

The kinetics and mechanism of the reaction of *p*-nitrocumyl bromide with nitrite ions in dimethyl sulfoxide. Evidence for a non-chain reaction giving a high nitro/nitrite ratio in the product

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Stuart W. Paine and John H. Ridd*

Chemistry Department, University College, 20 Gordon Street, London, UK WC1H 0AJ

The reaction of *p*-nitrocumyl bromide (RBr) with sodium nitrite in [²H₆]dimethyl sulfoxide gives none of the conventional evidence for an S_{RN}1 chain reaction but the initial values of the [RNO₂]/[RONO] ratio (2.5–5) are far higher than would be expected for the attack of a nitrite ion on the carbocation R⁺ and increase with the concentration of nitrite ions. The high values of [RNO₂]/[RONO] are considered to derive from a mechanism in which a nitrite ion attacks a π-complex derived from the carbocation R⁺ and a second nitrite ion. This interpretation is supported by a kinetic term that is second order with respect to nitrite ions. An attempt to provide evidence for alternative radical pair intermediates from ¹⁵N CIDNP effects was unsuccessful.

Introduction

Since the nitrite ion is an ambident nucleophile, the relative rates of attack at nitrogen and at oxygen can be used to provide information on the type of transition state involved in the nucleophilic substitution. Studies of the factors determining the relative proportions of nitro compounds and nitrites in the reaction product have a long history¹ but, following the work of Kornblum and his co-workers,² the generally accepted view³ is that changing from an S_N2-type to an S_N1-type transition state decreases the proportion of nitro compounds in the reaction product. Thus, in the reaction of silver nitrite with substituted benzyl bromides in ether,² the *para*-nitro derivative gives a nitro/nitrite ratio of 5.25 (an S_N2-type reaction) and the *para*-methoxy derivative gives a nitro/nitrite ratio of 0.64 (an S_N1-type reaction). Calculations of reaction potential maps for the nitrite ion⁴ support the view that the oxygen atoms should be the most reactive centres towards hard electrophiles (*e.g.*, carbocations) and the nitrogen atom the most reactive centre towards soft electrophiles.

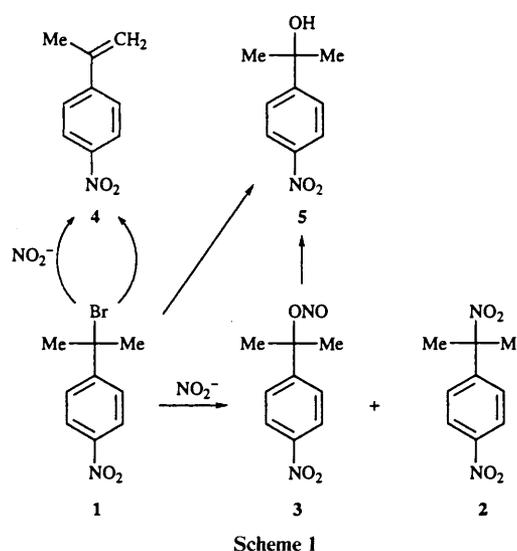
The reaction of *p*-nitrocumyl chloride with sodium nitrite in dimethyl sulfoxide would be expected to be an S_N1-type reaction and so the observed formation of the corresponding dinitro-compound in a yield⁵ of 92–95% does not accord with the expected product ratios. However, Kornblum and co-workers^{6,7} have shown that this reaction in dipolar aprotic solvents has the characteristics of an S_{RN}1 reaction: it is catalysed by light and by one-electron donors (*e.g.*, sodium metal), and it is inhibited by *p*-dinitrobenzene. The high yield of the dinitroproduct was therefore considered to derive from the attack of the nitrite ion on the effectively neutral α-carbon atom in the *p*-nitrocumyl radical.

As outlined previously,⁸ we were interested in the possible application of ¹⁵N CIDNP effects to short chain or non-chain radical reactions but the above reactions of *p*-nitrocumyl chloride proved too slow for our purposes. We therefore investigated the reactions of *p*-nitrocumyl bromide with nitrite ions and, as with the corresponding reaction with azide ions,⁸ found that the change from the chloride to the bromide caused a major change in the mechanism of substitution.

Results

Products

A solution of *p*-nitrocumyl bromide **1** (Scheme 1, 0.10 mol dm⁻³) and sodium nitrite (0.26 mol dm⁻³) in [²H₆]dimethyl sulfoxide was stirred for 5 h at room temperature under an argon



atmosphere; after extraction and purification of the products by HPLC, the product composition was *α,p*-dinitrocumene **2** (51%), *p*-nitro-*α*-methylstyrene **4** (17%) and *p*-nitrocumyl alcohol **5** (19%). Under the work-up procedure, any *p*-nitrocumyl nitrite **3** formed would have been transformed into the corresponding alcohol **5**.

The reactions were then followed from the changes in the 400 MHz ¹H NMR spectra of the reaction mixture (Fig. 1) and the product compositions obtained are shown in Table 1. In addition to the peaks from the identified products, an additional peak is present at δ 0.06 to high field of the methyl protons of the nitro-compound; this peak decreases towards the end of reaction and a corresponding increase is observed in the height of the signal for the alcohol **5**. The additional signal was therefore attributed to the nitrite **3**. Other studies have shown that ¹H NMR signals for methyl groups on a carbon atom carrying a nitrite group are slightly to high field of those on a carbon atom carrying a nitro group.⁹ The results in Table 1 show that when the initial concentration of the substrate is held constant, the percentage of nitrocompound formed increases steadily with the initial concentration of sodium nitrite.

Kinetics

Under our conditions, the reactivity of nitrite ions towards *p*-nitrocumyl bromide is less than that of azide ions by about a

Table 1 The reaction of *p*-nitrocumyl bromide (RBr) with sodium nitrite in [²H₆]dimethyl sulfoxide at 30 °C. The variation of the product composition with the initial concentrations of the reactants. The sodium perchlorate is present to maintain the total salt concentration constant

Reactants			Products		
[RBr]/mol dm ⁻³	[NaNO ₂]/mol dm ⁻³	[NaClO ₄]/mol dm ⁻³	[2] (%)	[4] (%)	[5] ^a (%)
0.1	0.2	0.8	29	29	42
0.2	0.2	0.8	20	35	45
0.2	0.4	0.6	38	27	35
0.2	0.6	0.4	47	24	29
0.2	0.8	0.2	54	20	26
0.2	1.0	0.0	55	22	23

^a These measurements refer to a time after the complete conversion of the nitrite 3 to the alcohol 5.

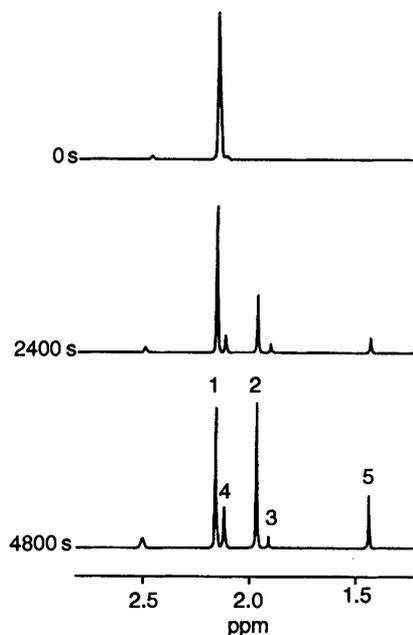


Fig. 1 The change in the ¹H NMR spectrum during the reaction of *p*-nitrocumyl bromide (0.2 mol dm⁻³) with sodium nitrite (0.8 mol dm⁻³) in [²H₆]dimethyl sulfoxide at 30 °C. Sodium perchlorate (0.2 mol dm⁻³) was also present. The numbers refer to the structures in Scheme 1.

factor of 10. In consequence, the underlying elimination reaction of *p*-nitrocumyl bromide forms a much greater part of the overall reaction than was observed in the reaction of 1 with azide ions.⁸ As outlined previously,⁸ the elimination reaction follows eqn. (1) and, by analogy with the reaction with azide

$$\text{Rate} = k_1[\text{RBr}] \quad (1)$$

ions, the substitution reaction would be expected to follow eqn. (2). It would seem therefore appropriate to analyse each

$$\text{Rate} = k_2[\text{RBr}][\text{NO}_2^-] \quad (2)$$

kinetic run as an example of parallel first- and second-order reactions.¹⁰

Unfortunately, the accuracy of the NMR method of analysis is not sufficient for the extraction of two rate coefficients from each kinetic run; the relative values of k_1 and k_2 obtained are very sensitive to the inclusion or omission of individual points. Fortunately, all of the kinetic runs give first-order rate coefficients with correlation coefficients >0.995 and it is therefore convenient to report the reaction rates in this way. This agreement with first-order kinetics arises because, with low concentrations of sodium nitrite, the formation of the alkene 4 is the predominant reaction and, with high concentrations of sodium nitrite, the concentration of nitrite ions changes little in the course of the reaction. The first-order rate coefficients are listed

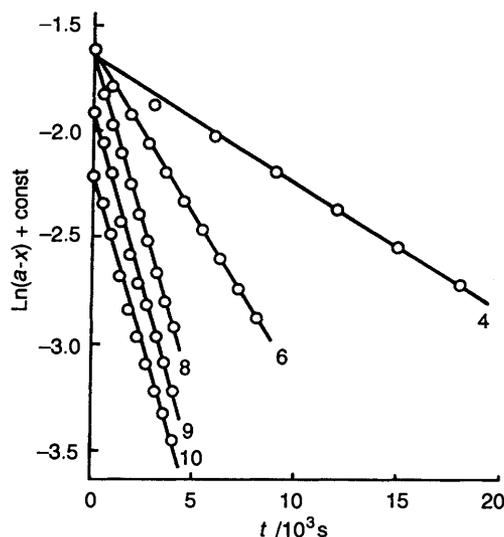


Fig. 2 First-order plots for the reaction of *p*-nitrocumyl bromide (0.2 mol dm⁻³) with sodium nitrite (0.2–1.0 mol dm⁻³) in [²H₆]dimethyl sulfoxide at 30 °C. The numbers refer to the runs listed in Table 2. For clarity, two of the plots have been displaced on the *y* axis by the following amounts: run 9, -0.3; run 10, -0.6. Runs 9 and 10 show the absence of any retardation by *p*-dinitrobenzene and 4-hydroxyTEMPO respectively.

in Table 2 together with the second-order rate coefficients where appropriate. Plots 4, 6 and 8 in Fig. 2 illustrate the agreement with first-order kinetics for runs without added species.

The results in Table 2 also include the rate coefficients for kinetic runs carried out in the presence of various added species. High concentrations of nitrite ions were used in these runs so as to make the underlying elimination reaction relatively unimportant. The comparison of these results with those for the relevant kinetic runs in the absence of the added species shows that neither *p*-dinitrobenzene nor 4-hydroxyTEMPO cause any significant change in the overall rate coefficients but these additives to introduce some slight curvature into the plots (Fig. 2, plots 9 and 10). The comparison of runs 11 and 7 (Table 2) shows that the presence of sodium bromide (0.2 mol dm⁻³) has no significant effect on the rate of reaction. The presence of water (5%) causes a slight decrease in this rate (compare runs 8 and 12).

In one kinetic run, the reaction mixture was irradiated with a mercury arc lamp for 15 min before being placed in the NMR instrument. Comparison with an identical sample kept in the NMR instrument showed that the irradiation produced a slight increase (14%) in extent of reaction at the time of the first reading (50 min).

One kinetic run was carried out using ¹⁵N-labelled sodium nitrite (1 mol dm⁻³) and *p*-nitrocumyl bromide (0.2 mol dm⁻³) in [²H₆]dimethyl sulfoxide at 30 °C. It was followed from the intensity of the ¹⁵N NMR signal for the nitro product 2 relative to [¹⁵N]nitromesitylene present as a standard. A steady growth

Table 2 The effect of the concentrations of the reactants and of various additives (X) on the rate coefficients [k_1 , eqn. (1), k_2 , eqn. (2)] for the reaction of *p*-nitrocumyl bromide (RBr) with sodium nitrite in [$^2\text{H}_6$]dimethyl sulfoxide at 30 °C

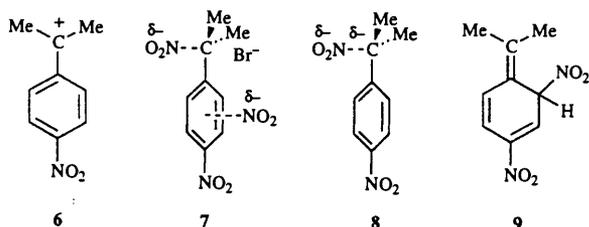
Run no.	[RBr]/mol dm ⁻³	[NaNO ₂]/mol dm ⁻³	[NaClO ₄]/mol dm ⁻³	X	[X]/mol dm ⁻³	$k_1/10^{-5} \text{ s}^{-1}$	$k_2/10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1	0.2	0.0	1.0	—	—	4.36	—
2	0.1	0.2	0.8	—	—	6.58	—
3	0.2	0.2	0.8	—	—	5.79	—
4	0.2	0.2	0.0	—	—	7.20	—
5	0.2	0.4	0.6	—	—	9.10	—
6	0.2	0.6	0.4	—	—	14.9	2.99
7	0.2	0.8	0.2	—	—	22.7	3.25
8	0.2	1.0	0.0	—	—	30.5	3.40
9	0.2	1.0	0.0	<i>p</i> -DNB ^a	0.1	30.7	2.83
10	0.2	1.0	0.0	4-HT ^b	0.02	31.9	3.55
11	0.2	0.8	0.0	NaBr	0.2	23.4	3.40
12	0.2	1.0	0.0	H ₂ O	(5%)	28.3	3.11

^a *p*-Dinitrobenzene. ^b 4-HydroxyTEMPO (the 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy radical).

of the ¹⁵N NMR signal for the nitro product was observed corresponding approximately to the expected half-life of the reaction. There was no evidence of the enhanced absorption or emission signals characteristic of ¹⁵N nuclear polarisation and observed in aromatic nitration.¹¹

Discussion

The absence of significant catalysis by light and the failure of *p*-dinitrobenzene and 4-hydroxyTEMPO to inhibit the reaction shows that an S_{RN}1 reaction is not involved; the similar absence of retardation by bromide ions (compare runs 7 and 11 in Table 2) shows that reaction does not occur through an equilibrium concentration of the carbocation **6**. These arguments are



similar to those used in discussing the reaction of **1** with azide ions in the preceding paper and will not be considered in detail again.

One key quantity in the interpretation of these results is the ratio $[\text{RNO}_2]/[\text{RONO}]$ characteristic of the substitution reaction. The results in Fig. 3 illustrate that the products **2–5** are all formed from the start of reaction but that, in the later stages of the reaction, some of the nitrite **3** is converted into the alcohol **5**; a small amount of the alkene **4** may also be present in the initial solution of **1**. The initial rate of formation of the alcohol **5** is very similar to that observed in the reaction of the substrate **1** with azide ions although, since the reaction with azide ions is much faster, the overall amount of alcohol formed is then much less. We have therefore assumed that the alcohol is initially derived from a separate reaction involving the solvent and that the ratio $[\text{RNO}_2]/[\text{RONO}]$ at or near the start of reaction is characteristic of the mechanism of substitution.

The upper set of results in Table 3 provide some support for this since, in the fastest reaction, the ratio $[\text{RNO}_2]/[\text{RONO}]$ remains effectively constant for ca. 30 min and then increases as the nitrite is converted into the alcohol. In the slowest reaction, the first point was not taken until 50 min and so it is reasonable that this ratio should then increase steadily during the reaction. These results suggest that the true $[\text{RNO}_2]/[\text{RONO}]$ ratio increases from 2.5 to about 5 as the concentration of nitrite ions is increased. Both of these ratios are much greater than would be expected from the attack of the nitrite ion on the carbocation **6**. The variation of the ratio with the concentration of

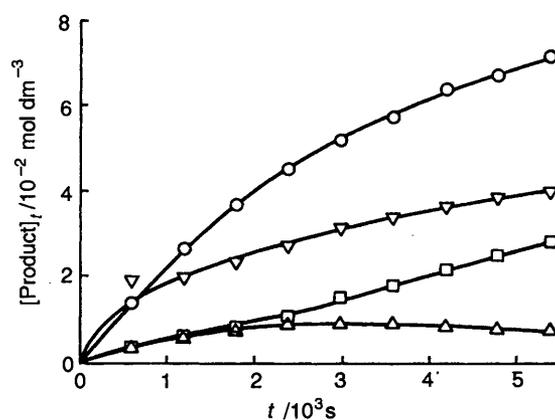


Fig. 3 The variation in the concentrations of the products with time for run no. 7 (Table 2); ○ α,p -dinitrocumene; ▽ *p*-nitro- α -methylstyrene; □ *p*-nitrocumyl alcohol; △ *p*-nitrocumyl nitrite

Table 3 The effect of additives and of the concentration of sodium nitrite on the product ratio $P = [\text{RNO}_2]/[\text{RONO}]$ during the initial stages of kinetic runs carried out with *p*-nitrocumyl bromide (0.2 mol dm⁻³) in [$^2\text{H}_6$]dimethyl sulfoxide at 30 °C. Sufficient sodium perchlorate was present to bring the total salt concentration to 1.0 mol dm⁻³

[NO ₂ ⁻] = 1.0		[NO ₂ ⁻] = 0.6		[NO ₂ ⁻] = 0.2	
Time/s	<i>P</i>	Time/s	<i>P</i>	Time/s	<i>P</i>
450	4.8	900	4.7	3000	3.11
900	4.7	1800	4.6	6000	3.85
1350	4.8	2700	5.0	9000	4.95
1800	5.02	3600	5.4		
2250	5.37				

[NO ₂ ⁻] = 1.0 [DNB] ^a = 0.1		[NO ₂ ⁻] = 1.0 [4-HT] ^b = 0.02		[NO ₂ ⁻] = 1.0 5% v/v water	
Time/s	<i>P</i>	Time/s	<i>P</i>	Time/s	<i>P</i>
450	5.7	450	4.5	450	4.6
900	5.0	900	4.1	900	2.8
1350	4.6	1350	4.0	1350	2.6
1800	4.8	1800	4.4	1800	2.5
2250	5.1	2250	4.6	2250	2.6

^a *p*-Dinitrobenzene. ^b 4-HydroxyTEMPO.

nitrite ions suggests that at least two reaction paths are involved and that the reaction path giving the higher ratio has also the higher order with respect to nitrite ions.

The lower set of results in Table 3 shows that the presence of *p*-dinitrobenzene and 4-hydroxyTEMPO has no significant effect on the $[\text{RNO}_2]/[\text{RONO}]$ ratio but that the presence of a large amount of water does significantly reduce the ratio. The ratio for the first point of the run with added water appears

anomalous; this may be because the error is greatest for this point since the concentrations of both the nitro compound and the nitrite are then very small.

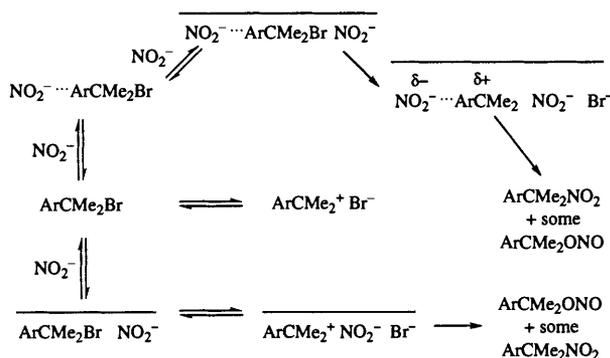
The order of the reaction with respect to nitrite ions has been examined by plotting the initial rate of reaction calculated from the first-order rate coefficients in Table 2 against the initial concentration of nitrite ions. The resulting plot (Fig. 4) has been fitted to a quadratic equation and corresponds to the kinetic form shown in eqn. (3). The values of the rate coefficients

$$\text{Rate} = k_1'[\text{RBr}] + k_2'[\text{RBr}][\text{NO}_2^-] + k_3'[\text{RBr}][\text{NO}_2^-]^2 \quad (3)$$

are: $k_1' = 4.15 \times 10^{-5} \text{ s}^{-1}$, $k_2' = 4.52 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_3' = 2.22 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

The curvature of the plot in Fig. 4 and the resulting importance of the second-order term with respect to nitrite ions was unexpected. The curvature does not seem to be an accidental consequence of the inorganic equilibria in the solutions. The runs shown on the plot have the total salt concentration brought to 1 mol dm^{-3} by added sodium perchlorate and if this is omitted the slower runs become faster (compare runs 3 and 4 in Table 2) but not by a sufficient amount to make the plot a linear one. The first kinetic term clearly derives from the reactions with the solvent leading to the alkene and the alcohol, and from the concurrent change in the $[\text{RNO}_2]/[\text{RONO}]$ ratio it appears that the other two terms derive from separate reaction paths leading to different ratios of the nitro compound and the nitrite. One or both of the rate coefficients k_2' , k_3' must have a component derived from the elimination reaction since the rate of elimination shows a small increase with the concentration of nitrite ions.

Although the possible complications from ion pair equilibria cannot be completely eliminated, both the anomalous product composition and the unexpected kinetic form can be explained if, in one reaction path, a second nitrite ion is present in the transition state and if this reduces the charge on the α -carbon atom. One possible transition state involving a π -complex between a nitrite ion and the aromatic ring of the substrate is shown in structure 7 and the corresponding overall reaction is shown as the upper reaction path in Scheme 2. The



transition state 7 carries two negative charges and, in its charge distribution, is intermediate between that for attack on the carbocation 6 and the possible $S_{RN}1$ transition state for attack on the radical 8.

The yellow-brown colour formed on mixing solutions of sodium nitrite and *p*-nitrocumyl bromide in dimethyl sulfoxide is consistent with some charge transfer interaction between the reagents. The decrease in the ratio $[\text{RNO}_2]/[\text{ROMO}]$ in the presence of water (Table 3) is also consistent with this interpretation since, in purely aqueous solutions, charge transfer interaction between nucleophiles and electron deficient aromatic systems is not found.¹² The high concentration of sodium nitrite used makes it more plausible for two nitrite ions to be about the *p*-nitrocumyl bromide molecule at the moment of ionisation for

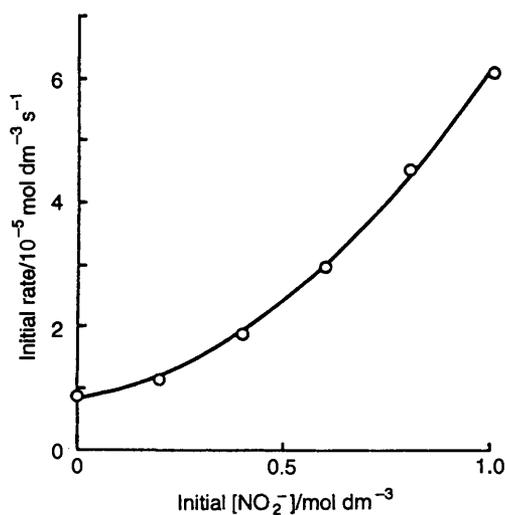


Fig. 4 The variation of the initial rate of reaction of *p*-nitrocumyl bromide with the initial concentration of sodium nitrite. The line is calculated from eqn. (3) using the listed rate coefficients.

a 1 mol dm^{-3} solution of sodium nitrite in dimethyl sulfoxide has one nitrite ion to every 13 solvent molecules.

Two other transition states related to 7 have been considered. One involves the initial transfer of one electron from a nitrite ion to the aromatic ring of the carbocation to form a radical pair immediately before the attack of the second nitrite ion at the α -carbon. Such a transition state is equivalent to condensing two stages of the $S_{RN}1$ reaction into one step. However, this process would offer the possibility of some concurrent separation of the radical pair if the second nitrite ion were not available. As outlined above, the ^{15}N CIDNP effects which might derive from such a separation have been sought but not found. Also, if such radical pairs are formed, a contribution from the $S_{RN}1$ reaction might be expected.

The other possible transition state involves the initial reversible addition of one nitrite ion to the aromatic ring as shown in structure 9, followed by an $S_{N}2'$ substitution by another nitrite ion at the α -carbon. Additions of nucleophiles at unsubstituted positions of an aromatic ring are well known¹³ but, if addition occurred at the *ortho* position, some such addition would be expected at the *para* position and this would then have a 50% chance of leading to the exchange of the original nitro group for the incoming nitro group. Such exchange was looked for in the reaction with sodium ^{15}N nitrite but was not found. The transition state 7 appears therefore to provide the most likely explanation of these results.

One remaining problem is why a kinetic term analogous to the third term in eqn. (3) was not found in the reaction of 1 with azide ions.⁸ A plausible explanation comes from the restriction of this work to a lower range of concentrations of the nucleophile ($0\text{--}0.4 \text{ mol dm}^{-3}$) for, in dimethyl sulfoxide, lithium azide is less soluble than sodium nitrite. The much greater reactivity of azide ions over nitrite ions in the second-order reaction may also make any contribution from the third-order term relatively less important.

Experimental

Materials

Sodium nitrite and sodium perchlorate were obtained from Aldrich, sodium ^{15}N nitrite was obtained from MSD isotopes; all salts were dried under reduced pressure.⁸ $^2\text{H}_6$ Dimethyl sulfoxide and *p*-nitrocumyl bromide were obtained and purified as described previously.⁸ The ^{15}N nitromesitylene was provided by Dr J. F. Johnston. *p*-Nitrocumyl alcohol was prepared from *p*-nitrocumene by the method of Kornblum, Ackermann and Swiger¹⁴ (Found: C, 59.4; H, 6.1; N, 7.7. Calc. for $\text{C}_9\text{H}_{11}\text{NO}_3$; C,

59.7; H, 6.1; N, 7.7%); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.18 (2 H, d), 7.66 (2 H, d), 2.11 (1 H, s), 1.62 (6 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 156.4, 146.6, 125.4, 123.4, 72.5, 31.7.

***α,p*-Dinitrocumene**

2-Nitropropane (17.02 g) were added to a well stirred solution of lithium methoxide (5.23 g) in methanol (100 cm³) under argon. After the solution had been stirred for 10 min, the solvent was removed under reduced pressure and diethyl ether was added. The precipitate was washed with ether and dried under reduced pressure to give lithium dimethylnitromethide (12.42 g, yield 94%).

A solution of *p*-dinitrobenzene (0.82 g) in dimethyl sulfoxide (20 cm³) was added to a solution of lithium dimethylnitromethide (0.51 g) in dimethyl sulfoxide (20 cm³) under argon. The reaction mixture was stirred for 30 min and then poured onto ice. A conventional work-up followed by recrystallisation from ethanol gave *α,p*-dinitrocumene (0.9 g, yield 87%) as white crystals, mp 68–70 °C (lit.,¹⁵ 67–68 °C) (Found: C, 51.5; H, 4.7; N, 12.9. Calc. for C₉H₁₀N₂O₄: C, 51.4; H, 4.8; N, 13.3%); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.26 (2 H, d), 7.60 (2 H, d), 2.04 (6 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 146.6, 142.3, 126.5, 124.0, 89.3, 27.3.

Products

A solution of *p*-nitrocumyl bromide (0.501 g) in dimethyl sulfoxide (20 cm³) was added to a solution of sodium nitrite (0.714 g) in dimethyl sulfoxide (20 cm³) under argon. The reaction mixture was stirred for 5 h at room temperature and then poured onto ice (100 g). A conventional work-up followed by purification of the products by HPLC (eluting with 60% hexane–40% ethyl acetate) gave *α,p*-dinitrocumene (0.221 g, 51%), *p*-nitrocumyl alcohol (0.072 g, 19%) and *p*-nitro-*α*-methylstyrene (0.058 g, 17%). The first two products were shown to be identical with the authentic compounds described above. The *p*-nitro-*α*-methylstyrene had mp 51–53 °C (lit.,¹⁶ 51–54 °C) (Found: C, 66.0; H, 5.6; N, 8.5. Calc. for C₉H₉NO₂: C, 66.2; H, 5.6; N, 8.6%); $\delta_{\text{H}}(\text{CDCl}_3)$ 8.19 (2 H, d), 7.6 (2 H, d), 5.53 (1 H, dd), 5.30 (1 H, dd), 2.19 (3 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$ 147.6, 146.9, 141.5, 126.2, 123.6, 116.4, 21.6.

The experiment with sodium [¹⁵N]nitrite was carried out in the same way but on half the scale. The products were *p*-nitro-*α*-[¹⁵N]nitrocumene (50%), *p*-nitrocumyl alcohol (19%) and *p*-nitro-*α*-methylstyrene (18%).

Kinetics

The procedure for the kinetic runs followed that described previously.⁸ As before, the calculations of the integrated rate coefficients omitted the point at $t = 0$.

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