spectral Parameters of the Species Produced in the Reaction of 2,4,6-Trinitrotoluene with Methoxide Ion in Me_2SO–Methanol Solutions

	NMR (Chemical shift data, δ ppm)					uv–visible spectra			
Species	Solvent	T, K	H_1	H_2	$(H_3, H_4)^a$	Solvent	T, K	$\lambda_{1,\max}$, mμ (ϵ_1)	$\lambda_{2,\max}$, mμ (ϵ_2)
 **4**	93% Me_2SO–7% MeOH	300	6.18	8.45		98% Me_2SO–2% MeOH	300	433 (1.8×10^4)[b]	505 (1.7×10^4)[b]
 **3**	93% Me_2SO–7% MeOH	300	8.18	8.18	5.53, 5.53	98% Me_2SO–2% MeOH	300	520 (1.7×10^4)	640 (1)
Isolated K^+ Salt of 3[c,d]	$CDCl_3$	243	9.09	9.09	6.43, 6.43	$CHCl_3$	300	524	630
Isolated Ph_4As[d] Salt of 3	C_5D_5N	244	8.52	8.52	5.90, 5.90	C_5H_5N	300	530	640
 **6**	93% Me_2SO–7% MeOH	300	6.18	8.45	6.42, 6.52	98% Me_2SO–2% MeOH	300	550 (1.5×10^4)	

[a] Peaks not assigned to specific nuclei. [b] Approximate value as determined using short path length flow uv cell. [c] 18-Crown-6 added to give appropriate concentration in solution. [d] Chemical shift values reported with respect to external Me_4Si lock

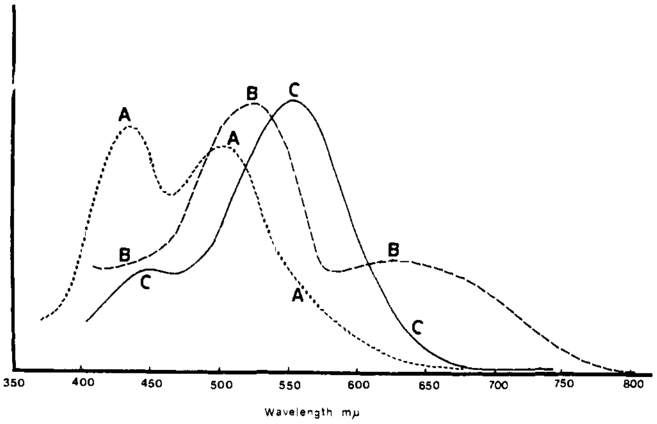


Figure 3. Uv visible spectra recorded using short path length cell after the reaction of trinitrotoluene (0.02 M in Me_2SO): A, with methoxide ion (0.02 M in 98% Me_2SO-2% MeOH), recorded under flowing conditions at a flow rate of 30 ml/min; B, with 0.02 M methoxide ion as in A, recorded after stopping the flow; C, with methoxide ion (0.04 M in 98% Me_2SO-2% MeOH), recorded under flowing and static conditions are identical.

work[13] as its production involves a proton abstraction, it was thought that the presence of **6** might go undetected in a mixture of **3** and **6** and a definite attempt was made to relate the present measurements to those of previous investigations.

(d) Dependence of the Reaction on Solvent Composition. The major difference between the present work and that of previous investigators is that previous work has been done in alcoholic solvents, whereas that reported above involves solvent mixtures of high Me_2SO content. The dependence of the reaction on the Me_2SO content of the solvent has been investigated and is presented in Figure 4 as a function of the solvent composition. The various peaks in the spectra have been assigned to the species **3**, **4**, and **6**.

The bottom spectrum, recorded at a flow rate of 30 ml/min, is that from the reaction of 0.25 M TNT and is similar to that

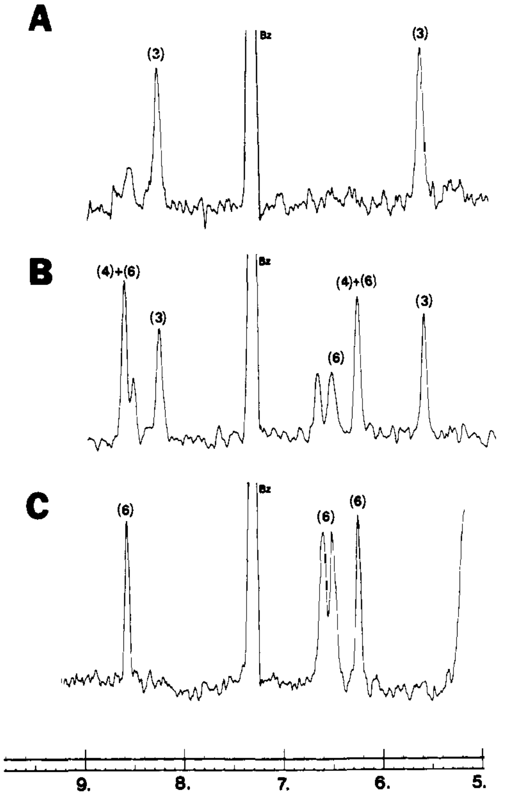


Figure 4. Flow NMR spectra of the reaction mixture from the reaction of trinitrotoluene (0.25 M in Me_2SO) with methoxide ion (0.5 M in various Me_2SO-methanol solvent mixtures). The spectra were all recorded at identical flow rates of 30 ml/min, and therefore at identical times after mixing. The single peak at −7.3 ppm is due to benzene used as internal reference to estimate concentrations. The peaks in the spectra are assigned to the species **3**, **4**, and **6**, discussed in the text: A, reaction with methoxide ion (0.5 M in 100% MeOH); B, reaction with methoxide ion (0.5 M in 50% Me_2SO-50% MeOH); C, reaction with methoxide ion (0.5 M in 75% Me_2SO-25% MeOH).

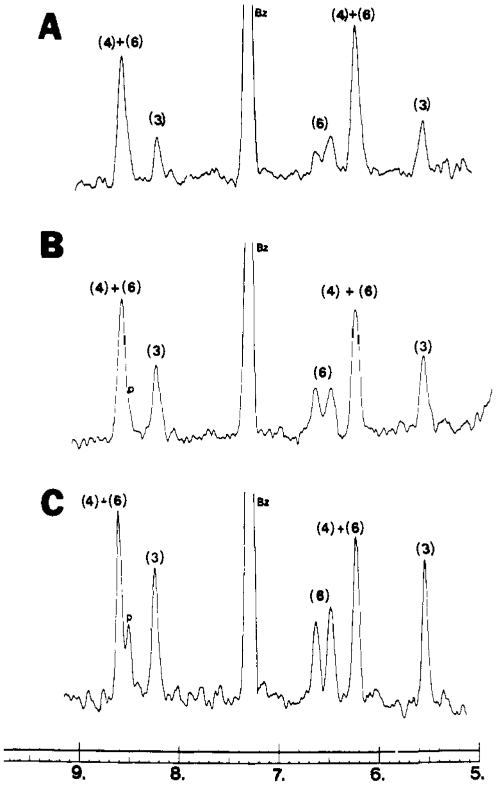


Figure 5. Flow NMR spectra of the reaction mixture from reaction of trinitrotoluene (0.25 M in Me_2SO) with methoxide ion (0.5 M in 50% Me_2SO-50% MeOH) recorded at various flow rates (and therefore various times after mixing). The single peak at −7.3 ppm is due to benzene used as internal reference. The various peaks in the spectra are assigned to the species **3**, **4**, and **6**, discussed in the text: A, flow rate 80 ml/min; B, flow rate 60 ml/min; C, flow rate 40 ml/min.

observed in solutions of higher Me_2SO content and is assigned to the dianion. The solution shows little change when the flow is stopped. The middle spectrum, which was recorded at the same flow rate (and therefore at the same time after mixing) with the Me_2SO-MeOH ratio of the methoxide ion solution lowered to 50:50 shows a much more complex mixture of intermediates. In fact, all three species **3**, **4**, and **6** are present, as indicated in the spectrum. It is important to note that the ring proton absorptions of **6** and **4** occur at almost identical chemical shifts and that the absorption at δ 8.45 is in fact due to a mixture of these species, as can be seen from the low intensity of the multiplet at δ 6.55 due to the methylene hydrogens in **6** relative to the single absorption at δ 6.25 due to the single hydrogen on the sp^3 hybrid carbon in the *same* species. As the Me_2SO-MeOH ratio in the alkoxide solution is further reduced and pure methanol used, only the anion is observed under identical conditions of flow rate and concentration as used to obtain the previous spectrum (top spectrum, Figure 4).

At Me_2SO-MeOH ratios less than 75:25, the spectra are quite time dependent. Since this might indicate the order in which the species are produced, this also was investigated. These results are presented in Figure 5 for the case of TNT (0.25 M in Me_2SO) plus methoxide ion (0.6 M in 50% Me_2SO-50% MeOH). The figure from bottom to top shows spectra recorded at increasing flow rates and indicates clearly that the Meisenheimer complex is formed first and subsequently the anion and dianion. When methoxide ion in pure methanol is used, the σ-complex is not observed: in this case also, no dianion is observed. It is not possible to deduce from this data whether the σ-complex is not formed at all, is formed with a very small K (formation), or is formed but decomposes very rapidly in this case.

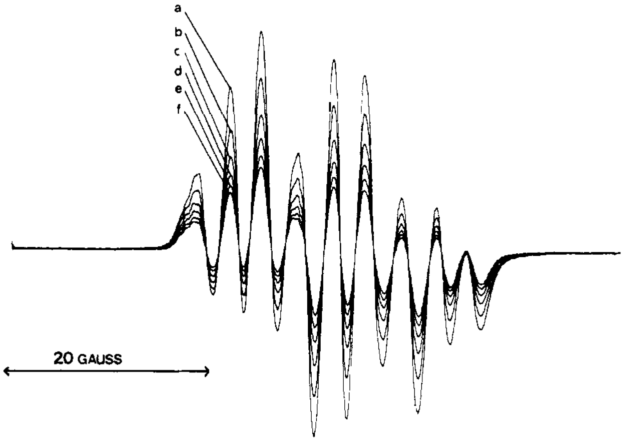


Figure 6. ESR spectra recorded during the decay of the radicals formed from reaction of 0.5 M TNT in Me_2SO with methoxide ion (0.5 M in 87.5% Me_2SO-12.5% MeOH): a, maximum concentration of radicals 240 s after mixing; b, 320 s; c, 400 s; d, 480 s; e, 560 s; f, 640 s.

Using the uv assignments given in Table I, these conclusions have been confirmed by uv-visible spectroscopy. Thus the reaction is very dependent on solvent composition, the formation of the dianion being favored by high Me_2SO concentrations, and the rate and extent of anion formation by high methanol concentrations. The anion also is favored in more dilute solutions.

Thus the relation to the previous work is that the NMR data clearly indicate that the species observed in these studies were the Meisenheimer complex **4** and the anion **3**. However, a change in the species produced should occur on increasing the Me_2SO content of the solvent and it would be of interest to study the solvent dependence of this reaction quantitatively in dilute solution using uv-visible spectroscopy, as the derived kinetic and thermodynamic parameters should yield information regarding the stabilizing forces in these three very closely related species. Such an investigation is currently in progress.

(e) **Free Radicals Produced in the Reaction.** As described above in section a the NMR results suggested the presence of substantial quantities of free radicals in the reaction mixture. Previous ESR investigations of this reaction indicated only small quantities of radicals compared to those produced by the action of base on *o*- and *p*-nitrotoluenes. The reaction was investigated by ESR using the same mixing chamber and concentrations as described in section a and a quartz flow ESR cell. Very large quantities of radicals were found (Figure 6) whose concentration reached a maximum and whose rate of disappearance was similar to that of the disappearance of the anion in Figure 1. Under some conditions it became apparent that in fact a mixture of radicals is formed, one of which may be the anion radical of TNT. Work is continuing in this area.

Conclusions

Thus, the use of high-resolution nuclear magnetic resonance spectroscopy in flowing systems has made possible the detection and characterization of the intermediate species **3**, **4**, and **6** in the reaction of trinitrotoluene with methoxide ion and the subsequent unambiguous assignment of their uv-visible absorption spectra. It is in this latter application that the technique is considered most useful, as the reaction and its solvent dependence are now amenable to direct investigation by uv-visible spectroscopy in dilute, ideal solutions.

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References and Notes

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Gas-Phase Methylene Reactions with Carbonyls. 1. Propanal

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Abstract: Gas-phase reactions of methylene with propanal in oxygen scavenged systems have been studied over a pressure range of 8 to 100 Torr. The reaction products were butanal, 2-methylpropanal, epoxybutane, and methyl propionate. No chemically activated isomerization or decomposition was observed over the pressure range. Large yields of methyl ethyl ketone were observed but were formed almost entirely from direct reaction of propanal with diazomethane, the methylene precursor. The relative reactivity of singlet methylene with C=O:C-H(α):C-H(β) is 1.0:0.05:0.08; the C=O reactivity relative to the C-H bonds in neopentane was 4.8. A direct insertion reaction into the C=O bond is thought to be a more likely pathway to the epoxide than a biradical intermediate formed by addition of the methylene to the oxygen end of the C=O. Methyl propionate is attributed to reaction by $^3CH_2$ with popanal, followed by reactions of the intermediate with oxygen.

Introduction

The reactions of methylene (CH_2), the simplest carbene, have been of continued interest since Doering's initial work in 1956.[1] Nevertheless, a perusal of the recent reviews[2,3] indicates that there is little qualitative, and virtually no quantitative, information on the gas-phase reactions of methylene with carbonyls.

Back's[4] studies of reactions of methylene produced by photolysis of ketene in unscavenged propanal and ethanal systems is of limited value because of (1) the substantial reaction of methylene with ketene itself, (2) the occurrence of both triplet and singlet state methylene reactions, and (3) the significant photodecomposition of the carbonyl reactants and products at the wavelengths employed. Thus even such basic questions as the relative reactivity of C=O addition to C-H insertion and the mechanism of C=O addition are largely unanswered.

Some studies have been reported on methylene interactions with CO_2[5] and a great deal of work has been done on the ketene system.[5a,6,7] Although these molecules contain a C=O bond rather different from the carbonyl compounds, three general observations are relevant. Matrix isolation studies[5b] on CO_2 showed that the intermediate has spectral characteristics most indicative of an α-lactone structure, although the presence of the open chain biradical $O{=}\dot{C}\text{-}O\text{-}\dot{C}H_2$ could not be completely excluded. Both product formation in the gas-phase[6] and matrix studies[7] on ketene support a mechanism involving C=C addition as the primary adduct rather than interaction with the C=O end of the molecule. Finally, the rate of $^1CH_2$ reaction with ketene is probably over a 100 times faster than the $^3CH_2$ rate.[6d]

Bradley and Ledwith have considered the mechanism of singlet methylene reaction with the carbonyl group in liquid acetone.[8] In addition to direct addition across the C=O bond they proposed a singlet dipolar intermediate I which can close