Nitrosation by Alkyl Nitrites. Part 5.[1] Kinetics and Mechanism of Reactions in Acetonitrile

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Simple alcohols and thioglycolic acid react with alkyl nitrites and nitrous acid in acidic acetonitrile solution to give the *O*- and *S*-nitrosated products, in reactions which are kinetically zero order in the alcohol or thiol concentration. The results are consistent with rate-limiting NO^+ formation. On addition of the parent alcohol (derived from the alkyl nitrite) reactions are slower and there is a change towards a first-order dependence upon the substrate concentration, indicating that under these conditions the reaction of NO^+ with the substrate is partly rate limiting. The reactivity order is found to be HNO_2 > t-butyl nitrite > i-propyl nitrite > isopentyl nitrite. Similarly aromatic amines yield nitrosamine or diazonium ion products, but now the kinetics are consistent with rate-limiting attack of NO^+ with the unprotonated amine. At higher acidities it is proposed that reaction occurs with the protonated form of the amine. The mechanistic implications of the kinetic results are discussed.

Alkyl nitrites have been much used as nitrosating agents in a variety of solvents. In aqueous acid solution hydrolysis occurs and the effective nitrosating agent is derived from the nitrous acid liberated.[2] In acidic alcohol solution, reactive substrates such as thiourea and thioglycolic acid react directly with the protonated form of the alkyl nitrite,[1] or possibly with the free nitrosonium ion. Amines are not reactive towards acidic solutions of alkyl nitrites,[3] unless there is a nucleophile present (such as halide ion), which results in the equilibrium formation of a nitrosyl species (such as a nitrosyl halide) which then brings about nitrosation or diazotisation. In basic alcohol solution reaction occurs readily between alkyl nitrites and amines[4] and alcohols.[5] Similarly, in the pH range 7–13 alkyl nitrites react directly with the thiolate anion RS^- derived from thiols such as cysteine.[6]

There have been several reports[7–10] of nitrosation using alkyl nitrites in dipolar aprotic solvents, using alcohols, amines, amides, and thiols. In most cases reaction takes place readily even without any added acid catalyst, and these systems are thought to have significant advantages for synthesis over earlier methods. Very little mechanistic work has been reported for reactions in these solvents, the only kinetic studies[11] concerned reactions of alkyl nitrites with amides in various solvents. Here the kinetics were consistent with a mechanism involving nucleophilic attack by the $-NH_2$ function of the amide at the nitrogen centre of the alkyl nitrite in an S_N2 type process. Since many of these reactions have considerable synthetic potential we have examined the kinetics of some of them. Here we report the results of a study carried out in acetonitrile solvent. Some of the results have been presented in a preliminary communication.[12]

Experimental

All three alkyl nitrites used, t-butyl nitrite (TBN), isopropyl nitrite (IPN) and isopentyl nitrite (IPeN) were prepared by the normal procedure[13] by the nitrosation of the corresponding alcohol. Each was purified by fractional distillation before use. Acetonitrile (h.p.l.c. grade) was purified by reflux over calcium hydride, followed by fractional distillation from calcium hydride. Stock solutions of sulphuric acid in acetonitrile were prepared by addition of the required small amount of sulphuric acid (98% analytical reagent grade) to ice-cooled acetonitrile. These solutions were standardised by titration and normally used within 8 h of preparation. Deuteriated compounds D_2SO_4 and CH_3OD were obtained commercially. Dry hydrogen chloride gas was dissolved in acetonitrile to prepare solutions of the same. All the alcohols and amines used were purified by fractional distillation or recrystallisation as appropriate. All other reagents were of the highest purity available.

Equilibrium constants for the reaction of the three alkyl nitrites with methanol in acetonitrile were measured spectrophotometrically (in the 330–420 nm region) at 25 °C. Kinetic measurements were also obtained at 25 °C by the use of either conventional or stopped-flow spectrophotometry, as appropriate. Reactions with thioglycolic acid were carried out at 330 nm following the appearance of the thionitrite, alkyl nitrites with methanol in the range 400–410 nm following the disappearance of the alkyl nitrite, nitrous acid with alcohols at 260 nm following the appearance of the alkyl nitrite, and the reactions with amines were monitored in the range 280–330 nm and the formation of the nitrosamine or the diazonium ion was measured. All kinetic experiments were carried out with $[\text{substrate}]_0 \gg [\text{RONO}]_0$ or $[\text{HNO}_2]_0$, and excellent first-order behaviour was noted for at least 2–3 half lives. The reported first-order rate constant k_0 is the mean of at least five separate measurements.

Results and Discussion

(*a*) *Equilibrium Measurements.*—Equilibrium concentrations of methyl nitrite were rapidly produced within 1–2 min when each of the alkyl nitrites was added to a solution of methanol in acetonitrile. The equilibrium constant in each case [equations (1) and (2)] was obtained by measurement of the u.v. spectra in

$$\text{RONO} + \text{MeOH} \rightleftharpoons \text{ROH} + \text{MeONO} \quad (1)$$

$$K = [\text{ROH}][\text{MeONO}]/[\text{RONO}][\text{MeOH}] \quad (2)$$

the range 330–420 nm at 25 °C. The values are given in Table 1. The value of K drops as the alkyl nitrite structure is changed from a tertiary structure to a secondary and a primary one. This trend has previously been reported,[9,10] for nitrosyl-group exchange between alkyl nitrites and alcohols in other solvents

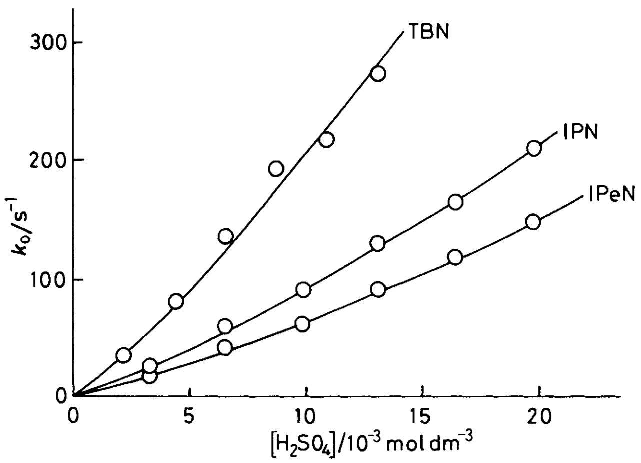

Figure. Acid catalysis in the nitrosation of methanol by alkyl nitrites in acetonitrile.

Table 1. Equilibrium constant values K determined for RONO + R′OH $\rightleftharpoons$ ROH + R′ONO.

	R	R′	K
(*a*) In CH_3CN			
	Bu^t	Me	13.0 ± 0.5
	Pr^i	Me	3.8 ± 0.3
	Pe^i	Me	2.5 ± 0.2
(*b*) In $CHCl_3$			
	Bu^t	Pr^i	4.0 ± 0.3
	Pr^i	Bu^t	0.3 ± 0.02
	Bu^t	Et	10.1 ± 0.4
	Bu^t	Me	20.5 ± 0.6
	Bu^t	Bu^t	1.0[a]
	Bu^t	Pr^i	4.2[a]
	Bu^t	Et	10.6[a]
	Bu^t	Pr	10.0[a]

[a] From ref. 9.

Table 2. Effect of the 'age' of the acid solution upon the rate constant for reaction of IPN with methanol in acetonitrile.

Time after solution preparation/min	$k_0/10^{-2}$ s^{-1}
8	2.40
16	4.69
27	4.96
34	5.01

such as chloroform. The same trend also occurs for such an exchange between alkyl nitrites and water (hydrolysis of alkyl nitrites).[14] In all cases the origin of the effect is likely to be steric; kinetic measurements of the latter example[15] show that the effect arises mainly from the effect on the rate constant of the reverse reaction of alkyl nitrite hydrolysis (*i.e.* the nitrosation of the alcohol by nitrous acid), which decreases along the series R = Me, Et, Pr^i, Bu^t. Table 1 also shows some K values measured in chloroform solution. Again the same trends are evident, and some of the values are in good agreement with literature values.[9]

(*b*) *Kinetics of Alcohol and Thioglycolic Acid Nitrosation.*—By working with [R′OH] or [R′SH] $\gg$ [RONO] we ensured that the reaction occurred effectively quantitatively from left to right in equation (1). Even in the absence of added acid catalysts the reaction occurs rapidly in acetonitrile. Even though each kinetic run was perfectly first order in [RONO] the first-order rate constants, k_0, increased markedly with the 'age' of the alkyl nitrite stock solution. Results for the reaction of IPN with methanol are shown in Table 2. Given the later results which demonstrate pronounced acid catalysis, it is likely that this effect arises from the production of nitrous acid formed by the decomposition of the alkyl nitrite. A similar explanation has been advanced to account for other alkyl nitrite nitrosation reactions in formally neutral solution.[16]

Table 3. First-order rate constants (k_0) for the nitrosation of alcohols and thioglycolic acid by TBN, IPN, and HNO_2 in acetonitrile.

Nitrite	[Substrate]/mol dm^{-3}		$[H_2SO_4]$/mol dm^{-3}	k_0/s^{-1}
TBN	MeOH	0.0233	2.18 × 10^{-3}	31.7 ± 0.7
		0.0699	2.18 × 10^{-3}	31.5 ± 1.4
		0.117	2.18 × 10^{-3}	33.3 ± 0.5
	TGA	4.73 × 10^{-3}	2.33 × 10^{-3}	27.9 ± 1.4
		9.46 × 10^{-3}	2.33 × 10^{-3}	38.7 ± 0.4
		14.2 × 10^{-3}	2.33 × 10^{-3}	37.1 ± 1.0
IPN	MeOH	0.0434	1.43 × 10^{-3}	11.9 ± 0.3
		0.0651	1.43 × 10^{-3}	12.9 ± 0.3
		0.0996	1.43 × 10^{-3}	11.5 ± 0.2
	TGA	5.85 × 10^{-3}	5.61 × 10^{-4}	3.08 ± 0.1
		11.7 × 10^{-3}	5.61 × 10^{-4}	2.97 ± 0.1
		17.6 × 10^{-3}	5.61 × 10^{-4}	2.99 ± 0.1
HNO_2	MeOH	9.96 × 10^{-3}	8.68 × 10^{-4}	21.9 ± 0.9
		19.9 × 10^{-3}	8.68 × 10^{-4}	21.2 ± 1.2
		24.9 × 10^{-3}	8.68 × 10^{-4}	26.9 ± 2.7
		49.8 × 10^{-3}	8.68 × 10^{-4}	24.8 ± 1.9
		76.7 × 10^{-3}	8.68 × 10^{-4}	22.8 ± 1.1
	Pr^{i}OH	0.0149	8.68 × 10^{-4}	24.6 ± 1.3
		0.0446	8.68 × 10^{-4}	26.0 ± 1.3
		0.0744	8.68 × 10^{-4}	21.9 ± 1.1
	TGA	8.87 × 10^{-3}	8.46 × 10^{-4}	15.8 ± 0.6
		17.7 × 10^{-3}	8.46 × 10^{-4}	19.6 ± 0.4
		26.6 × 10^{-3}	8.46 × 10^{-4}	21.7 ± 0.4
		44.3 × 10^{-3}	8.46 × 10^{-4}	23.4 ± 0.5

Acid catalysis is quite marked for all three alkyl nitrites in reaction with both methanol and thioglycolic acid. However values of k_0 were somewhat dependent on the 'age' of the acetonitrile acid solution. There was a tendency for k_0 values to increase, although they do so somewhat erratically, with increasing 'age' of the acid solution up to *ca.* 15 min. Thereafter values of k_0 remained constant for many hours. Over a much longer time scale, when the acid solution had been left to stand for many days the value of k_0 dropped quite markedly even though the titratable acid remained constant. To explain these rather unusual results we must consider acid–base equilibria in acetonitrile. Measurements of the hydrogen ion activity in this solvent[17,18] show similar time-variable behaviour. The value increased during the first 30 min after sulphuric acid had been added, and then reached a steady value. Over a much longer period (several weeks)[19,20] the measured hydrogen-ion activity dropped markedly, even though, again, the stoicheiometric acid concentration measured by titration remained constant. The initial increase has been attributed[21,22] to the occurrence of a slow equilibrium process, possibly involving proton transfer from the acid to the solvent, the formation of nitrilium-like salts of empirical formula $CH_3CN{\cdot}2HX$, or formation of salts of the type $CH_3C(X){=}\overset{+}{N}H_2X^-$. The decrease in hydrogen-ion activity over a much longer time period has been explained[18,23] in terms of the formation of a basic species, possibly acetamide or a polymer of acetonitrile,[20] which thus causes a reduction in the hydrogen-ion activity. The physical

Table 4. Dependence of k_0 on [TGA] in the nitrosation of TGA by IPN using HCl catalyst (2×10^{-3} mol dm^{-3}).

[TGA]/mol dm^{-3}	k_0/s^{-1}
0.0057	4.15 ± 0.04
0.0114	4.66 ± 0.37
0.0171	3.95 ± 0.05

Table 5. Effect of added Bu^{t}OH on k_0 for nitrosation of methanol by TBN.

[Bu^{t}OH]/mol dm^{-3}	k_0/s^{-1}
0	143 ± 2
0.0108	89 ± 2
0.0323	51 ± 1
0.0539	39.1 ± 0.5
0.108	25.1 ± 0.3
0.216	16.0 ± 0.4
0.323	9.8 ± 0.2
0.431	6.3 ± 0.1
0.539	4.5 ± 0.1

Table 6. Dependence of k_0 on [MeOH] for the nitrosation of MeOH by IBN in the presence of t-butyl alcohol (0.414 mol dm^{-3}).

[MeOH]/mol dm^{-3}	k_0/s^{-1}
0.0417	0.788 ± 0.006
0.0626	0.944 ± 0.017
0.0958	1.07 ± 0.05
0.192	1.33 ± 0.01
0.287	1.52 ± 0.04

measurements parallel our kinetic findings quite well. Consequently we have worked throughout with acid solutions which had been prepared at last 15 min prior to use, after which consistent reproducible rate constants were obtained over several hours.

Perhaps the most striking kinetic results concern the nitrosation by IPN, TBN, and HNO_2 of methanol and thioglycolic acid (and in the case of HNO_2 reactions, of isopropyl and t-butyl alcohol also). In all cases the reactions were found to be completely zero order with respect to the substrate concentration under our experimental conditions. This is clearly shown in Table 3 which includes some of our results; others were obtained at different acidities, and also showed the same zero-order substrate kinetic dependence. The small increase in k_0 for the reaction of HNO_2 with TGA may arise from extra acid catalysis brought about by TGA itself. The conclusion must be that the rate-limiting step occurs before substrate nitrosation and does not involve the substrate. The most obvious explanation is that we are observing rate-limiting formation of NO^+, starting from either one of the alkyl nitrites or from nitrous acid. Acid catalysis is pronounced under these conditions. Data for the nitrosation of methanol by three alkyl nitrites TBN, IPN, and IPeN are shown in the Figure. This means that reaction probably involves rapid equilibrium protonation of the alkyl nitrites or of nitrous acid, followed by unimolecular loss of NO^+, as outlined in the Scheme.

The general rate equation expected from such a mechanism is given in equation (3), which reduces to equation (4) if $k_2[\text{substrate}] \gg k_{-1}[\text{ROH}]$. The results in Table 3 shows clearly that for each alkyl nitrite or nitrous acid, the value of k_0 depends only upon the acidity. The stoicheiometric $[H_2SO_4]$ is not a correct measure of acidity here, since the plots in the Figure are not quite linear, but we use it for convenience. One unlikely alternative is that protonation of the alkyl nitrite is rate limiting. This possibility can be discounted since the solvent isotope effect k_H/k_D for the reactions of MeOD using D_2SO_4 is *ca.* 0.8 (for two alkyl nitrites and for several different acidities). This result is not consistent with rate-limiting proton transfer.

$$\mathrm{RONO} + \mathrm{H_2SO_4} \overset{K}{\rightleftharpoons} \mathrm{R\overset{+}{O}(H)NO} + \mathrm{HSO_4^-}$$

$$\mathrm{R\overset{+}{O}(H)NO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ROH} + \mathrm{NO^+}$$

$$\mathrm{NO^+} + \text{Substrate} \xrightarrow{k_2} \text{Product}$$

R = Bu^t, Pr^i, isopentyl, or H

Scheme.

$$k_0 = k_1K[H_2SO_4]k_2[\text{substrate}]/(k_{-1}[\text{ROH}] + k_2[\text{substrate}]) \quad (3)$$

$$k_0 = k_1K[H_2SO_4], \text{ if } k_2[\text{substrate}] \gg k_{-1}[\text{ROH}] \quad (4)$$

For the alkyl nitrite reactions another possible explanation of the results is that rate-limiting hydrolysis by traces of water present occurs to give nitrous acid. This cannot be the explanation when the reactant is nitrous acid. We do, however, observe equilibrium concentrations of nitrous acid spectrophotometrically when IPN is added to an acid solution of acetonitrile. When traces of water are rigorously excluded, by using super-dried acetonitrile and TGA as the substrate and also source of the acidity, reaction still occurs readily with IPN, which is markedly catalysed by the addition of dried HCl gas, when k_0 is again independent of [TGA], as shown in Table 4. Presumably the 'acid catalysis' component due to TGA is swamped by HCl. We suggest that the hydrolysis when it occurs is a side reaction.

A further test of the mechanism comes from the results of experiments carried out when the parent alcohol of the alkyl nitrite is added to the reaction solution. This results in a marked reduction in the value of k_0 (shown in Table 5) and also the reaction loses its zero-order dependence upon the substrate concentration (see Table 6). This is fully in accord with the Scheme and the general rate equation (3), since now with added ROH, the $k_{-1}[\text{ROH}]$ term competes more effectively with $k_2[\text{substrate}]$ and so the earlier limiting form [equation (4)] no longer prevails. It is possible that at the higher concentrations of added ROH, the reduction in the measured rate constant may also have a component due to a medium solvent effect. The same effect can be achieved by the addition of small amounts of water. It is known[24] that water and alcohols generally act as bases in acidic acetonitrile. An explanation based on this has previously been advanced[16] to explain the reduction of k_0 in acidic alcohol solution by the addition of small amounts of water.

The relative reactivities of HNO_2 and three alkyl nitrites in acetonitrile under zero-order (in substrate) conditions is HNO_2 > TBN > IPN > IPeN. The acid dependence is not strictly first order in $[H_2SO_4]$ but nevertheless this reactivity order is quite clear, and can be estimated as 6:3:1.5:1. The 'reactivity' includes the equilibrium constant for protonation as well as the rate constant for the loss of NO^+, and in the absence of pK_a data in this solvent, the two effects cannot be separated. However the trend in reactivity of the alkyl nitrites (tertiary > secondary > primary) is probably steric in origin from comparisons with the hydrolysis of alkyl nitrites[15] and their exchange reactions with alcohols.[10]

Finally in this section, it is worth noting that there is an obvious comparison between the formation of the nitronium ion in nitration[25] and the nitrosonium ion in nitrosation. Hitherto, in spite of claims to the contrary, there as been no convincing kinetic evidence of a fully zero-order dependence upon the substrate concentration in nitrosation. This has now

Table 7. Variation of k_0 with $[H_2SO_4]$ for reaction of aniline (1.9×10^{-3} mol dm^{-3}) with TBN (1×10^{-4} mol dm^{-3}) in acetonitrile.

$[H_2SO_4]$/mol dm^{-3}	k_0/s^{-1}
0.0155	0.023 ± 0.001
0.0310	0.026 ± 0.001
0.0466	0.026 ± 0.002
0.0776	0.039 ± 0.003
0.109	0.047 ± 0.001
0.140	0.060 ± 0.002
0.233	0.130 ± 0.01

been established in acetonitrile solvent for very reactive species (alcohols and a thiol).

(*c*) *Kinetics of Aromatic Amine Nitrosation.*—Aniline, *N*-methylaniline, and 4-methylaniline all react readily with TBN in acetonitrile, even in the absence of an added acid catalyst, to give, initially, the corresponding diazonium ions or nitrosamine. However, in each case side reactions or subsequent reactions (coupling *etc.*) prevented a kinetic study of the reaction. However, with sulphuric acid in excess over the amine, the reaction proceeded quantitatively to give the diazonium ions, for both primary aromatic amines. With *N*-methylaniline, the initially formed nitrosamine underwent further reaction, probably involving the Fischer–Hepp rearrangement to the 4-nitroso isomer.[26] Fortunately the second reaction was sufficiently slow to allow the nitrosamine formation to be studied kinetically. In all cases reaction conditions were $[\text{amine}]_T$ (*i.e.* the total stoicheiometric amine concentration) $\gg$ [RONO]. Throughout, reactions were strictly first order in [RONO] and also first order in $[\text{amine}]_T$, contrasting markedly with the corresponding reactions of alcohols and TGA. For both primary amines there was no acid catalysis at low acid concentration, but some degree of catalysis at higher concentration. The results for aniline are shown in Table 7. The difference between the behaviour of these amines and the alcohols (and a thiol) probably arises as a concentration effect rather than from an intrinsic reactivity difference. The amines will be substantially protonated in these acid solutions thus reducing the concentration of the reactive free-base form. So at low acidities reaction occurs by rate-limiting attack of NO^+ on the free amine. No acid catalysis is expected, since the protonation of the alkyl nitrite is offset by the protonation of the amine. At higher acid concentrations it is possible that another component to the reaction is called into play *viz.* the rate-limiting attack of NO^+ with the protonated form of the amine. This is well-known in the corresponding reactions in aqueous solution at moderate acidities[27] and also in aqueous solution when nitrosation of amines is effected by nitrosamines.[28] In both cases it has been suggested that NO^+ becomes attached initially to the aromatic system, possibly *via* a π-complex, before rearrangement to the amino group occurs.

Similar results[29] *i.e.* which show rate-limiting NO^+ attack have been obtained for reactions in acetonitrile using alkyl nitrites as nitrosating agents with the enols and enolate ions derived from pentane-2,4-dione, 1,1,1-trifluoro- and 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

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References

1 Part 4. M. J. Crookes and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1989, 759.
2 M. J. Crookes and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1339.
3 S. E. Aldred and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1021.
4 J. H. Bayless, F. D. Mendicino, and L. Friedman, *J. Am. Chem. Soc.*, 1965, **87**, 5790; S. Oae, N. Asai, and K. Fujimori, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1124; J. Casado, A. Castro, F. Lorenzo, and F. Meijide, *Monatsh. Chem.*, 1986, **117**, 335.
5 A. D. Allen and G. R. Schonbaum, *Can. J. Chem.*, 1961, **39**, 940.
6 H. M. S. Patel and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1989, 339.
7 J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.
8 J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc. C*, 1966, 1249.
9 M. P. Doyle, J. W. Terpstra, R. A. Pickering, and D. M. Le Poire, *J. Org. Chem.*, 1983, **48**, 3379.
10 S. A. Glover, A. Goosen, C. W. McCleland, and F. R. Vogel, *S. Afr. J. Chem.*, 1981, **34**, 96.
11 Z. Kricsfalussy and A. Bruylants, *Bull. Soc. Chim. Belg.*, 1964, **73**, 96; *ibid.*, 1965, **74**, 17; Z. Kricsfalussy, A. Bruylants, and A. Dalco, *ibid.*, 1967, **76**, 168.
12 M. J. Crookes and D. L. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1988, 571.
13 W. A. Noyes, *Org. Synth.*, Coll. Vol. II, 1943, pp. 108, 204, 263.
14 D. L. H. Williams, 'Nitrosation,' Cambridge University Press, 1988, p. 151 and references therein.
15 S. E. Aldred, D. L. H. Williams, and M. Garley, *J. Chem. Soc., Perkin Trans. 2*, 1982, 777.
16 A. D. Allen and G. R. Schonbaum, *Can. J. Chem.*, 1961, **39**, 947.
17 I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, 1962, **66**, 1675.
18 I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 4428.
19 I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, 1961, **65**, 1020.
20 I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmilk, *Anal. Chem.*, 1967, **39**, 1627.
21 G. J. Janz and S. S. Danyluk, *J. Am. Chem. Soc.*, 1959, 3846.
22 M. Kinugasa, K. Kishi, and S. Ikedo, *J. Phys. Chem.*, 1973, **77**, 1914.
23 I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 1961, **83**, 3927.
24 I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 1968, **90**, 3320.
25 K. Schofield, 'Aromatic Nitration,' Cambridge University Press, 1986, pp. 8–14.
26 Ref. 14, p. 113.
27 J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.
28 J. T. Thompson and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1932.
29 M. J. Crookes, P. Roy, and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1015.

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