Catalysis of Aromatic Nitration by the Lower Oxides of Nitrogen

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Summary In the absence of nitrous acid traps, the nitration of phenol in 56·2% sulphuric acid displays autocatalytic behaviour; on the other hand, the isomer ratio of the products is inconsistent with the commonly accepted prior nitrosation scheme, and some other route for the promotion of nitration must be operative.

WE report here on anomalous nitration patterns of phenol in mineral acid nitration media which suggest an unusual catalysis of the nitration. Such nitrations of phenol and other substrates activated toward electrophilic substitution are recognized to be subject to the catalytic effects of nitrous acid and perhaps other lower oxides of nitrogen, and the mode of action is assumed to be prior nitrosation followed by oxidation of the nitrosoaromatic.[1] We have found that this reaction scheme is not necessarily operative, or, at the very least, is not alone in promoting nitration.

We used phenol at 25 °C in 56·2% sulphuric acid with no added nitrous acid trap. Aliquots of sodium nitrate and nitrite solutions served as fresh sources of the N^V and N^{III} species, respectively, in each run.† We added the two oxyacids to phenol–sulphuric acid solutions either alone or sequentially, with 30 s between additions. The reactions were quenched and worked up after either 30 s or 7 min total reaction time. The analyses were carried out by h.p.l.c., and the data are presented in the Table.

oxidation of the nitroso compound by addition of N^V was isolated and found to have an $o:p$ ratio of $(0.03 \pm 0.02):1$.

Next, in run 3 we see that with only N^V, after 7 min the nitration is effectively complete, in contrast with the 30 s result of run 1. Clearly some sort of catalysis is operative in the 7 min run, since from our measured initial rate constant for phenol nitration in these media ($k_{NO_2} = 3.9 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹) only about 7% of the phenol should have been nitrated over that period. This value is in fair agreement with the value for nitration at that acidity in studies with added HONO traps.[1b] However, the product $o:p$ ratio is $0.78:1$, a value clearly inconsistent with a prior nitrosation route, which should yield an $o:p$ ratio of about $0.03:1$.

Finally, in accord with this assessment is the result of run 4 in which N^V was added 30 s before N^{III}. While small in an absolute sense, the product $o:p$ ratio of $(0.11 \pm 0.01):1$ shows that 3—4 times more *ortho* nitration is taking place in this mixture than would be expected from the essentially pure prior nitrosation route operative in run 5.

If we assume that in run 3 both nitrosation and nitration are proceeding in parallel, then, given the nitrosation $o:p$ ratio of $0.03:1$, and recognizing that the $o:p$ ratio for straight nitration is about $2.0:1$,[1b] it can be shown that the observed product mixture can be obtained only if the nitration rate is about 1·9 times greater than the rate of

TABLE. Nitration of phenol in 56·2% sulphuric acid at 25 °C[a]

Run	Mode	Reaction time	Nitrophenol[b] (%)	Ratio $o:p$	Material balance[c] (%)	Remarks
1	N^V alone	30 s	< 1	—	98	98% phenol recovered
2	N^{III} alone[d]	30 s	quantitative (nitrosophenol)	—	—	—
3	N^V alone	7 min	87	0·78	87	No phenol observed in product
4	N^V first[e]	7 min	98+	0·11 ± 0·01	98	No phenol observed in product
5	N^{III} first[e]	7 min	98+	0·03 ± 0·02	98	No phenol observed in product

[a] The volume of the solutions was 3·3 ml. Initial concentrations: N^V, 6·1—9·7 × 10⁻² M; phenol, 6·1 × 10⁻³ M; N^{III}, 6·1 × 10⁻² M. Analyses on quenched samples by h.p.l.c. [b] Fraction of starting phenol converted into nitrophenols. [c] Fraction of starting phenol accounted for. [d] Performed in a spectrophotometer; no product isolated. [e] Both N^{III} and N^V added. Second component added 30 s after first.

First, we see that whereas the intervention of NO_x catalysis of phenol nitration can bring about autocatalysis,[1] in the brief 30 s period employed in run 1 almost no nitration took place.

We then established that, in accord with work of Challis and Lawson, phenol nitrosation is rapid and yields almost entirely the *para*-isomer.[2] In our work the conversion was complete and quantitative within 30 s (run 2), with a measured second-order rate constant of $k_{NO} = 92$ dm³ mol⁻¹ s⁻¹. A measure of the very small degree of substitution was obtained from runs, shown collectively as run 5, in which the nitrophenol formed from the subsequent

nitration *via* nitrosation and oxidation. In addition, since the reaction is complete in 7 min, a lower limit can be calculated for the apparent second-order rate constant for the catalysed component of the aromatic nitration, $k_{NO_2}^{cat}$ > 5·0 × 10⁻² dm³ mol⁻¹ s⁻¹.

This value is an order of magnitude greater than that for the conventional nitration, and clearly a potent catalyst not involving nitrosation is operative. It is not clear if in fact the reaction is truly catalysed or merely promoted, and we use the former term here with reservation.

The chemistry in effect here must be elucidated. It can be suggested that phenol may be a special case, since at

† The oxidation states of the oxyacids of nitrogen are used here because more than one specific form is present for both nitrous and nitric acids in 50—60% sulphuric acid. Thus, N^{III} in these solutions is both NO^+ and HONO; N^V is both HNO_3 and NO_2^+.

least in acetic anhydride its nitration is more sensitive to promotion by the lower nitrogen oxides than that of anisole.[4] On the other hand, our results can be compared with those recently presented by Giffney and Ridd,[3] who suggest that the lower oxides of nitrogen play a non-nitrosative role in the reaction of NN-dimethylaniline in nitration media. Their proposed scheme includes electron transfer from the protonated substrate to NO^+, followed by

radical cation reactions. The possibility of radical cation intermediates in aromatic nitration more generally has been recently raised,[5] and it seems the entire question of nitration mechanism is yet to be resolved.[6]

[1] (a) J. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, in 'Nitration and Aromatic Reactivity,' Cambridge University Press Cambridge, 1971, p. 57; (b) R. G. Coombes, J. G. Golding, and P. Hadjigeorgiou, *J. Chem. Soc., Perkin Trans.* 2, 1979, 1451.

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

[3] J. C. Giffney and J. A. Ridd, *J. Chem. Soc., Perkin Trans.* 2, 1979, 618.

[4] J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Commun.*, 1969, 605.

[5] C. L. Perrin, *J. Am. Chem. Soc.*, 1977, **99**, 5516; L. Eberson, L. Johnson, and F. Radner, *Acta Chem. Scand., Ser. B*, 1978, **32**, 749.

[6] R. G. Coombes in 'Comprehensive Organic Chemistry,' Vol. 2, ed. I. O. Sutherland, Pergamon, Oxford, 1979, p. 309.