The Chemistry of Nitroso-compounds. Part III.[1] The Nitrosation of Substituted Benzenes in Concentrated Acids

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Rates of nitrosation are reported for benzene, toluene, diphenyl ether, anisole, and phenol in 10·4M-$HClO_4$ at 52·9 °C, for benzene in 12·2M-H_2SO_4, and for [$^2H_6$]benzene in 12M-D_2SO_4. The effective reagent under these conditions is NO^+ and substitution occurs predominantly at the *para*-position of monosubstituted substrates. Benzene reacts about 50 times more rapidly in H_2SO_4 than in $HClO_4$ of the same H_0 acidity, and about 8·5 times more rapidly than [$^2H_6$]benzene in D_2SO_4, which shows that H^+-loss from the Wheland intermediate is rate-limiting. Rates of nitrosation are moderately increased by electron-donating substituents and log (partial rate factors) for the *para*-position correlate with σ^+ parameters to give $\rho = -6·9$. This relatively low ρ value is consistent with the rate-limiting step suggested. The reactivity of NO^+ is discussed and it is shown to be at least 10^{14} times less reactive than NO_2^+. The significance of the findings to recent explanations of aromatic reactivity in nitrations is also discussed.

THE reaction of nitrous acid with aromatic substrates is usually difficult in the absence of powerfully activating substituents such as OH, OR, and NR_2. Often the nitroso-product formed initially undergoes further transformation [2] and nitrous acid is unstable in moderately acidic solutions at high temperatures.[3] This combination of adverse factors has discouraged detailed investigation of these reactions and relatively little is known about their mechanism. In concentrated acids, oxidation to the nitro-derivative is commonly observed and the overall transformation in nitric acid has been extensively investigated by Ingold and his colleagues [4] as the 'special nitrous acid-catalysed' mechanism of nitration. Although information about the initial nitrosation is latent in their results, it is difficult to abstract because of competition in concentrated acids from the 'general' mechanism of nitration involving the nitronium ion (NO_2^+).[5]

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[1] Previous paper, C. N. Berry and B. C. Challis, *Chem. Comm.*, 1972, 627.

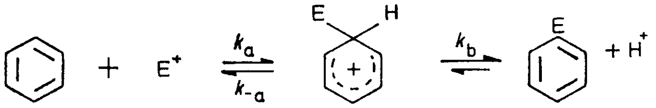
[2] J. H. Boyer, 'Chemistry of the Nitro- and Nitroso-groups, Part 1,' ed. H. Feuer, Interscience, London, 1969, p. 215.

[3] N. S. Bayliss and D. W. Watts, *Austral. J. Chem.*, 1963, **16**, 927.

[4] C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, G. J. Minkoff, and R. I. Reed, *J. Chem. Soc.*, 1950, 2628; J. Glazer, E. D. Hughes, C. K. Ingold, A. T. James, G. T. Jones, and E. Roberts, *ibid.*, p. 2657.

[5] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Bell, London, 1969; J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge Univ. Press, 1971; P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution, Nitration, and Halogenation,' Butterworths, London, 1959.

Kinetic studies of phenol and anisole[6] showed that nitrosation in concentrated $HClO_4$ (>5M) proceeded by the nitrosonium ion (NO^+), which is the major component of 'nitrous' acid under these conditions.[7] In more dilute acid, the reagent could not be positively identified. Perhaps the most important characteristic of these nitrosations, however, was the incidence of substantial primary isotope effect for deuteriated substrates, showing that decomposition of the Wheland intermediate (k_b) was rate-limiting if the reaction proceeded by the usual A-S_E2 mechanism (Scheme 1). This step is usually rapid for other electrophilic aromatic substitutions,[8] implying that nitrosation is unusual in this respect. Careful and extensive work by Zollinger and his colleagues[8,9] on aromatic azo-coupling reactions has shown that, in the absence of steric congestion to increase the rate of k_{-a}, large $k_H : k_D$ ratios are usually observed when the acidity of the leaving proton is low (*i.e.*, for reactive basic substrates and for unreactive electrophiles). It is not clear which of these factors is of prime importance for the nitrosation of phenol and anisole.



SCHEME 1 A-S_E2 Mechanism for electrophilic aromatic substitution

Reliable information on the efficacy of various nitrosating agents towards aromatic substrates is not available. However, several reagents (*e.g.*, H_2ONO^+, NOCl, and NOBr) are known to combine on encounter with the nitrogen of relatively basic amines and with anions,[10] and the nitrous acidium ion (H_2ONO^+) is believed to react readily with anilinium ions in diazotisation.[11] Despite these indications of considerable reactivity, the nitrosonium ion (NO^+) is one of the more basic[7] (and presumably less reactive) positively charged electrophilic species, with a noted tendency to discriminate towards the *para*-position of even highly activated substrates.[6] At least some of the low reactivity evident for aromatic substitution, however, may arise from the instability of nitrous acid solutions even at ambient temperatures.[3]

We have therefore extended our investigation of aromatic nitrosation to less reactive aromatic substrates, including benzene. To avoid complications arising from reaction *via* a spectrum of nitrosating agents, these studies have been conducted in concentrated mineral acids where the major species is thought to be NO^+.[7]

EXPERIMENTAL

Substrates and Reagents.—AnalaR benzene and toluene, and $[^2H_6]$benzene (Koch–Light), were each fractionally distilled, and the middle cut taken: benzene, $n_D^{20} = 1{\cdot}5008$ (lit.,[12] $n_D^{20} = 1{\cdot}5011$); $[^2H_6]$benzene, $n_D^{20} = 1{\cdot}5013$ (lit.,[12] $n^{20} = 1{\cdot}5011$); toluene, $n_D^{20} = 1{\cdot}4955$ (lit.,[13] $n_D^{20} = 1{\cdot}4961$). Reagent grade diphenyl ether was shaken with 3M-NaOH solution to remove phenolic impurities, and then washed well with water. Repeated recrystallisation from EtOH gave white leaves, m.p. 27·5 °C (lit.,[14] 27·5 °C). The purification of phenol and anisole was described.[6]

AnalaR $NaNO_2$ (vacuum dried), $HClO_4$, and H_2SO_4 were used without further purification. D_2SO_4 (98%) was prepared by distilling SO_3 into 99·7% D_2O (Koch–Light). The SO_3 itself was distilled from 30% oleum solution, after refluxing for 10 h over CrO_3 to remove SO_2, and redistilled twice before use.

Kinetics.—Rates of nitrosation of all the substrates were determined from measurement of the concentration of unchanged nitrous acid with respect to time, by use of a modification[6] of Shinn's method[15] in which an azo-dye is produced whose concentration, proportional to the nitrous acid concentration, can be assayed spectrophotometrically.

Experiments with phenol, anisole, diphenyl ether, and toluene were carried out in $HClO_4$ at 52·9 °C in volumetric flasks. Under these conditions spontaneous decomposition of nitrous acid is sufficiently rapid to compete with the nitrosation of toluene. This unproductive loss was ascertained by independent, concurrent measurements of the nitrous acid concentration in flasks containing the reaction solution but no toluene. Numerical details are in the Results section.

Experiments with benzene and $[^2H_6]$benzene were carried out in $HClO_4$, H_2SO_4, and D_2SO_4 at 52·9 °C in sealed tubes containing aliquot portions of the reaction solution to minimise unproductive loss of nitrous acid. Despite this precaution, spontaneous decomposition was still significant and, as for toluene, concurrent 'blank' experiments were carried out to ascertain the rate of this process.

Products were identified in most cases by spectral comparison with authentic compounds.

RESULTS

Diphenyl Ether.—With an excess of diphenyl ether, as in the kinetic runs, the major product (>95%) was *p*-nitrosophenol with traces of the *ortho*-isomer. This can be explained, as in the nitrosation of anisole,[6] by rapid hydrolytic cleavage of the initial *p*-nitroso-ether to give *p*-nitrosophenol and phenol (Scheme 2). Phenol then reacts with further nitrous acid under the experimental conditions to give a second molecule of *p*-nitrosophenol. Evidence for this pathway was obtained independently. Thus diphenyl ether in 10·4M-$HClO_4$ at 52·9 °C showed no detectable hydrolysis to phenol on u.v. spectral examination after 24 h. Also with a 100-fold excess of nitrous acid the only product obtained was 2,4-dinitrophenol at twice the initial diphenyl ether concentration. The same dinitro-product was obtained from the reaction of *p*-nitrosophenol with nitrous acid under similar conditions.

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[6] Part II, B. C. Challis and A. J. Lawson, *J. Chem. Soc.* (*B*), 1971, 770.

[7] N. S. Bayliss, R. Dingle, D. W. Watts, and R. J. Wilkie, *Austral. J. Chem.*, 1963, **16**, 933, and references therein.

[8] H. Zollinger, *Adv. Phys. Org. Chem.*, 1964, **2**, 163.

[9] See E. Berliner, *Progr. Phys. Org. Chem.*, 1964, **2**, 253.

[10] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

[11] B. C. Challis and J. H. Ridd, *J. Chem. Soc.*, 1962, 5208.

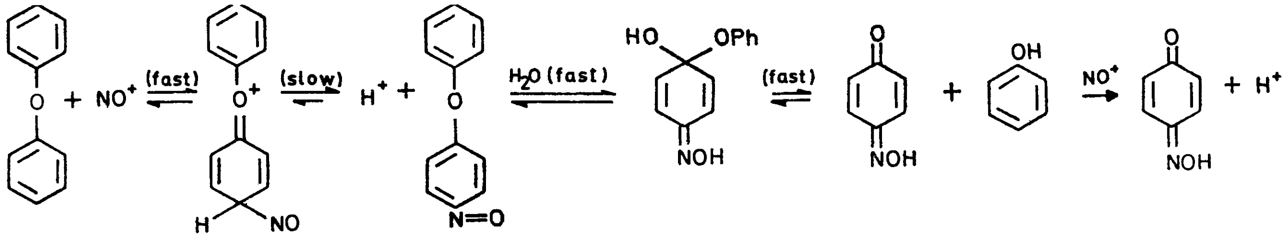
[12] I. Heilbron and H. M. Bunbury, 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 4th edn., vol. 1, p. 325.

[13] Ref. 12, vol. 5, p. 3069.

[14] Ref. 12, vol. 3, p. 1280.

[15] M. B. Shinn, *Ind. Eng. Chem. Anal.*, 1941, **13**, 33; N. F. Kershaw and N. S. Chamberlin, *ibid.*, 1942, **14**, 312.

For the kinetic experiments with a 10-fold excess of diphenyl ether, the disappearance of nitrous acid as shown in Figure 1 was a pseudo-first-order process [equation (1)].



SCHEME 2 Nitrosation of diphenyl ether in concentrated $HClO_4$

In the computation of the actual nitrosation rate of diphenyl ether, however, uptake of nitrous acid by phenol

$$-d[HNO_2]/dt = k_0[HNO_2] \qquad (1)$$

produced during the reaction has to be taken into account. Since phenol reacts much more rapidly than diphenyl ether with nitrous acid (see later), it follows that the pseudo-first-order coefficient for nitrosation of diphenyl ether (Rate = $k_1[HNO_2]$) is half the observed rate coefficient (*i.e.*, $k_0 = 2k_1$). Values of these rate coefficients in 10·4M-$HClO_4$ at 52·9 °C are listed in Table 1, together with second-order coefficients calculated from equation 2. From the consistency of k_2 it is evident that the reaction has a first-order dependence on both substrate and nitrous acid concentrations, as expected from previous studies.[6]

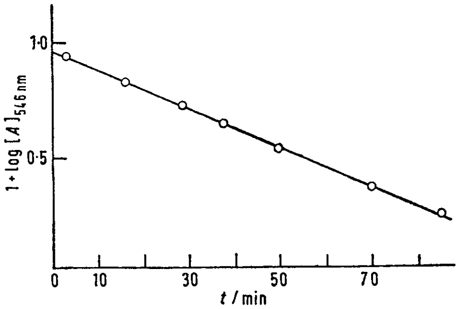


FIGURE 1 Nitrosation of diphenyl ether in 10·4M-$HClO_4$ at 52·9 °C; initial [PhOPh] = 3·45 × 10^{-4}M; $[HNO_2]$ = 3·5 × 10^{-5}M

TABLE 1

Experimental rate coefficients (k_0, k_1, and k_2) for nitrosation of diphenyl ether, phenol, and anisole in 10·4M-$HClO_4$ at 52·9 °C

10^4[Substrate]/ M	$10^4[HNO_2]$/ M	$10^3k_0/s^{-1}$	$10^3k_1/s^{-1}$	$10k_2$ / l mol^{-1} s^{-1}
Diphenyl ether				
10	1·01	0·96	0·480	4·80
4·8	0·40	0·484	0·242	5·05
3·45	0·35	0·331	0·166	4·80
Phenol				
2·90	1·00			109[a]
Anisole				
2·30	1·00			137[a]

[a] k_2 Calculated directly from equation (2).

$$\text{Rate} = k_2\,[\text{Substrate}][HNO_2] \qquad (2)$$

Phenol and Anisole.—Nitrosation of these two compounds in $HClO_4$ at 0·7 °C was reported in Part II.[6] A modest increase in reaction temperature is unlikely to occasion any radical change of mechanism, which at 0·7 °C involved interaction between the neutral substrate and the nitrosating agent, with proton loss from the Wheland intermediate as the rate-limiting step. For comparison with other substrates, the nitrosation rate of phenol and anisole in 10·4M-$HClO_4$ was also measured at 52·9 °C, and values of k_2 [equation (2)] are also listed in Table 1.

Toluene.—Spontaneous decomposition of nitrous acid and the nitrosation of toluene proceeded at similar rates under our conditions. The decomposition is known to have a first-order dependence on $[HNO_2]$,[7] and our results confirm this for at least 70% reaction. For experiments with excess of toluene, where the nitrosation followed a pseudo-first-order rate equation (Rate = $k_1[HNO_2]$), the observed rate of disappearance of nitrous acid will also follow equation (1). In this case, however, k_0 is the sum of the spontaneous decomposition rate (k') and the nitrosation rate (k_1), *i.e.*, equation (3). Values of k' (obtained

$$k_0 = k' + k_1 \qquad (3)$$

from concurrent measurements in the absence of toluene), k_0, and k_1 are in Table 2 for reaction in 10·4M-$HClO_4$ at 52·9 °C. The second-order coefficient, k_2, is reasonably constant (±10%) for a 20-fold change in toluene concentration, confirming the validity of equation (2) for this reaction.

Benzene and [$^2H_6$]*Benzene*.—The normal isomer was examined in both 10·4M-$HClO_4$ and *ca.* 12M-H_2SO_4, and the deuteriated isomer in *ca.* 12M-D_2SO_4, in sealed vials to minimise spontaneous decomposition of nitrous acid. Despite this precaution, the rate of decomposition (k'), measured by concurrent experiments in the absence of substrate, was appreciable, and the error (±20%) in the nitrosation rates is much higher than for the other compounds. The experimental data were treated in the same way as for toluene, and values of the various coefficients are listed in Table 2.

With excess of benzene, as in the kinetic experiments, the product from reaction in H_2SO_4, identified spectrally and by t.l.c., was nitrosobenzene, but appreciable amounts of nitrobenzene were obtained from similar reactions carried out with excess of nitrous acid. This is not unexpected as NO^+ is an oxidising agent.[16] For reaction in $HClO_4$, however, the sole product even with excess of benzene was nitrobenzene, again identified spectrally and by t.l.c. in almost quantitative yield after allowance for spontaneous loss of nitrous acid. As far as our results are concerned, it is important to establish that the nitrobenzene resulted from oxidation of nitrosobenzene by reagents other than

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[16] T. Moeller, 'Inorganic Chemistry,' Wiley, New York, 1952, ch. 8.

nitrous acid. Direct nitration of benzene can be ruled out immediately because our reaction rates are several orders of magnitude less than those reported[17] for nitration in concentrated $HClO_4$ and because we observe a significant primary isotope effect for our reactions, whereas none has been reported for the nitration of benzene.[18] Independent experiments established that nitrosobenzene was readily oxidised to nitrobenzene by $HClO_4$ in the absence of nitrous acid, and the efficacy of $HClO_4$ relative to NO^+, their relative concentrations being borne in mind, is readily established by comparison of their standard oxidation potentials [$E°_{298}(NO + H_2O \rightleftharpoons HNO_2 + H^+ + e^-) = -0{\cdot}99$ V; $E°_{298}(ClO_3^- + H_2O \rightleftharpoons ClO_4^- + 2H^+ + 2e) = -1{\cdot}00$ V].[16] We therefore believe the k_1 values obtained for benzene in both $HClO_4$ and H_2SO_4 refer to rates of nitrosation only.

TABLE 2

Experimental rate coefficients (k_0, k_1, and k_2) for nitrosation of toluene and benzene at 52·9 °C; initial $[HNO_2] = 10^{-4}$M

Acid	10^4[Substrate]/ M	10^5k_0[a]/ s^{-1}	10^5k_1/ s^{-1}	$\frac{10^3k_2}{l\ mol^{-1}\ s^{-1}}$
Toluene				
10·4M-$HClO_4$		2·08		
10·4M-HClO	160	12·4	10·3	6·44
10·4M-$HClO_4$	40·0	4·86	2·78	6·95
10·4M-$HClO_4$	20·0	3·45	1·37	6·85
10·4M-$HClO_4$	8·00	2·56	0·48	6·00
Benzene				
10·4M-$HClO_4$		1·22		
10·4M-$HClO_4$	90	1·57 (1·58)	0·35 (0·36)	0·39
12·46M-H_2SO_4		2·83 (2·65)		
12·12M-H_2SO_4	119·0	21·5	18·8	15·8
12·24M-H_2SO_4	120·0	19·7	17·0	14·2
[$^2H_6$]Benzene				
11·7M-D_2SO_4		0·20		
11·8M-D_2SO_4	110·0	2·21	2·01	1·83
12·0M-D_2SO_4	110·0	1·96	1·76	1·60

[a] Duplicate values in parentheses.

DISCUSSION

Mean values of the second-order coefficients (k_2) derived from equation (2) by use of stoicheiometric reactant concentrations are summarised in Table 3. Under our conditions, none of the substrates is appreciably protonated and nitrous acid exists mainly (>99%) as the nitrosonium ion (NO^+).[7] Although homolytic pathways become more likely at high temperatures, we found no evidence for free radicals in our reaction solutions and neither the substrate selectivity nor the product orientation is consistent with this kind of process. Thus the k_2 values in Table 3 are equivalent to molecular rate coefficients for reaction by NO^+.

TABLE 3

Mean second-order rate coefficients (k_2^x) and partial rate factors (f_p^x) for the nitrosation of monosubstituted benzenes at 52·9 °C

Substnt. (X)	$\frac{10k_2^x}{l\ mol^{-1}\ s^{-1}}$	f_p^x	$-\sigma^+_{p\text{-}X}$ [a]
H	0·0039	1·0	0
Me	0·066	$1{\cdot}02 \times 10^2$	0·311
PhO	4·9	$3{\cdot}78 \times 10^3$	0·50
OMe	137	$2{\cdot}10 \times 10^5$	0·778
OH	109	$1{\cdot}68 \times 10^5$	0·92

[a] From ref. 19.

For phenol,[6] anisole,[6] and diphenyl ether, there is experimental proof that nitrosation takes place mainly at the *para*-position. Assuming this is also true for toluene, we have calculated partial rate factors (f_p^x) (Table 3) for *para*-substitution in 10·4M-$HClO_4$ from equation (4), where k_2^x and k_2^H are the molecular NO^+ coefficients for the X-substituted compound and benzene, respectively. Evidently f_p^x increases by a factor of *ca.*

$$f_p^x = 6k_2^x/k_2^H \qquad (4)$$

$1{\cdot}7 \times 10^5$ in going from benzene to phenol, showing that NO^+ is a fairly selective electrophile. With the exception of the datum for phenol (whose deviation is discussed below), log f_p^x correlates satisfactorily with Stock and Brown's[19] σ^+ substituent parameters (Figure 2) to give a slope (ρ) = $-6{\cdot}9$. Several mechanistic deductions can be drawn from the linearity of this plot. Phenol apart, there is no obvious discontinuity indicative of a change of either mechanism or rate-limiting step; it supports our earlier conclusion that no significant free-radical substitution occurs; it also rules out the possibility that π-complex formation between the aromatic substrate and NO^+ is kinetically significant. The last deduction is particularly important because π-complexes appear to form in concentrated sulphuric acid and when the substrate and nitrous acid concentrations are relatively high.[20] Detailed spectral examination, however, gives no positive evidence for their formation under our conditions.

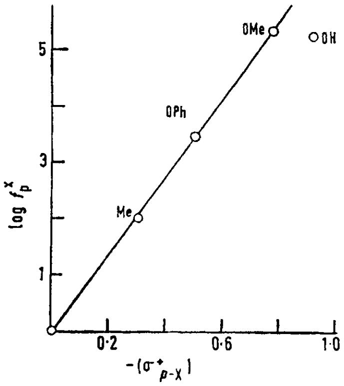

FIGURE 2 Linear free-enery plot for the nitrosation of monosubstituted benzenes in 10·4M-$HClO_4$ at 52·9 °C

We noted that f_p^x for phenol is lower than expected, by a factor that is well outside the estimate of experi-

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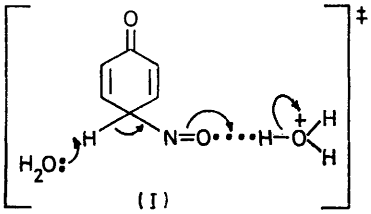
[17] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

[18] L. Melander, *Arkiv Kemi*, 1959, **2**, 211.

[19] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[20] Z. J. Allan, J. Podstata, D. Snobl, and J. Jarkovsky, *Coll. Czech. Chem. Comm.*, 1967, **32**, 1449.

mental error. No firm explanation can be given for this deviant behaviour, but it may well be consequential to the rate-limiting proton transfer, with the transition state involving protonation of the nitroso-oxygen [as in (I)] rather than the phenolic oxygen.



(I)

All the mechanistic deductions from the $\rho\sigma^+$ plot are nicely confirmed by examination of the primary isotope effects. Substantial rate retardations for *para*-[$^2H_1$]-isomers were noted [6] for phenol and anisole at 0·7 °C [k_H/k_D (phenol) $= 3{\cdot}8 \pm 0{\cdot}5$; k_H/k_D (anisole) $= 2{\cdot}7 \pm 0{\cdot}3$] and Table 2 shows that [$^2H_6$]benzene in D_2SO_4 reacts about 8·5 times more slowly than ordinary benzene in H_2SO_4. Since the H_0 acidity of the two solvents for these experiments is closely similar [21] and, in any event, the reaction rate is not strongly dependent on acidity under our conditions, the rate difference for the benzene isomers indicates a substantial primary isotope effect. Thus rate-limiting proton transfer seems to be characteristic of aromatic nitrosation with substrates of widely different reactivity, and is not a special effect related to the relatively low acidity of the leaving proton for the compounds such as phenol and anisole. The data for benzene in Table 2 show that the reaction rate depends on the nature of the solvent acid even when nitrous acid is totally converted into NO^+. Thus for solvents of similar H_0 acidity [22] nitrosation of benzene in H_2SO_4 is *ca.* 50 times faster than in $HClO_4$. This difference cannot be attributed to sulphonation of the substrate, which is at least 30 times slower than the rate of nitrosation,[23] but it is a direct consequence of the rate-limiting proton loss from the Wheland intermediate and reflects the presence of basic species (*e.g.*, HSO_4^-, SO_4^{2-}) other than H_2O present in H_2SO_4 solutions. Accordingly, the large rate retardation noted for [$^2H_6$]benzene in D_2SO_4 arises from the change of solvent as well as from the incidence of a primary isotope effect.

Reactivity of the Nitrosonium Ion.—Nitrosation of phenol and aromatic ethers proceeds mainly at the most reactive *para*-position, as is observed for bromination in acetic acid,[24] for mercuriation,[25] and for high-temperature sulphonation.[26] The rate, however, is only moderately dependent on electron donation by the substituent but, as we discuss below, this is a poor criterion of reagent reactivity. The most satisfactory assessment therefore comes from direct comparison with the rates of other substitutions. Under somewhat milder conditions (61·5% $HClO_4$, 25 °C) than ours, the nitration of benzene is believed to be encounter-controlled,[17] which suggests that NO_2^+ is at least 10^{14} times more effective than NO^+. It is significant, too, that rates of acid-catalysed halogenation by HOBr and HOCl, similar to those for the nitrosation of benzene, are usually observed in dilute $HClO_4$ (0·1—1·0M),[27,28] where the concentrations of positively charged reagents are extremely low. Thus our results confirm that NO^+ is a weak electrophile, but to a lesser extent than previously supposed, and investigations with benzene and toluene demonstrate that one of the major difficulties in effecting reaction is the low thermal stability of nitrous acid solutions.

The low reactivity of NO^+ is not reflected by its selectivity towards substrates of differing reactivity. The value of $\rho = -6{\cdot}9$ (Figure 2), which we have since confirmed by more extensive studies of low-temperature *ortho*-nitrosation of *para*-substituted phenols ($\rho = -6{\cdot}2$),[29] is significantly smaller than those found for other weak electrophilic reagents (*e.g.*, bromination in HOAc, $\rho = -12{\cdot}1$).[24] It is, in fact, of similar magnitude to values obtained for the very reactive reagents effective in acid-catalysed nitration ($\rho = -6{\cdot}2$) [30] and bromination by HOBr ($\rho = -5{\cdot}78$).[27] Evidently the rate-limiting step has an important influence on substrate selectivity as proton-loss from the Wheland intermediate is slow for nitrosation, but not for the other reactions. The magnitude of ρ *vis-à-vis* the reagent reactivity is therefore a useful mechanistic criterion for aromatic substitution in the absence of direct kinetic evidence from isotopic studies. For aromatic nitrosation, and for other substitutions with a similar rate-limiting step, substituent effects on k_a and k_{-a} must approximately cancel (*cf.* Scheme 1, $k_{-a} \gg k_b$, therefore $k_2 \simeq k_a k_b/k_{-a}$), so the experimental ρ reflects a substantial sensitivity of proton loss (k_b) to electron supply. A good model for these reactions is therefore aromatic hydrogen exchange and the relatively low value of $\rho = -8{\cdot}75$ for exchange in $CF_3{\cdot}CO_2H$ [31] agrees nicely with our results.

Inasmuch as substantial primary isotope effects persist over a 10^5-fold range of substrate reactivity, there is no positive evidence that slow proton loss for nitrosation is related to the low acidity of the Wheland

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[21] E. Högfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.

[22] C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970, p. 21.

[23] A. W. Kaandorp, H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1962, **81**, 969.

[24] P. B. D. de la Mare, *J. Chem. Soc.*, 1954, **4450**; H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421, 5175.

[25] H. C. Brown and M. Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 1939.

[26] B. H. Chase and E. McKeown, *J. Chem. Soc.*, 1963, 50.

[27] P. B. D. de la Mare and I. C. Hilton, *J. Chem. Soc.*, 1962, 997, and references therein.

[28] P. B. D. de la Mare, A. D. Ketley, and C. A. Vernon, *J. Chem. Soc.*, 1954, 1290.

[29] B. C. Challis and R. J. Higgins, to be published.

[30] J. D. Roberts, J. K. Sandford, F. L. J. Sixma, H. Cerfontain, and R. Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

[31] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

intermediate. It seems unlikely, too, that NO^+, despite its small size, is extensively solvated, because the reaction rate in concentrated acids is not strongly dependent on a_{H_2O}.[6] This rules out the importance of steric factors in determining the rate-limiting step as in azo-coupling reactions.[8,32] The nitrosonium ion is, however, a relatively stable species ($pK = -6{\cdot}12$ on the H_R scale) [7] compared with other positively charged electrophiles, so that the k_{-a} step (Scheme 1) should be particularly rapid. This factor is of over-riding importance in determining the rate-limiting step.

Nitrous Acid-catalysed Nitration.—Our findings have an important bearing on recent discussions [33] of partial rate factors for the nitration of reactive aromatic compounds. Schofield and his colleagues,[17,34] in particular, have gathered convincing evidence that the nitration rates of benzene and more reactive substrates under a range of conditions are virtually independent of the substrate reactivity, because these reactions are encounter-controlled. They believe that an oxidative–nitrosation pathway, rather than direct nitration, may then explain earlier contradictory evidence that nitration of these substrates is strongly dependent on their reactivity. This hypothesis is entirely consistent with our findings. Further, the incidence of nitration *via* nitrosation should be readily detected by examination of deuteriated (or tritiated) substrates. These experiments were carried out several years ago for the nitration of benzene and toluene and no substantial primary hydrogen isotope effect was apparent [8,18] The result is ambiguous, however, because concurrent substrate reactivity was not measured, but experiments are in hand to remedy the deficiency.

We thank the S.R.C. for a maintenance grant (to A. J. L.).

[2/564 *Received*, 10*th March*, 1972]

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[34] S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2448, and references therein,