8. *Kinetics and Mechanism of Aromatic Nitration. Part IX.* Nitrosating Agents in Nitrations catalysed by Nitrous Acid.*

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The kinetics of nitration of *p*-chloroanisole by nitric acid in acetic acid under catalysis by nitrous acid (Part VI) has been further studied, using conditions which isolate the nitration process dependent on catalysis by nitrous acid, a catalysis believed to operate by preliminary nitrosation of the aromatic molecule (Part VI). The object was to determine the active nitrosating agents, and the method has been to examine the kinetic effect of added ionising nitrates and of water. The analysis shows that two nitrosating agents are at work, the nitrosonium ion and the dinitrogen tetroxide molecule, the former being specifically more than ten times faster in reaction than is the latter.

The catalysis, by nitrous acid, of the nitration of aniline and phenol and their derivatives, and also, as was shown, of other sufficiently reactive aromatic compounds, has already been studied kinetically (Part VI, *J.*, 1950, 2628), most thoroughly in the examples of the nitration of *p*-chloroanisole and of *p*-nitrophenol by nitric acid in constant excess in solvent acetic acid. It was thus shown that the total nitration process consists of two parts, which could be isolated. One was the now familiar nitronium-ion reaction, which is anti-catalysed by nitrous acid, according to the law,

$$\text{Rate} = k_0(1 + a[\text{HNO}_2]^{1/2})^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the other was a kinetically new reaction of the form,

$$\text{Rate} = k_2[\text{ArH}][\text{HNO}_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

to which the positive catalysis of nitration is due. The latter reaction could be made negligible by cutting out the nitrous acid as completely as possible, and raising the concentration of nitric acid sufficiently to render the nitronium ion freely available; or it could be made dominating by providing an ample supply of nitrous acid, and so reducing the concentration of nitric acid as to repress strongly the production of nitronium ions. It will be understood that by " nitrous acid " and by " HNO_2 " is here meant stoicheiometric nitrous acid, that is, the whole of the material, which in the water-diluted solution, could be collectively estimated as nitrous acid.

The observed kinetic form of the reaction responsible for the catalysis was regarded as giving strong support to a theory, which had often been inconclusively discussed, namely, that catalysed nitration depends on initial nitrosation, followed by a rapid oxidation of the

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* Part VIII, *J.*, 1950, 2678.

formed nitroso-compound, with restoration of as much nitrous acid as was consumed in the original slow stage :

$$\left.\begin{array}{l} ArH + HNO_2 \xrightarrow{\text{slow}} ArNO + H_2O \\ ArNO + HNO_3 \xrightarrow{\text{fast}} ArNO_2 + HNO_2 \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Here again " nitrous acid " and " HNO_2 " mean stoicheiometric nitrous acid.

The obvious next step in the development of this theory was to identify the nitrosating agent; and this is the object of the present paper. Possible nitrosating agents are the nitrosonium ion, and any accessible molecule or ion of the form NOX, where X is a strong electron-attractor—any " nitrosonium-ion carrier," as we call such compounds. At the outset, the species NO^+, $H_2NO_2^+$, N_2O_4, N_2O_3, and HNO_2, to list only the more obvious, all qualify for consideration. For although the free nitrosonium ion should be the most reactive of these, so much more of one of the others may be present in the system employed, as to give that one a dominating kinetic importance. Moreover concurrent investigations of *O*- and *N*-nitrosation, diazotisation, and deamination lead to the belief that several of the compounds listed above can act as nitrosating agents under appropriate conditions (cf. Hughes, Ingold, and Ridd, *Nature*, 1950, **166**, 642; Yoffe and Gray, *J.*, 1951, 1412). It will be understood that the chemical names and formulæ in this paragraph, contrary to the preceding usage, mean what they look like, HNO_2 referring to molecular nitrous acid, N_2O_4 to undissociated dinitrogen tetroxide, and so on.

It is first necessary to consider, for each of the possible nitrosating agents, whether, and if so with what restrictions, a rate-determining nitrosation by that agent, followed by rapid oxidation of the nitroso-compound as described (reactions I), would lead to a catalysed nitration of the observed kinetic form (equation 2), in the experimental conditions of the kinetic investigation.

It was shown kinetically in Part II (*J.*, 1950, 2400), and the conclusion was confirmed by a study of physical properties, that, in the presence of a great excess of nitric acid in organic solvents such as acetic acid, stoicheiometric nitrous acid is stored mainly as molecular dinitrogen tetroxide. That being so, an assumption that the effective nitrosonium-ion carrier, in the conditions of the kinetic experiments, is dinitrogen tetroxide would clearly be consistent with the kinetics : molecular dinitrogen tetroxide passes the kinetic test unconditionally.

However, there are other, if conditional, possibilities. It was shown in Part II that, in the presence of excess of nitric acid in a solvent such as acetic acid, the dinitrogen tetroxide molecule is slightly ionised to the nitrosonium ion and the nitrate ion (cf. Goulden and Millen, *J.*, 1950, 2620) :

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

Now this nitrate ion could be, and indeed is likely to be, thus produced in amounts considerably smaller than the buffered quantity provided by the various ionisation equilibria of nitric acid, for example, the equilibrium,

$$HNO_3 + HOAc \rightleftharpoons NO_3^- + H_2OAc^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

It follows that, provided the ionisation of dinitrogen tetroxide is not so extensive as to upset the buffering of nitrate ion, the concentration of free nitrosonium ion will bear a constant ratio to that of molecular dinitrogen tetroxide, and therefore to that of stoicheiometric nitrous acid. Therefore, given the condition stated, the hypothesis of nitrosation by the free nitrosonium ion is consistent with the observed kinetics.

We have no exact knowledge of the equilibria of self- or mutual dehydration which determine the active mass of water in these nearly anhydrous solutions. But if, by any means, this quantity were buffered sufficiently to experience no disturbance from equilibria involving molecular nitrous acid, then an assumption that nitrosation takes place by an attack of this molecule on the aromatic substance can easily be shown to be in agreement with the kinetics.

Finally, if conditions of both the stated types were simultaneously fulfilled, in particular, if the active masses of both nitrate ion and water were so buffered that neither suffered disturbance from equilibria involving the nitrous acidium ion, then the hypothesis that this ion is the nitrosating agent can be seen to accord with the kinetics.

Thus, of the listed nitrosating agents, all satisfy, or might satisfy, the already ascertained kinetic laws, with the single exception of dinitrogen trioxide, which, at best, would require the stoicheiometric nitrous acid to enter through the square of its concentration, instead of through the first power, into the rate equation.

We have sought to distinguish between the remaining possibilities by examining the kinetic effect of nitrate ion and of water, added in quantities greater than those produced from nitric acid, or from the catalysing nitrous acid. According to the identity of the nitrosating agent, the second-order rate constant k_2 for catalysed nitration should then suffer modification according to the law

$$k_2 \propto [\mathrm{NO_3^-}]^x[\mathrm{H_2O}]^y$$

where the powers x and y have the following values for the nitrosating agents under consideration :

	NO^+	$H_2NO_2^+$	N_2O_4	HNO_2
x	-1	-1	0	0
y	0	$+1$	0	$+1$

Clearly it should be possible to obtain the required distinction on this basis.

It has been found that the rate of the catalysed reaction, as expressed by the second-order constant k_2 of equation (2), is strongly depressed by added ionising nitrates. Added water exerts a relatively trivial retarding effect, which we shall neglect, believing it to arise from less direct causes than are of present concern. This much was indicated in Part VI, though only in experiments at higher and more scattered solute concentrations than are quantitatively significant. It has been found, moreover, that the alkali-metal nitrates formerly employed are not fully dissociated in the medium at kinetically useful concentrations. And, therefore, in developing the work we have gone over to tetra-alkylammonium nitrates, which seem to be free from this difficulty.

A quantitative study of the kinetic effect of nitrates has shown that the rate-constant k_2 of catalysed nitration is additively composed of two parts : one part is unaffected by nitrates (x zero) ; the other is diminished by added nitrates (x negative). This result, together with the relative indifference of the rate to water (y zero), suggests the hypothesis that the total nitrosating activity is being shared between two agents, namely, the dinitrogen tetroxide molecule and the nitrosonium ion.

A first kinetic expression of this hypothesis is as follows :

$$\mathrm{Rate} = k_2'[\mathrm{ArH}][\mathrm{N_2O_4}] + k_2''[\mathrm{ArH}][\mathrm{NO^+}]$$

Since in organic solvents containing nitric acid, dinitrogen tetroxide is only slightly ionised, the above equation can be rewritten thus :

$$\mathrm{Rate} = [\mathrm{ArH}][\mathrm{N_2O_4}]\{k_2' + (Kk_2'')/[\mathrm{NO_3^-}]\}$$

K being the ionic dissociation constant of dinitrogen tetroxide. Since the concentration of molecular dinitrogen tetroxide, as it appears in these equations, must be nearly identical with the concentration of stoicheiometric nitrous acid, as contained in equation (2), our expression for the above hypothesis of dual action can be put in the following form :

$$k_2 = k_2' + (Kk_2'')/[\mathrm{NO_3^-}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When testing equation (3), one has to deal with the slight complication that the concentration of nitrate ion which here appears is not simply the known concentration of added salt, but is the total concentration of nitrate ion present in the medium, including the not exactly known portion derived from the ionisation of nitric acid and nitrous acid. The procedure employed is best explained with reference to some actual measurements.

The table records a set of data for the effect of added tetramethylammonium nitrate and tetraethylammonium nitrate on the rate of nitration of *p*-chloroanisole by nitric acid in fixed concentration in acetic acid at a fixed temperature, under catalysis by stoicheiometric nitrous acid. With the chosen concentrations of nitric acid and of nitrous acid, equation (1), representing nitronium-ion nitration, is entirely unimportant; and equation (2), representing the catalysed reaction, expresses the whole of the rate. Since nitrous acid is neither formed nor destroyed, each kinetic run yields a first-order rate constant k_1, from which, by division by the concentration of nitrous acid present during the run, the second-order constant k_2 of equations (2) and (3) can be deduced.

Effect of added tetramethylammonium and tetraethylammonium nitrates on rate of nitration of p-*chloroanisole by* 4·44M-*nitric acid in acetic acid at* 35·0° *under catalysis by nitrous acid.*

(Initially, [$Cl \cdot C_6H_4 \cdot OMe$] ~ 0·08M.; k_1 in sec.$^{-1}$; k_2 in sec.$^{-1}$ mole^{-1} l.)

Run no.	[Nitrate]	[HNO_2]	10^4k_1	10^3k_2
12	None	0·075	26·1	34·9
	$NMe_4^+NO_3^-$			
16	0·0070	0·058	17·3	29·9
18	0·0097	0·050	13·6	27·0
26	0·0126	0·024	6·15	25·9
17	0·0167	0·058	13·7	23·5
14	0·0208	0·062	13·3	21·4
15	0·0234	0·066	13·8	21·0
19	0·0800	0·048	7·40	15·4
	$NEt_4^+NO_3^-$			
27	0·0242	0·025	4·88	19·8
	0·0115	0·021	5·17	25·2

Fig. 1.

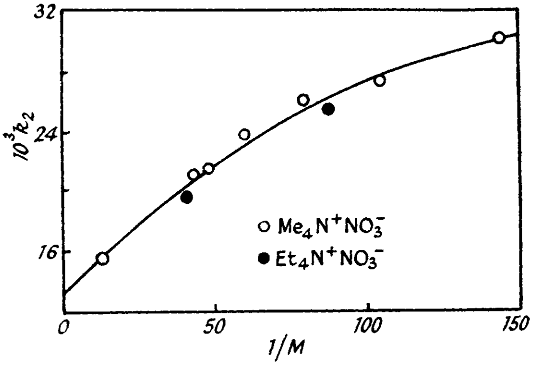
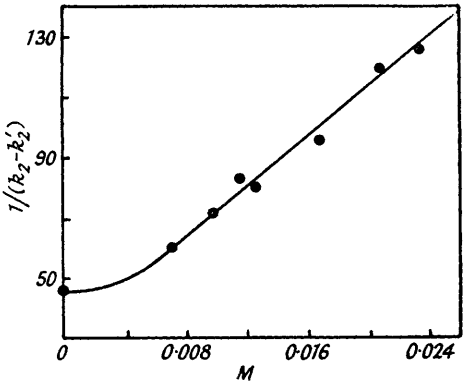


Fig. 2.



The first step in the reduction of these data is to plot k_2, the second-order rate constant, against 1/M., the reciprocal of the concentration of *added* nitrate. The resulting graph is in Fig. 1; and from it a limiting value of k_2 at (1/M.) = 0 can be read. Now although this graph will not strictly coincide with the graph that we cannot plot of k_2 against $1/[NO_3^-]$, where NO_3^- means *total* nitrate ion, as in equation (3), the two graphs should merge at the high-concentration end, and hence should run to the same limit at (1/M.) = 0 = ($1/[NO_3^-]$). Thus the observed limit of k_2 at (1/M.) = 0, namely 13 × 10^{-3} sec.$^{-1}$ mole^{-1} l., should be the value of k_2' in equation (3), that is, the rate constant for nitrosation by molecular dinitrogen tetroxide.

This value of k_2' is now used, in conjunction with each determined value of k_2, for the purpose of constructing a graph of $1/(k_2 - k_2')$ against M. Bearing in mind the form of equation (3), and the circumstance that M. and $[NO_3^-]$ must converge to congruence at higher concentrations, one sees that this graph should be asymptotic to a straight line, and that the reciprocal of its limiting slope should be equal to Kk_2''. The actual graph is in Fig. 2, and it has the expected asymptotically linear form. From its steady slope, the value 2·5 × 10^{-4} sec.$^{-1}$ can be deduced for Kk_2''.

This composite constant, the product of the dissociation constant of dinitrogen tetroxide and the rate constant for nitrosation by nitrosonium ion, cannot be exactly factorised on the basis of the present data. Yet the analysis can be pushed a little further as follows.

First, the value of k_2 observed in the absence of any added salt, combined with values of k_2' and of Kk_2'' given above, enable equation (3) to be used for the purpose of deducing the related value of $[NO_3^-]$, that is, the concentration of nitrate ion present in the salt-free nitration medium. This value is 0·011M. Under the extreme (but probably approximate) assumption that all this comes from nitric acid (reaction III) and none from dinitrogen tetroxide (reaction II), it would represent, as an upper limit, a degree of dissociation of only 0·2% of the 4·44M.-nitric acid in acetic acid at 35°, consistently with our previous knowledge that nitric acid behaves as a weak electrolyte in solvent acetic acid.

Secondly, under the other extreme (probably not approximate) assumption, that the whole of the nitrate ion comes from dinitrogen tetroxide (reaction II), and none of it from nitric acid (reaction III), we may derive an upper limit for the ionic dissociation constant of dinitrogen tetroxide. It is $K < 1{\cdot}9 \times 10^{-3}$ mole l.$^{-1}$, consistently with our previous knowledge that dinitrogen tetroxide, though a strong electrolyte in nitric acid, becomes a weak electrolyte, obeying Ostwald's dilution law, in mixtures of nitric acid with organic solvents.

Thirdly, using the above upper limit of K, and the determined value of $k_2''K$, we can derive a lower limit for k_2'', the rate constant for nitrosation by the nitrosonium ion. The value is below, and it is of interest to compare it with the rate constant for nitrosation by dinitrogen tetroxide :

$$k_2'' > 132 \times 10^{-3}\ \text{sec.}^{-1}\ \text{mole}^{-1}\ \text{l.} \qquad k_2' = 13 \times 10^{-3}\ \text{sec.}^{-1}\ \text{mole}^{-1}\ \text{l.}$$

The figures show that the nitrosonium ion is specifically more than ten times faster as a reagent for nitrosation than is the dinitrogen tetroxide molecule. The actual factor may be much greater than ten.

EXPERIMENTAL

Materials.—The nitrating mixtures were made from absolute nitric acid, acetic acid, and dinitrogen tetroxide, each purified as directed in Part II (*J.*, 1950, 2400). Solutions containing suitable amounts of stoicheiometric nitrous acid were prepared by mixing a solution free from nitrous acid with a solution to which freshly distilled dinitrogen tetroxide had been added. The *p*-chloroanisole was obtained as directed in Part VI (*J.*, 1950, 2628). Tetramethylammonium nitrate (Found by use of Devarda's alloy: NO_3^-, 46·0. Calc. for $C_4H_{12}N{\cdot}NO_3$: NO_3^-, 45·5%) and tetraethylammonium nitrate (Found : NO_3^-, 31·9. Calc. for $C_8H_{20}N{\cdot}NO_3$: NO_3^-, 32·2%) were prepared by way of the iodides and hydroxides, and after crystallisation were carefully dried.

Kinetics.—The dilatometric method was employed, using tapless dilatometers, as in Part VI. The first-order rate law, checked graphically, was well obeyed by the individual runs. Best values of first-order rate constants were calculated by Guggenheim's pairing method. During preparation for a set of runs, including the final series reported in the table, a bulk solution of nitric acid in acetic acid was made up, in order to secure constancy in the concentration of nitric acid. But it was not found possible similarly to standardise the concentrations of nitrous acid, and therefore this was introduced (as dinitrogen tetroxide) and analytically determined on the occasion of each run. It was determined both before and after each run, always with substantially identical results.

Analysis.—The dilatometric indication of reaction progress had already been checked for this nitration by chemical analysis (Part VI). Concentrations of nitrous acid were estimated by the colorimetric method (Part II).

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