Average magnetic shielding values for NH_3 and H_2CO have recently been calculated from molecular orbital theory by Ditchfield.[34] These calculated values for hydrogen are $\bar{\sigma}(H_2CO) = 22.3$ and $\bar{\sigma}(NH_3) = 33.6$ ppm and for nitrogen $\sigma(NH_3) = 267.8$ ppm. The agreement with our above results is reasonably good in view of the difficulty of ab initio calculations of the paramagnetic term.

Acknowledgment. The writer wishes to thank Dr. Michael Barfield for helpful discussion on this work. The support of the National Science Foundation, Structural Chemistry Section, was greatly appreciated.

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High Resolution Nuclear Magnetic Resonance Studies of Chemical Reactions Using Flowing Liquids. Investigation of the Kinetic and Thermodynamic Intermediates Formed by the Attack of Methoxide Ion on 1-X-3,5-dinitrobenzenes[1]

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Abstract: High resolution nuclear magnetic resonance spectroscopy in a flowing system has been used to investigate both the kinetic and the thermodynamic distributions of the isomeric complexes formed by the attack of methoxide ion on 1-X-3,5-dinitrobenzenes (where X = CN, CF_3, $COOCH_3$, $COOCH_2CH_3$) by the direct observation of these species at various reaction times in a flowing, chemically reacting system. In all cases a *mixture* of the two species is formed initially under kinetic control and the conversion from kinetically to thermodynamically controlled distributions occurs in less than 2 sec for all the compounds investigated. The results are compared with data on the reactions from previous uv-visible spectroscopic measurements and a reinterpretation of these data is given.

The various spectroscopic techniques used for kinetic measurements of chemical reactions all have their unique advantages and disadvantages. Thus, uv-visible spectroscopy has the advantage that it is a very sensitive technique and it is by far the most widely used method for making flow and stopped-flow kinetic measurements in reacting chemical systems. It does, however, have a severe disadvantage in that it is relatively nondiagnostic, the results leaving the identity of many observed species uncertain and in some cases depending on spectral assignments which may directly affect the interpretation of the kinetic data. Ir spectroscopy is less sensitive but is somewhat more diagnostic, depending on the presence of specific, often identifiable groupings of atoms in the molecule. It is used only infrequently, however, mainly due to its lack of sensitivity. ESR combines a high degree of sensitivity with a considerable amount of diagnostic character but is obviously applicable only to a restricted class of compounds. However, it has found wide application for radical reactions and is often used where the species observed are in a flowing chemically reacting system, permitting the observation of relatively short-lived species.

High-resolution nuclear magnetic resonance spectroscopy is much less sensitive than uv-visible spectroscopy (often by several orders of magnitude) but has a great advantage as a diagnostic tool and can provide much more information about the detailed molecular structure of the species observed. Because of this, it has become one of the most widely used spectroscopic techniques for the identification of compounds in equilibrium systems, and systems where chemical reactions are occurring slowly in a static system. However, despite its obvious advantages as a diagnostic tool, high-resolution nuclear magnetic resonance spectroscopy has not been used to date to make measurements in flowing, reacting chemical systems. The reason for this is that, in magnetic resonance experiments (either NMR or ESR), the spins must attain their Boltzmann distribution between the energy levels produced by the application of the magnetic field before reliable experimental measurements can be made. A time interval of $\sim 3T_1$ (where T_1 is the spin-lattice relaxation time of the spin particle, characterizing its first-order attainment of the equilibrium distribution between the levels) is needed to attain ~95% of the equilibrium magnetization. In the case of unpaired electron spins, T_1 is very short, and, in practice, the attainment of the equilibrium is instantaneous and places no restriction on the use of flow systems. For nuclear spins, T_1 is characteristically long (of the order of several seconds or more) and thus a severe restriction is placed on the use of flowing systems for making high resolution nuclear magnetic resonance measurements. The reliable observation of chemical species is thus precluded, and the potential advantage of the diagnostic character of high resolution NMR in these situations is lost.

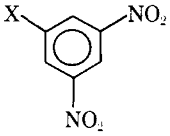
Techniques and equipment have been developed which circumvent these problems, and allow the use of high resolution NMR for the direct observation of short-lived species in flowing, chemically reacting systems. A preliminary account of this technique and its application to the investigation of the products formed from kinetic and thermodynamic control in the reaction of methoxide ion with 3,5-dinitrocyanobenzene has been given.[3]

The purpose of the present paper is to present a full account of the work on this and other related systems, including the use of the technique to give reliable and quantitative kinetic data and the results of a direct comparison of the NMR and uv-visible spectroscopic measurements by the investigation of the reaction by both techniques under comparable conditions.

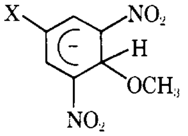
The systems chosen for study belong to the general class of compounds known as Meinsenheimer complexes, the formal analogs of the postulated intermediates in nucleophilic aromatic substitution reactions, an area in which there has been considerable interest in recent years.[4]

A point of particular interest is the relationship between kinetic and thermodynamic control of the reactions in cases where a mixture of isomeric complexes is formed, a distinction first demonstrated by Servis.[5]

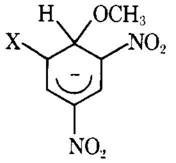
The substrates chosen for study were of the general form I (X = CN, CF_3, $COOCH_3$, $COOCH_2CH_3$, COO-*i*-Pr, COO-*t*-Bu). Attack of alkoxide ion on I may yield either one or both of the complexes II, III depending on whether the attack is between the two NO_2 groups or between X and one NO_2 group, respectively.



I



II



III

X = CN, CF, $COOCH_3$, $COOCH_2CH_3$, COO-*t*-Bu

In the case of I (X = CN), Foster and Foreman showed by NMR that there was one major thermodynamically stable product species, which they identified as III (X = CN).[6,7]

Terrier and coworkers have shown by uv-visible spectroscopy that there is another species formed in the kinetically controlled reaction to which they assigned the structure II (X = CN).[8] They were able to detect by NMR the existence of II to about 5% in the reaction mixture in DMSO solution with very little methanol present and assigned its ^1H NMR spectrum.

The kinetics of the reaction of methoxide ion with 3,5-dinitrobenzonitrile to form III (X = CN) in methanol and methanolic DMSO solutions has also been investigated by Fendler and coworkers.[9] They reported no prior formation of II to yield 1-methoxy-3-cyano-5-nitrobenzene. Foster and Foreman also investigated I (X = CF_3)[6] and Crampton and coworkers[10,11] have given a detailed investigation of the series of complexes formed from the series of compounds I (X = CF_3, $COOCH_3$, ...) by both NMR and uv-visible spectroscopy. In these studies, the NMR measurements clearly indicate that for these compounds both II and III are present in the equilibrium mixture, to the extent of $\simeq 3{:}7$ ratio making the identification and detection of II much more straightforward than the case of II (X = CN).

For all compounds I (X= CN, CF_3, $COOCH_3$, ...) the uv-visible spectra show initially a spectrum consisting of two absorptions at $\simeq 500$ and $\simeq 545$ mμ which changes to a larger absorption at $\simeq 495$ mμ and the peak at $\simeq 545$ mμ becomes smaller and in the case of X = CN almost disappears altogether. These have been interpreted[10,11] as indicating the following scheme.

$$\mathrm{I} \xrightarrow{\text{fast}} \mathrm{II} \xrightarrow{\text{slow}} \mathrm{III}$$

On the basis of this assignment, species of type II are proposed to have a characteristic absorption spectrum[8,10,11] λ_1 505 mμ, ϵ 16.800; λ_2 555 mμ, ϵ 11.700 and complexes of type III to have a characteristic spectrum λ_{max} 500 mμ and ϵ 22,800.

In the present work we have used the technique of flow nuclear magnetic resonance spectroscopy to investigate the exact relationship of II and III *throughout* the complete course of the reaction. Since the half-life for the establishment of the thermodynamic equilibrium mixture is in all cases less than 3 sec it is not possible to investigate this change using conventional NMR spectroscopy. This application of the diagnostic character of NMR will provide a sound basis for the interpretation of the uv-visible spectra from which technique more exact data can subsequently be obtained.

Experimental Section

Flow NMR measurements were made using a suitably modified H.A.100 spectrometer of which a detailed description will be given in a forthcoming publication.[12]

A system is used which includes two reservoirs to permit one or both of the reacting solutions to come to equilibrium in the applied magnetic field before they are mixed together. They are then mixed in a high-pressure mixing chamber and flowed continuously through the measuring coils of the probe. There is some line broadening as a function of the flow rate, but at suitable flow rates the signal to noise ratio is appreciably better than for a stationary sample, as the nuclei cannot be saturated by the irradiating field. There is a limitation on both the flow rate and the length of time the flow can be continued imposed by the capacity of the reservoirs. This can be maximized by using a probe design in which the transmitter/receiver coupling is minimized by time-sharing techniques[13] and the space occupied by the balance "paddles" in the usual probe design is made available.

Uv-visible spectroscopic measurements were made using a Unicam SP 800 spectrophotometer and a Cary spectrophotometer. For the flow uv measurements a specially constructed straight-through flow cell was used of pathlength < 1 mm.

Chemicals used were from commercial sources or were prepared by literature methods and had mp's and spectroscopic properties consistent with those previously reported. NMR measurements were made by mixing equimolar solutions containing 0.5 or 0.2 *M* of each reactant nitroaromatic substrate in DMSO solution with methoxide ion in a solvent system of 87.5% DMSO/12.5% methanol (v/v).

Results and Discussion

Although the systems investigated all conform to the same general scheme, there are significant differences between some of them, both in their chemical behavior and also in the previous work which has been done, and for clarity of presentation they will be discussed separately.

A. 3,5-Dinitrocyanobenzene and Methoxide Ion. (a) Qualitative. Typical spectra obtained for the reaction of 3,5-dinitrocyanobenzene (0.5 *M*) in DMSO solution with methoxide ion (0.5 *M*) in DMSO/methanol solution (87.5/12.5 (v/v) are shown in Figure 1. The spectra show only the low-field resonances due to the hydrogens on the aromatic rings. The lock signal for all the measurements is the methyl resonance of the solvent DMSO.

The top spectrum shows the absorptions due to the ring hydrogens of 3,5-dinitrocyanobenzene. As can be seen from the figure, it is possible to obtain good, well-resolved high-resolution nuclear magnetic resonance spectra from stationary samples, provided care is taken to make the magnetic field as homogeneous as possible. There is some loss of resolution in subsequent spectra in the figure, which is at least partly due to the effect of the flow,[14] but the spectra are quite adequate for the assignment of structures. The decrease in the S/N ratios between this and the other spectra is to some extent due to broadening of the signals, but is also due to the twofold dilution which occurs during the mixing of the two streams of reactant solutions.

The bottom spectrum was obtained by flowing the reacting solutions and then stopping the flow and is the equilibrium situation. The three resonances of equal intensity at τ 1.5, 2.24, and 4.38 correspond to those reported by Foster and Foreman[6,7] which they assigned to structure III (X = CN). The values found in the present work[7] correspond closely to those reported by Terrier et al.[8]

The intermediate spectra in Figure 1 are recorded at the flow rates indicated. The flow rate increases from top to bottom, hence the time from mixing to observation decreases. In these spectra, in addition to the resonances assigned to III (X = CN) there are two other signals at τ 2.15 and 3.79 in the relative ratios 2:1. As previously shown by Terrier,[8] these can be assigned to the thermodynamically less stable isomer II (X = CN). In the present instance, however, this species is present at a stable, time-independent concentration at any particular flow rate chosen. As the flow is increased, that is as the time interval between mixing and observation is decreased, the proportion of II in the mixture of II and III increases. Qualitatively, it is observed that at the faster flow rates a limiting situation is apparently reached, with a ratio of II:III of approximately 6:4 as indicated in the last spectrum in the series. A complete, quantitative treatment of the data will be needed before one can say that this is the true limiting situation, corresponding to the mixture formed by kinetic control of the methoxide ion attack on the substrate, as the possible effects due to the efficiency of the mixing cannot be deduced from these qualitative observations, but it should be noted that this observation is in apparent conflict with the interpretation of the uv-visible spectroscopic results. When the flow is stopped, the spectrum changes almost immediately to the lowest one in the series, corresponding to the thermodynamically stable product III (X = CN). Under the conditions of the experiment, this change takes place in much less than 10 sec, and thus it would not be possible to make any reliable measurements on the reacting solutions by conventional NMR spectroscopy.

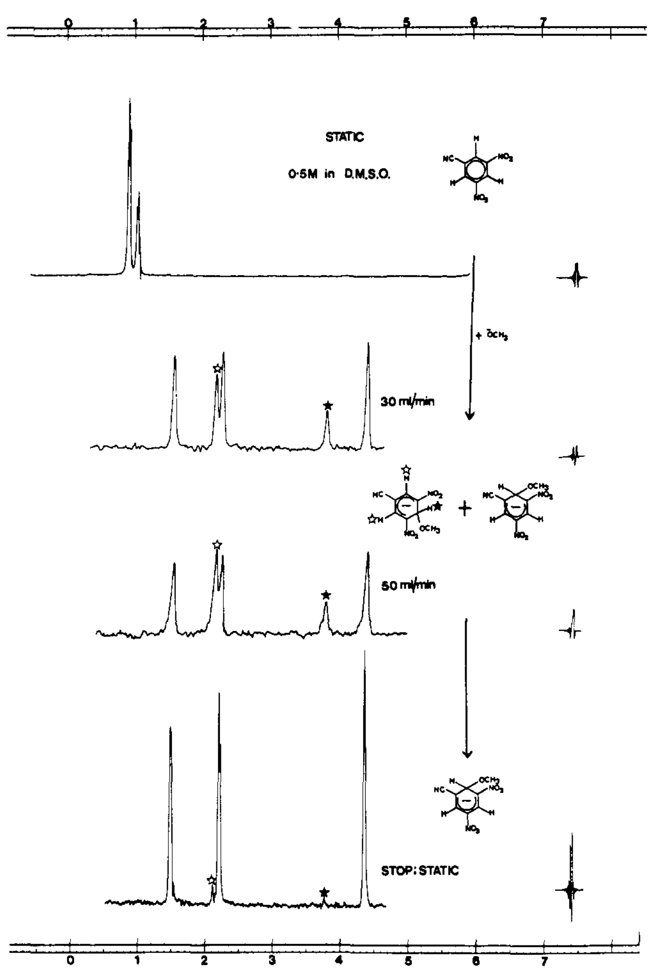
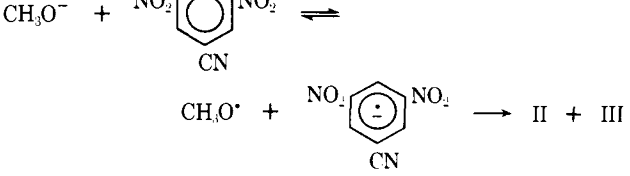


Figure 1. Representative ^{1}H NMR spectra recorded at 100 MHz, 0.5 *M* in DMSO, showing the ring proton absorptions of 3,5-dinitrocyanobenzene alone (top spectrum) and during its reaction with 1 equiv of methoxide ion (in 87.5% DMSO/12.5% MeOH) under the conditions of flow rate indicated.

One point of interest which emerges from the present work is that there is no evidence in Figure 1 or in any of the spectra recorded of enhanced emission or absorption in the proton resonances due to nuclear polarization effects. The spectra of the intermediates were recorded within a very short time after mixing and such effects might well have been expected if the attack of the alkoxide ion had proceeded via a prior electron transfer reaction (Scheme A) as has been suggested.[16] The nonobservation of such effects does not, of course, preclude their occurence, but it does place severe limits on the lifetimes of the radical pair. Thus, although radical anions are definitely produced in these basic systems, there is no evidence in the present work that neces-

Scheme A



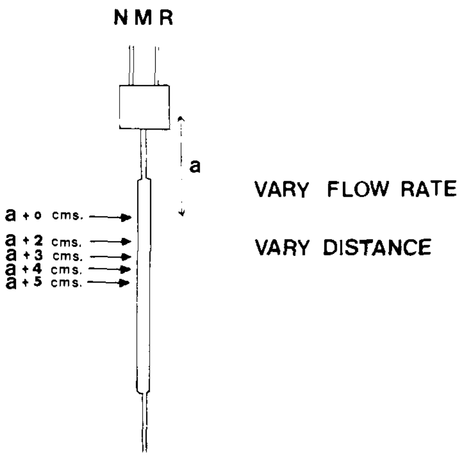


Figure 2. Schematic representation of the relationship between the high-pressure mixing chamber and the NMR detection coils indicating the two experimental variables which can be used to control the time interval between mixing and observation.

sitates postulating their involvement in the attack of the nucleophile on the aromatic substrate.

(b) **Quantitative Measurements.** Since the area of a signal due to a given nucleus is proportional to the concentration of this nucleus in solution, NMR can be used to make kinetic measurements, providing there are no saturation effects. An advantage of the use of NMR for this purpose is that measurements can be made of several nuclei within a single molecule, which should all yield the same answer and thus give a consistency check as well as additional data.

In making kinetic measurements, we wish to know the concentration of a given species as a function of time as the reaction proceeds. Consideration of the system used as shown schematically in Figure 2 indicates that there are two experimental parameters which can be varied to accomplish this. Thus we can, for a fixed observation point corresponding to the location of the receiver coil with respect to the tube, vary the flow rate of the liquids and thus alter the time between mixing and observation. If the volume between the point of mixing and this point of observation is known, we can deduce the time intervals involved. One limitation here will be that a minimum rate of flow is necessary for the high-pressure mixing chamber to work efficiently and thus long time intervals will be more difficult to measure. However, one can also vary the distance between the point of mixing and the point of observation and again make measurements as a function of flow rate as before. The results for all different flow rates and all the different distances should lie on the same kinetic curve and since there will be considerable overlap in the time intervals from these different combinations, a further internal consistency check is provided.

A plot of log percent concentration against time for the disappearance of II and the appearance of III in this system is shown in Figure 3. The open circles correspond to measurements made at varying flow rates with the point of observation as close as possible to the point of mixing. The other symbols correspond to measurements at different flow rates but at larger distances from the point of mixing. Each point corresponds to the average value obtained from measurements made on the signals in a given spectrum. Peak areas were measured using a planimeter to increase the accuracy. As can be seen from the figure, there is reasonable consistency between all the different sets of measurements.

These data are shown replotted in Figure 4. The data follow a reasonable first-order plot from which the kinetic parameters given in Table I can be extracted. The reaction is relatively fast, having a half-life, $t_{1/2} = 0.940 \pm 0.015$ sec, showing clearly the usefulness of the technique. Both this and the previous graph are drawn assuming that there is 100% efficiency in the mixing, and that all of the time interval between the mixing chamber and the point of observation is available for reaction within the mixed, flowing solu-

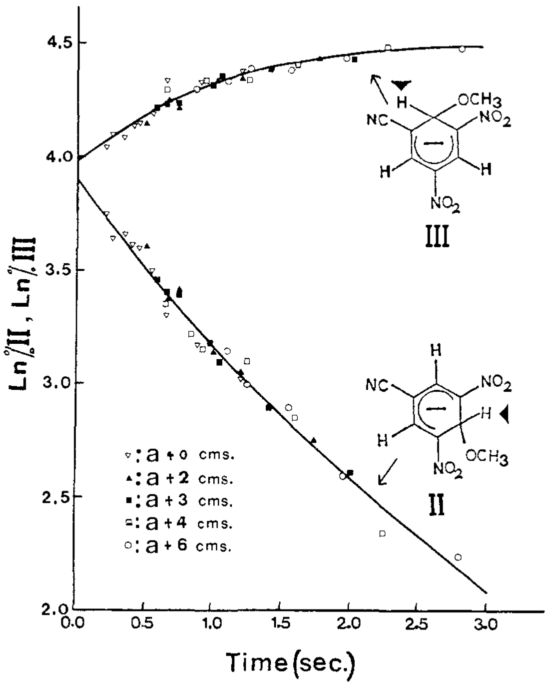


Figure 3. Plot of log % II and log % III against time (seconds) based on the areas of the resonance signals of the hydrogens attached to the sp^3 hybridized carbon atoms in these compounds. The points corresponding to each fixed distance between the mixing and observation are identified as inset in the figure.

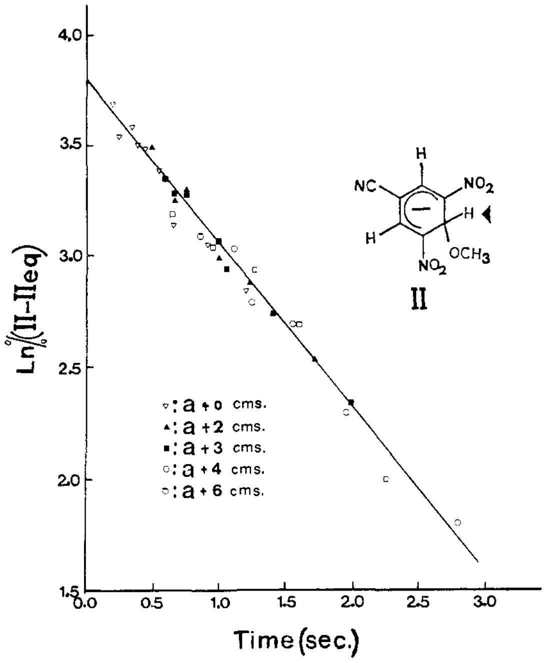


Figure 4. Plot of log $\%(\mathrm{II} - \mathrm{II}_\infty)/T$ (seconds) for the disappearance of the proton resonance of the hydrogen atom attached to the sp^3 hybridized carbon atom in complex II formed from 3,5-dinitrocyanobenzene. The points corresponding to measurements made at each fixed distance between mixing and observation are identified as inset in the figure. The solid line is a least-squares fit to the data yielding the kinetic parameters listed in Table I.

Table I. Kinetic and Thermodynamic Parameters Obtained from the Flow NMR Investigation of the Reaction of 1-X-3,4-dinitrobenzenes with Methoxide Ion and Hydroxide Ion Under the Conditions Indicated

X^a	OR	$II_{t=0}$ %	$III_{t=0}$ %	II_{eq}%	III_{eq}%	k_3, sec^{-1}	k_{-3}, sec^{-1}	K_3
$COOCH_3$	$OCH_3{}^b$	56 ± 6	44 ± 4	25 ± 3	75 ± 5	0.565 ± 0.065	0.188 ± 0.024	3.0 ± 0.4
$COOCH_2CH_3$	$OCH_3{}^b$	58 ± 6	42 ± 4	25 ± 3	75 ± 5	0.920 ± 0.12	0.307 ± 0.040	3.0 ± 0.4
CN	$OCH_3{}^b$	47 ± 5	53 ± 5	3.1 ± 0.4	96.9 ± 3	0.712 ± 0.093	0.023 ± 0.003	31.3 ± 5.0
CF_3	$OCH_3{}^b$	53 ± 5	47 ± 5	4.5 ± 5	95.5 ± 3	1.648 ± 0.215	0.078 ± 0.01	21.2 ± 2.5
$COOCH_3$	OH^c	49 ± 5	51 ± 5	25 ± 3^d	75 ± 5^d	0.413 ± 0.055	0.138 ± 0.018	3.0 ± 0.4
CN	OH^c	18 ± 2	82 ± 6	2.5 ± 0.5	97.5 ± 2.5	0.459 ± 0.060	0.012 ± 0.0015	39 ± 8

[a] 0.5 *M* in DMSO. [b] 0.5 *M* in 87.5:12.5 DMSO:MeOH (v/v). [c] 0.5 *M* in 7:3 DMSO:H_2 (v/v). [d] Decomposes on standing.

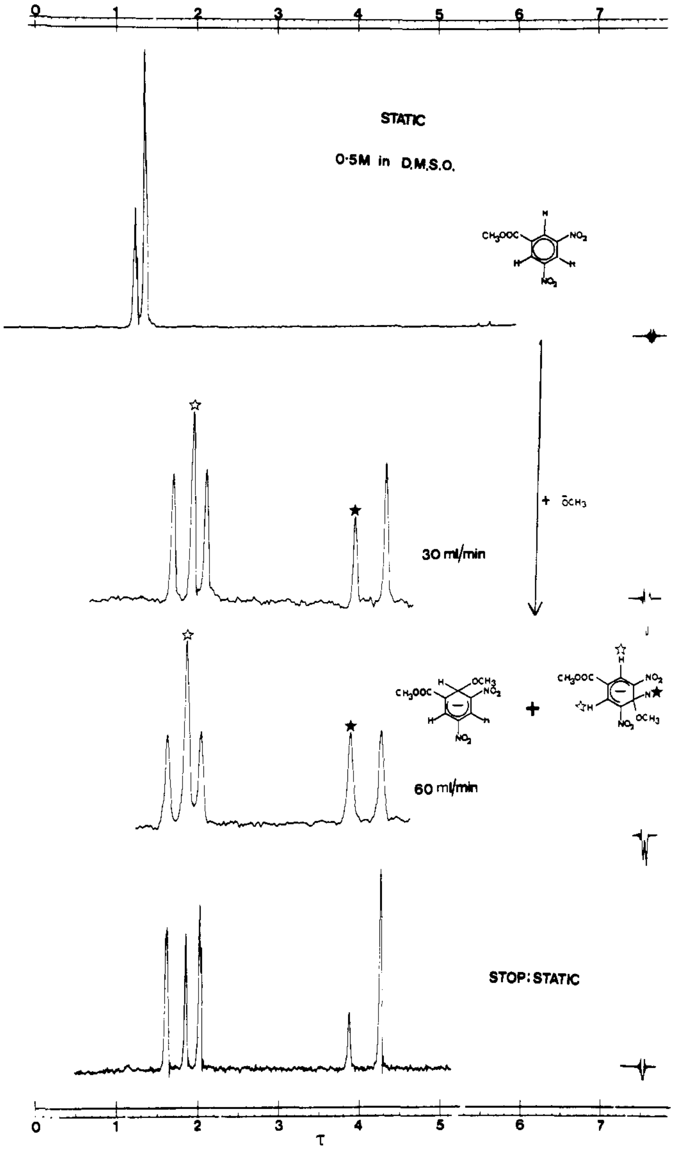


Figure 5. Representative ^1H NMR spectra showing the ring proton absorptions of 3,5-dinitrocarbomethoxybenzene (0.5 *M* in DMSO) alone (top spectrum) and during its reaction with 1 equiv of methoxide ion (in 87.5% DMSO/12.5% MeOH) at the rates of flow indicated.

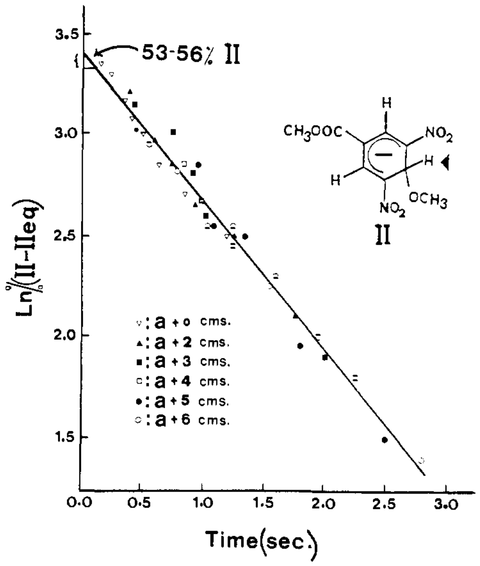


Figure 6. Plot of log %(II − II$_\infty$)/*T* (seconds) for the disappearance of the proton resonance of the hydrogen atom attached to the sp^3 hybridized carbon atom in complex II formed from 3,5-dinitrocarbomethoxybenzene. The points corresponding to measurements made at each fixed distance between mixing and observation are identified as inset in the figure. The solid line is a least-squares fit to the data yielding the rate constant and deviations given in Table I.

tion.[17] As indicated in Figure 4, the possible error from this source is not large, and can be estimated. For 100% efficient mixing, the initial kinetic mixture would contain 47% II and 53% III. The least efficient mixing possible consistent with the results would yield 43% II and 57% III. The relationship of these results to those from the uv-visible measurements from which they differ somewhat will be discussed in a later section.

B. Methyl 3,5-Dinitrobenzoate and Methoxide Ion. (a) Qualitative. Typical spectra obtained for this system are shown in Figure 5. Again, the spectra obtained under flowing conditions indicate the presence of two species (II and III, X = $COOCH_3$). The proportion of each species present is markedly dependent on the flow rate and, as before, there is a very fast decay of the spectrum to the equilibrium situation indicated in the bottom spectrum. The lowest of the spectra shown in Figure 5 represents a limiting situation similar to the 3,5-dinitrocyanobenzene system. In this case, however, both isomers are also present in the equilibrium mixture, the less stable one II (X = $COOCH_3$) to the extent of ~25%. There is no difficulty in measuring the NMR spectrum of the less stable isomer in this case, and the identification of both species in the system has been made previously by Crampton and coworkers.[10,11] Again, however, the change from the kinetic to the equilibrium distribution is very fast and cannot be investigated by conventional NMR spectroscopy.

(b) Quantitative. Spectra were recorded with variation of both the flow rate and also the distance between mixing and observation as in the previous example. The results are shown plotted assuming a simple first-order reaction in Figure 6. The kinetic parameters derived from this plot are presented in Table I. Again the initial kinetically controlled mixture contains both isomers II and III (X = $COOCH_3$), in similar proportions to those of the previous system. $t_{1/2}$ is again short, approximately 0.920 ± 0.015 sec.

C. Other Systems. Similar measurements were carried out on the series of substrates I (X = CF_3, $COOCH_2CH_3$, COO-*t*-Bu, . . .). In all cases, the spectra obtained were very

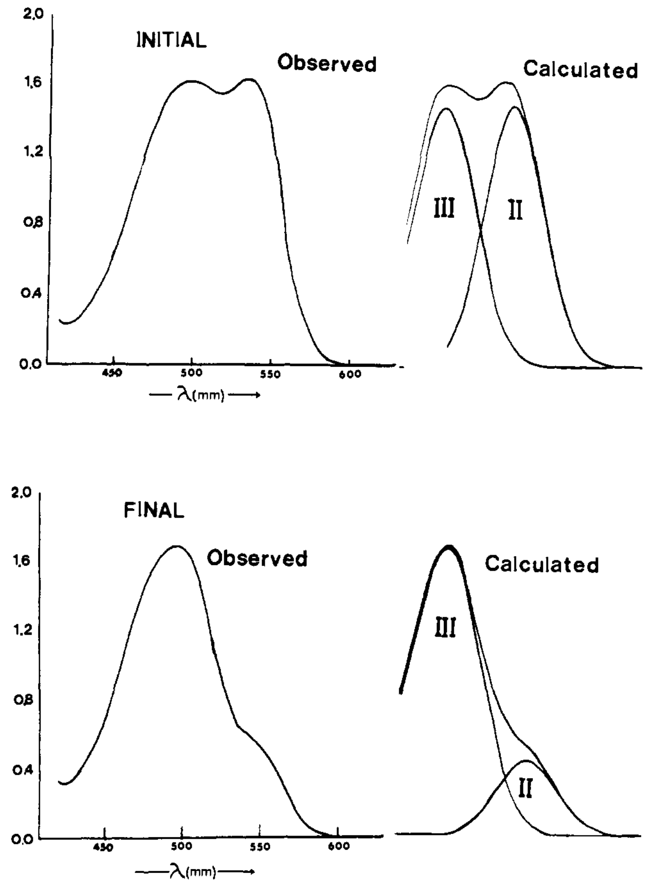
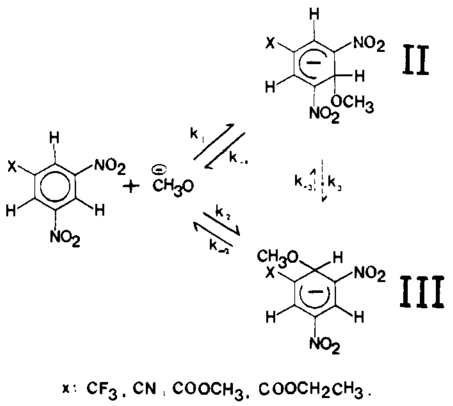


Figure 7. Uv-visible spectra recorded during the reaction of methyl 3,5-dinitrobenzoate with sodium methoxide (87.5% DMSO/12.5% MeOH) together with the resolution of the curves into two gaussian component curves.

dependent on the flow rate and there was a very fast conversion from the kinetic to the thermodynamic distributions of the two isomers II and III. Reasonably good kinetic plots were obtained, yielding the parameters listed in Table I. Similar results were also found for the attack of hydroxide ions on I (X = CN and X = COOCH$_3$) and these data are also included in the table. There is little difference in the initial percentages of the two isomers formed and the distributions are quite close to a statistical distribution between the two forms, which should be 2:1 in favor of III, indicating the attack of the methoxide ion in these systems is relatively unselective. This result is similar to that observed for the attack of carbanions[6,10,18,19] where there is either no interconversion between the two isomers or where it is very slow, and where the kinetic distribution of the two isomers can thus be measured directly by NMR. The thermodynamic distributions of the two isomers varies within the series of compounds studied, consistent with previous work, with X = CN being most different from the rest. However, only a small difference in energy between the two species would be necessary to cause this difference.

All the data can be discussed within the general framework of the reaction Scheme B as used previously.[8] Thus the formation of the kinetic mixture is very fast compared to the establishment of the thermodynamically controlled equilibrium, indicating that k_1 and k_2 are larger than k_{-1} and k_{-2}. The ratio of k_1/k_2 may be obtained from the initial kinetically controlled distribution of II and III. The conversion of II to III may be considered in terms of k_3 and k_{-3} which can be reexpressed in terms of k_1, k_{-1}, k_2, and k_{-2}. (Whether the actual conversion of II to III takes place by the direct route II → III or by II → I → III is a question of a chemical nature which the kinetic measurements cannot answer.) Thus, a large amount of kinetic data may be obtained from the NMR measurements which may be used to describe these systems. However, although the NMR measurements yield excellent diagnostic data, there are several limitations placed on the usefulness of NMR as a kinetic technique, due to the inherent low sensitivity of the method. This has the effect of first lowering the accuracy of individual measurements and second necessitating the use of very concentrated and thus nonideal solutions. Thus, the main usefulness of the flow NMR technique will be in the unambiguous identification of the species present and hence the assignment of their uv-visible spectra. The best kinetic data in the most ideal solution conditions may then be obtained by uv-visible spectroscopy. (In some cases this may not be possible as the species may not have uv-visible absorptions and the NMR data will thus be all that are available.) It has been possible to assign the uv-visible spectra of the two intermediates in this reaction using the flow NMR data and hence to resolve the apparent disagreement between the NMR data and the previous spectroscopic data concerning the percentages of the two isomers present.

Scheme B



D. Comparison of Results from NMR and Ultraviolet-Visible Spectroscopic Measurements. The uv-visible spectra have been previously measured for several of the compounds studied by Terrier and coworkers[8] and by Crampton and coworkers.[10,11] The spectral changes observed during the reaction are very similar for the whole series of compounds and they can all be discussed together. There is, in all cases, the initial very fast appearance of a spectrum with two peaks at λ_{max} ~505 mμ (e.g., Figure 7). The initial spectrum has been assigned to adducts of type II[8,10,11] which were thus considered to have two maxima, e.g., X = CN, λ_{1max} ~490 mμ, and λ_{2max} 550 mμ.[8,10,11] However, the NMR data suggest that both II and III are present in this mixture. It would be tempting to reinterpret the spectrum on this qualitative information, but *this would still be ambiguous*, and in any case there is (and often will be) a difference in the substrate concentration of ~10^4 fold between the two sets of measurements which may well change the chemical reaction, and a more quantitative comparison of the two sets of data is required.

The most direct comparison will be if measurements can be made using both NMR and uv-visible spectroscopy using the same flow equipment on solutions with identical concentrations of all reactant species for both sets of measurements. This is difficult to achieve because of the large concentration difference between the two techniques, but the difference has been minimized in the present instance by using the minimum concentration possible for the NMR measurements and a specially constructed very short path length flow uv cell.

The profiles of the uv spectra initially observed during the reaction and observed at equilibrium are independent of the reactant concentrations of the concentration range of 10^{-5} to 10^{-2} *M* in DMSO/methanol solution. The spectra shown in Figure 7 were recorded at 5×10^{-2} *M* concentrations of reactants using the very short path length cell and are very similar to those reported previously at much lower concentrations. It was not possible to record the flow NMR spectra at these concentrations, but it was possible to record reasonable spectra at 0.1 *M* concentrations. In the light of the concentration independence of the initial and final uv spectra over a considerable range of concentrations up to 0.05 *M* it is assumed that there will be no appreciable change in increasing the concentration to 0.1 *M*. A direct comparison of the uv and NMR data can be made for a whole series of measurements of both spectra, and the uv spectra of both species can be unambiguously deduced knowing their concentrations from the NMR data. (In the present case, only two species are involved, but the approach is applicable to much more complex systems.)

The results indicate clearly that species II and III each have single absorptions at ~500 and ~550 mμ, respectively, with similar extinction coefficients as indicated in Figure 7. This interpretation of the uv-visible spectral changes differs from those given previously and it is thought that these should be reevaluated in the light of the present work.[20]

Conclusions

The technique of flow nuclear magnetic resonance spectroscopy has been used to investigate both the kinetic as well as the thermodynamic distribution of the two isomeric complexes resulting from the attack of methoxide ion on 3,5-dinitro-X-substituted benzenes. The technique has been shown to yield useful quantitative kinetic data and a direct comparison of the results to those from optical spectroscopy has been made, including a suggested reinterpretation of the optical data.

It is in this sense that the technique described in the present work is considered most useful and it is thought that future applications of the technique to other systems will be most worthwhile if they follow this approach. That is, the flow NMR measurements should be used to identify the species present and hence assign their uv-visible absorptions unambiguously, and then the detailed kinetic measurements should be made using this technique which will permit working in dilute, relatively ideal solutions. It is expected, in general, that the technique and approach outlined in this work should find ready application in the understanding of many other chemical systems.

Note Added in Proof. Private communication from Dr. F. Terrier indicates that in his work[8] the measurements from which the extinction coefficients and absorption maxima of the two complexes were evaluated were made under different base concentrations from the kinetic measurements, and while the former are in error, the kinetic parameters are correct and are in reasonable agreement with those quoted in the present work.

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(14) Line broadening is introduced by the flow since $1/T_{2(\text{obsd})} = (1/T_2) + (1/\tau)$ where τ is the residence time of the sample in the coil.[15] Thus when τ is of the same order or less than the actual T_2 of the sample $1/T_{2(\text{obsd})}$ will be larger and hence the line width of the resonance $= 1/T_{2(\text{obsd})}$ will be larger. In cases of very fast flow $1/\tau$ will be the major contribution to the line width.

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(20) This interpretation of the uv-visible spectral changes was suggested independently to the author by M. R. Crampton (private communication) after publication of the first communication on this work which indicated qualitatively that a mixture of II and III was initially formed in the case of I (X = CN) but without knowing the results of the direct comparison of the uv-visible and NMR data presented above.