938. The Nitrosation of Phenol in Aqueous Perchloric Acid.

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The rate of *C*-nitrosation of phenol in aqueous 20—60% (w/w) perchloric acid has been determined. Possible mechanisms for the reaction in this region are discussed.

In aqueous perchloric acid nitrous acid in low concentration may be involved in two concurrent equilibria: $HO{\cdot}NO + H_3O^+ \rightleftharpoons H_2NO_2^+ + H_2O$ and $HO{\cdot}NO + H_3O^+ \rightleftharpoons NO^+ + 2H_2O$.[1] At higher concentrations of nitrous acid the equilibrium $2HO{\cdot}NO \rightleftharpoons N_2O_3 + H_2O$ can become important.[2] In acid solution, nitrous acid reacts readily with phenol by electrophilic substitution to form nitrosophenols. *p*-Nitrosophenol forms 90% of the product.[3]

In aqueous perchloric acid with nitrous acid at low concentration the potential nitrosating species, apart from nitrous acid which will be relatively ineffective, are the nitrous acidium ion ($H_2NO_2^+$) and the nitrosonium ion (NO^+).

When the rate of the reaction is governed by the equilibrium concentration of the reactive species it is theoretically possible to distinguish between a nitrous acidium attack and a nitrosonium-ion attack by considering the way in which the rate varies with acidity.[4]

For a reaction through the nitrous acidium ion

$$\mathrm{d}\,(\log k_2)/\mathrm{d}y = -\mathrm{d}H_0/\mathrm{d}y$$

while for the reaction through the nitrosonium ion

$$\mathrm{d}\,(\log k_2)/\mathrm{d}y = -\mathrm{d}J_0/\mathrm{d}y$$

where k_2 is the second-order rate constant, y is the percentage of acid, and H_0 and J_0 are the appropriate acidity functions.

Recent work in hydrochloric acid showed that the reaction is of first order with respect to nitrous acid and to phenol. The second-order rate constant for the reaction catalysed by hydrochloric acid (pH 1·3) at 0° is 0·135 l. mole^{-1} min.$^{-1}$.[5] Nitrosyl chloride may be a complicating factor in this reaction.

This paper deals with the kinetics of the nitrosation of phenol in aqueous perchloric acid. The reaction of nitrous acid with phenol under these conditions follows second-order kinetics and is acid-catalysed:

$$\text{Rate} = k_2(HO{\cdot}NO)(\text{phenol})$$

where k_2, the second-order rate constant, increases with acidity.

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[1] Hughes, Ingold, and Ridd, *J.*, 1958, 58.
[2] Bunton and Stedman, *J.*, 1958, 2440.
[3] Veibel, *Ber.*, 1930, **63**, 1577.
[4] de la Mare and Ridd, " Aromatic Substitution," Butterworths Scientific Publ., London, 1959, p. 37.
[5] Suzawa, Yasuoka, Manabe, and Hiyama, *Science and Ind.* (*Japan*), 1953, **27**, 349 (*Chem. Abs.*, 1956, **50**, 227); 1955, **29**, 7 (*Chem. Abs.*, 1955, **49**, 13,749).

Experimental.—Sodium nitrite, phenol, and perchloric acid, "AnalaR" quality, were used throughout.

To minimise decomposition of nitrous acid the reaction was carried out with both nitrous acid and phenol at 0·001N and at 0·6°. The nitrous acid was estimated by the Griess–Ilosvay method.[7]

Nitrous acid concentrations for each run were determined every 5 min. for the first half of the reaction and at longer intervals later.

The rate constants were found by a plot of $(a - c)/ac$ against t, where a is the initial concentration of nitrous acid and c the concentration after time t. Good second-order rate constants were found throughout. No account was taken of any decomposition of nitrous acid occurring during the reaction.

The ultraviolet absorption spectrum of the reaction product in 45·2% (w/w) perchloric acid was examined and shown to be similar to that of *p*-nitrosophenol. The bulk of the phenol is converted into *p*-nitrosophenol.

Results and discussion.—The experimental results are as follows:

$HClO_4$ (% w/w)	21·5	30·3	38·2	41·7	45·2	48·3	51·4	57·0
k_2 (l. mole^{-1} min.$^{-1}$)	1·5	3·3	9·6	24·5	57	95	120	155

From a plot of log k_2 against % w/w perchloric acid the following slopes are found which are tabulated with the values of $-\mathrm{d}H_0/\mathrm{d}y$ and $-\mathrm{d}J_0/\mathrm{d}y$ given by Deno *et al.*[8]

$HClO_4$ (% w/w) (y)	25	30	35	40	45	50	55
d (log k_2)/dy	0·04	0·05	0·06	0·12	0·10	0·04	0·02
dJ_0/dy	0·13	0·15	0·18	0·20	0·22	0·29	0·32
dH_0/dy	0·06	0·07	0·08	0·10	0·11	0·16	0·16

These results up to 45% acid support the view that $H_2NO_2^+$ is the active species. The falling off of rate beyond this point is probably due to protonation of the phenol.

The conclusion from these results is interesting in view of the fact that the spectroscopic results for nitrous acid in perchloric acid appear best interpreted as an equilibrium between HO·NO and NO$^+$.[9] We accordingly offer an alternative mechanism consistent with the experimental results:

$$C_6H_5{\cdot}OH + H^+ \rightleftharpoons C_6H_5{\cdot}OH_2^+ \quad \text{Rapid pre-equil.} \quad . \quad . \quad . \quad (1)$$

$$C_6H_5{\cdot}OH_2^+ + HO{\cdot}NO \longrightarrow p\text{-}HO{\cdot}C_6H_4{\cdot}NO \quad \text{Rate-determining} \quad . \quad . \quad (2)$$

For (1) $\quad H_0 = \mathrm{p}K + \log C_6H_5{\cdot}OH/C_6H_5{\cdot}OH_2^+$

For (2) $\quad \text{Rate} = k[C_6H_5{\cdot}OH_2^+][HO{\cdot}NO]$

Also $\quad \text{Rate} = k_{\text{exp}}\,[C_6H_5{\cdot}OH][HO{\cdot}NO]$

The concentration of the protonated species being assumed always to be effectively small, we then have

$$k_{\text{exp}} = k \times 10^{\mathrm{p}K - H_0}$$

$$\log k_{\text{exp}} = \log k + \mathrm{p}K - H_0$$

$$\mathrm{d}\,(\log k_{\text{exp}})/\mathrm{d}y = -\mathrm{d}H_0/\mathrm{d}y$$

which is again consistent with the experimental results, the falling off of the rate above 45% acid being due to the dissociation of nitrous acid to nitrosonium ion

Our present experiments do not enable us to distinguish between this mechanism and that involving attack by $H_2NO_2^+$ but they exclude NO$^+$ as the attacking species.

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[6] Hughes and Ridd, *J.*, 1958, 82.

[7] Rider and Mellon, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 96.

[8] Deno, Berkheimer, Evans, and Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344.

[9] Turney and Wright, *J.*, 1958, 2417.