The Nitrosation of Phenol and *p*-[^{2}H]Phenol

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ALTHOUGH extensive studies of the *N*-nitrosation of amines show that several species may function as nitrosating reagents in dilute aqueous acids, the nature of the reagent in strongly acidic solutions is speculative.[1] In particular, it is not clear whether the extremely rapid acid-catalysed nitrosations in concentrated acids involve either the nitrous-acidium ion (I) or the nitrosonium ion (II), or even if it is possible to distinguish between these potential reagents.

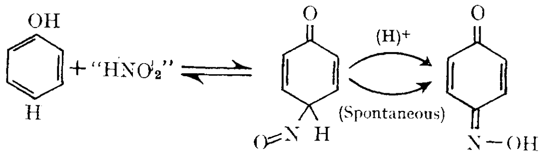
$$\mathrm{H^+ + HNO_2 \rightleftharpoons \underset{(I)}{H_2NO_2^+} \rightleftharpoons \underset{(II)}{NO^+} + H_2O}$$

Similar uncertainty is also evident from kinetic investigations of other reactions in which the character of the reagent has been deduced from the acidity dependence of the reaction rate. Thus Ladenheim and Bender[2] conclude from studies with benzamide in H_2SO_4, for which the rate is proportional to the h_R function, that (II) is the reagent, whereas Morrison and Turney[3] suggest the linear dependence between the rate of phenol nitrosation and the h_0 acidity function in $HClO_4$ is evidence for nitrosation by (I).

A possible explanation of this discordancy in the acidity function correlations is that initial attack by the electrophilic reagent is not entirely rate-controlling for the reaction of phenol, which would then invalidate Morrison and Turney's[3] conclusion. To check this possibility, we have compared the nitrosation rate of phenol and *p*-[^{2}H]phenol (both of which predominantly form *para*-substituted products) in aqueous $HClO_4$, and in the Table the experimental second order rate coefficients from equation (1) are listed:

$$\text{Rate} = k_2[\text{Phenol}]\,[\mathrm{HNO_2}] \qquad (1)$$

for reaction at 0·7°. The substantially reduced rate for the deuteriated substrate ($k_2^{\mathrm{H}}/k_2^{\mathrm{D}} \approx 3{\cdot}8 \mp 0{\cdot}4$) over a wide range of acidities is indicative of a primary isotope effect, and we conclude that proton-loss from some relatively stable intermediate is the rate-controlling process. The character of this intermediate may be deduced from the acidity dependence of the reaction rate as shown in the Figure. Thus the rate of phenol nitrosation, as reported earlier,[3,5] is virtually independent of acidity up to 1M-$HClO_4$, but thereafter increases rapidly with increasing acidity [$d(\log k_2)/d(-H_0) = 1{\cdot}3$] to reach a maximum in about 7·7M-$HClO_4$. This is consistent with the formation of a dienone intermediate (III), which may undergo slow product formation *via* both a spontaneous (at low acidities) and acid-catalysed path (at higher acidities) as shown below. It is not clear whether the acid-catalysed path involves protonation of the phenolic- or nitroso-oxygen atoms, but the steady decrease of reaction rate at very high acidities ([$HClO_4$] > 8M) suggests the



(III)

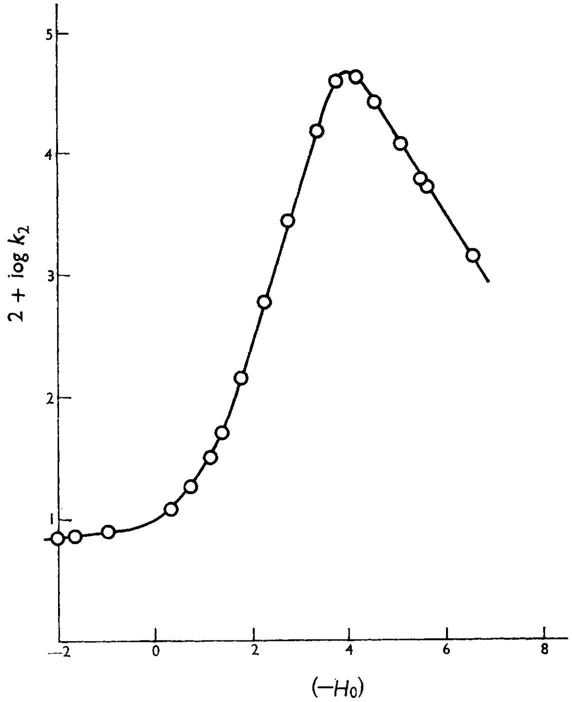


FIGURE. *Plot of log* k_2 *against* H_0 *acidity function for the nitrosation of phenol in aqueous* $HClO_4$ *at 0·7°.*

Second order coefficients [*equation* (1)] *for nitrosation of phenol and* p-[^{2}H]*phenol in* $HClO_4$ *at* 0·7°

[$HClO_4$]	$-H_0$[4]	k_2^H (min.$^{-1}$ mole^{-1} l.)	k_2^D (min.$^{-1}$ mole^{-1} l.)	k_2^H/k_2^D
0·105	—	0·081	0·021	3·9
1·67	0·74	0·181	0·043	4·2
2·25	0·98	0·262	0·064	4·1
3·86	1·72	1·30	0·39	3·3
4·13	1·85	1·85	0·52	3·6
4·87	2·23	5·25	1·60	3·4
5·89	2·82	33·0	9·4	3·6

protonated intermediate is in equilibrium with the reactants under these conditions.

It seems probable that electrophilic substitution of phenolic compounds generally involves ionization of the phenolic-hydrogen to form a dienone intermediate, with subsequent cleavage of the ring proton as the rate-determining process; with one exception,[6] substantial primary isotope effects have been reported for all the reactions studied so far.[7] It is also apparent from the above results that the kinetic acidity dependence for the nitrosation of phenol in aqueous $HClO_4$ provides no direct information on the reagent involved, and therefore it is not inconsistent with reaction *via* the nitrosonium ion (II).

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

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[3] D. A. Morrison and T. A. Turney, *J. Chem. Soc.*, 1960, 4827.

[4] K. Yates and H. Wai, *J. Amer. Chem. Soc.*, 1964, **86**, 5408.

[5] H. Schmid, G. Muhr, and P. Riedl, *Monatsh.*, 1966, **97**, 781.

[6] F. M. Vainstein, E. A. Shilov, and O. M. Grishin, *Zhur. Vsesoyuz Khim. obshch. im. D.I. Mendeleeva.*, 1960, **5**, 119.

[7] For a summary see H. Zollinger, *Adv. Phys. Org. Chem.*, 1964, **2**, 163.