large preponderance of NO_2^+ ions over $H_2NO_3^+$ ions, as there appears to be in pure nitric acid,[13] then $[NO_2^+] \approx [NO_3^-]$ and we can write

$$[NO_2^+] = (K_1K_2)^{\frac{1}{2}}[HNO_3]/[H_2O]^{\frac{1}{2}}, \tag{9}$$

where

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[NO_2^+][H_2O]}{[H_2NO_3^+]}. \tag{10}$$

The rate of nitration is thus

$$\frac{d[ArNO_2]}{dt} = k_3[NO_2^+][ArH]$$

$$= k_3(K_1K_2)^{\frac{1}{2}}[HNO_3][ArH]/[H_2O]^{\frac{1}{2}}. \tag{11}$$

This equation implies that the water formed in the nitration should have a retarding effect on the reaction. But it is an experimental fact that small amounts of water have only a slight effect on the rate,[2] perhaps because water forms a complex with nitric acid. We shall therefore assume that both $[HNO_3]$ and $[H_2O]$ are effectively unchanged during the reaction, and that the first-order rate constant is

$$k_{\text{first}} = \frac{1}{[ArH]}\frac{d[ArNO_2]}{dt} \propto k_3(K_1K_2)^{\frac{1}{2}}. \tag{12}$$

In our present experiments we have measured the quantities

$$\Delta V^{\ddagger}_{\text{zeroth}} = -RT\left(\frac{\partial \ln k_{\text{zeroth}}}{\partial P}\right)_{T,x}, \tag{13}$$

$$\Delta V^{\ddagger}_{\text{first}} = -RT\left(\frac{\partial \ln k_{\text{first}}}{\partial P}\right)_{T,x}. \tag{14}$$

It will be seen from (8) and (12) that these apparent volumes of activation are actually composite quantities made up of the following terms:

$$\Delta V^{\ddagger}_{\text{zeroth}} = \Delta V^{\ddagger}_2 + \tfrac{1}{2}\Delta V_1, \tag{15}$$

$$\Delta V^{\ddagger}_{\text{first}} = \Delta V^{\ddagger}_3 + \tfrac{1}{2}\Delta V_1 + \tfrac{1}{2}\Delta V_2, \tag{16}$$

where the $\Delta V^{\ddagger}$ are volumes of activation * and the ΔV are total volume changes for complete reaction. To interpret the results adequately, we need to separate these terms.

ZEROTH-ORDER REACTIONS

There is no way of measuring $\Delta V^{\ddagger}_2$ or ΔV_1 directly, but we can make a fair estimate of the magnitude of $\Delta V^{\ddagger}_2$ by considering an analogous reaction. Reaction 2 probably occurs by way of a heterolytic fission:[2]

$$(O)(O)N{-}\overset{+}{O}H_2 \rightarrow O{=}\overset{+}{N}{=}O + OH_2, \tag{17}$$

which is closely analogous to the rate-determining step in the unimolecular hydrolysis of acetals

$$(R_2)(RO)C{-}\overset{+}{O}HR \rightarrow R_2{=}C{=}\overset{+}{O}R + OHR. \tag{18}$$

* In the transition-state theory, certain approximations are involved in deriving the relationship $\Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)$. These have been discussed by Benson [14] and Hamann.[15]

Koskikallio and Whalley [6] have found that pressure has only a small influence on the rates of these hydrolyses, ΔV^{*} being either zero or slightly positive ($\leqslant 2$ cm^3/mole). We may safely assume that $\Delta V_2^{\ddagger}$ will be similarly small and can be neglected. It follows that $\Delta V^{*}_{\text{zeroth}} \approx \frac{1}{2}\Delta V_1$. From the values of $\Delta V^{*}_{\text{zeroth}}$ in tables 1 and 2 it would thus appear that ΔV_1 (the volume change for the autoprotolysis of nitric acid) must be about -20 cm^3/mole, which is close to the value -23 cm^3/mole for the autoprotolysis of water.[16] The large contraction is undoubtedly caused by electrostriction of the liquid around the $H_2NO_3^+$ and NO_3^- ions.[17]

We conclude that the acceleration of the zeroth-order reactions at high pressures arises principally from the enhanced ionization of nitric acid into nitric acidium ions and nitrate ions.

FIRST-ORDER REACTIONS

It is apparent from eqn. (12) and (16) that the increase in autoprotolysis will also tend to accelerate the first-order reactions. But here there are additional effects associated with the subsequent equilibrium 2 and the rate-determining step 3. It is possible, at least in principle, to measure $\Delta V_1 + \Delta V_2$ directly by observing the effect of pressure on the equilibrium,

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O, \qquad (19)$$

which exists in pure nitric acid.[13, 18] But the experiments would be difficult and we have not yet attempted them. Instead we have made use of the fact that the equilibrium 2 between $H_2NO_3^+$ and NO_2^+ ions is analogous to that between I_3^- and I^- ions:

$$I_3^- \rightleftharpoons I^- + I_2, \qquad (20)$$

for which $\Delta V = +5$ cm^3/mole.[19] In the absence of more direct information we have assumed that ΔV_2 also has this value, so that $\Delta V_1 + \Delta V_2 \approx -15$ cm^3/mole. It follows from the values of $\Delta V^{\ddagger}_{\text{first}}$ in tables 1 and 2 that $\Delta V_3^{\ddagger} \approx -15$ cm^3/mole. Without placing too much reliance on this value, we can be satisfied that the activation step involves a considerable contraction of the system. It is likely that most of the contraction arises from the partial formation of a covalent bond between the attacking ion and the benzene ring, and it is completely analogous to the contraction which is known to occur in S_N2 substitutions [20] (the present reaction is an S_E2 substitution).

We conclude, therefore, that an increase in pressure accelerates the first-order nitrations both because it favours the formation of nitronium ions and because it speeds up the rate at which they attack aromatic compounds.

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