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

$$[NO_{2}^{+}] = (K_{1}K_{2})^{\frac{1}{2}}[HNO_{3}]/[H_{2}O]^{\frac{1}{2}},$$
(9)

where

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[\text{NO}_2^+][\text{H}_2\text{O}]}{[\text{H}_2\text{NO}_3^+]}.$$
 (10)

The rate of nitration is thus

$$\frac{d[ArNO_2]}{dt} = k_3[NO_2^+][ArH]$$
$$= k_3(K_1K_2)^{\frac{1}{2}}[HNO_3][ArH]/[H_2O]^{\frac{1}{2}}.$$
(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,<sup>2</sup> perhaps because water forms a complex with nitric acid. We shall therefore assume that both [HNO<sub>3</sub>] and [H<sub>2</sub>O] are effectively unchanged during the reaction, and that the first-order rate constant is

$$k_{\text{first}} = \frac{1}{[\text{ArH}]} \frac{\text{d}[\text{ArNO}_2]}{\text{d}t} \propto k_3 (K_1 K_2)^{\frac{1}{2}}.$$
 (12)

In our present experiments we have measured the quantities

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

$$\Delta V_{\text{first}}^{\dagger} = -RT \left( \frac{\partial \ln k_{\text{first}}}{\partial P} \right)_{T,x}.$$
 (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 :

$$\Delta V_{\text{zeroth}}^{*} = \Delta V_{2}^{*} + \frac{1}{2} \Delta V_{1}, \qquad (15)$$

$$\Delta V_{\text{first}}^{*} = \Delta V_{3}^{*} + \frac{1}{2}\Delta V_{1} + \frac{1}{2}\Delta V_{2}, \qquad (16)$$

where the  $\Delta V^{\ddagger}$  are volumes of activation \* and the  $\Delta V$  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  $\Delta V_2^{\pm}$  or  $\Delta V_1$  directly, but we can make a fair estimate of the magnitude of  $\Delta V_2^{\pm}$  by considering an analogous reaction. Reaction 2 probably occurs by way of a heterolytic fission : <sup>2</sup>

$$\sum_{0}^{+} N - OH_2 \rightarrow O = N = O + OH_2,$$
 (17)

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

$$\begin{array}{c} R_2 \\ C \\ -OHR \end{array} \rightarrow R_2 = C = OR + OHR. \end{array}$$
 (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 <sup>14</sup> and Hamann.<sup>15</sup>

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#### CHEMICAL EFFECTS OF PRESSURE

Koskikallio and Whalley <sup>6</sup> have found that pressure has only a small influence on the rates of these hydrolyses,  $\Delta V^{\pm}$  being either zero or slightly positive ( $\leq 2 \text{ cm}^3/\text{ mole}$ ). We may safely assume that  $\Delta V_2^{\pm}$  will be similarly small and can be neglected. It follows that  $\Delta V_{\text{zeroth}}^{\pm} \approx \frac{1}{2} \Delta V_1$ . From the values of  $\Delta V_{\text{zeroth}}^{\pm}$  in tables 1 and 2 it would thus appear that  $\Delta V_1$  (the volume change for the autoprotolysis of nitric acid) must be about  $-20 \text{ cm}^3/\text{mole}$ , which is close to the value  $-23 \text{ cm}^3/\text{mole}$ for the autoprotolysis of water.<sup>16</sup> The large contraction is undoubtedly caused by electrostriction of the liquid around the H<sub>2</sub>NO<sub>3</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions.<sup>17</sup>

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,

# $2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O_3$ (19)

which exists in pure nitric acid.<sup>13, 18</sup> 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 :

$$I_3^- \rightleftharpoons I^- + I_2, \tag{20}$$

for which  $\Delta V = +5 \text{ cm}^3/\text{mole}.^{19}$  In the absence of more direct information we have assumed that  $\Delta V_2$  also has this value, so that  $\Delta V_1 + \Delta V_2 \approx -15 \text{ cm}^3/\text{mole}.$ It follows from the values of  $\Delta V_{\text{first}}^{\pm}$  in tables 1 and 2 that  $\Delta V_3^{\pm} \approx -15 \text{ cm}^3/\text{mole}.$ 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  $S_N 2$  substitutions <sup>20</sup> (the present reaction is an  $S_E 2$  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.

- 1 Gonikberg and Gavrilova, J. Gen. Chem. U.S.S.R., 1952, 22, 1388.
- <sup>2</sup> Hughes, Ingold and Reed, J. Chem. Soc., 1950, 2400. See also: Ingold, Structure and Mechanism in Organic Chemistry (Bell and Sons, London, 1953). de la Mare and Ridd, Aromatic Substitution (Butterworths, London, 1959).
- <sup>3</sup> Brown and Jensen, J. Amer. Chem. Soc., 1958, 80, 2291.
- <sup>4</sup> Weissberger, Proskauer, Riddick and Toops, Organic Solvents (Interscience, New York, 1955). <sup>5</sup> Perrin, Trans. Faraday Soc., 1938, 34, 144.
- 6 Koskikallio and Whalley, Trans. Faraday Soc., 1959, 55, 809.
- 7 Kolthoff and Robinson, Rec. trav. chim., 1926, 45, 169.
- 8 Zambelli, J. Chem. Soc. Abstr., 1887, 533.
- 9 Bellinger, Friedman, Bauer, Eastes and Bull, Ind. Eng. Chem., 1948, 40, 1320.
- 10 Cordes, Fetter and Happe, J. Amer. Chem. Soc., 1958, 80, 4802.
- 11 Hamann, Physico-Chemical Effects of Pressure (Butterworths, London, 1957), p. 166.

Melander, Nature, 1949, 163, 599; Acta Chem. Scand., 1949, 3, 95; Arkiv. Kemi, 1950, 2, 213.
 <sup>13</sup> Gillespie, Hughes and Ingold, J. Chem. Soc., 1950, 2552.

<sup>14</sup> Benson, *Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960), p. 510.
 <sup>15</sup> ref. (11), p. 161.
 <sup>16</sup> Owen and Brinkley, *Chem. Rev.*, 1941, 29, 461.

<sup>17</sup> ref. (11), p. 55; p. 152. <sup>18</sup> Ingold and Millen, J. Chem. Soc., 1950, 2612. <sup>19</sup> Ewald and Hamann, Austral. J. Chem., 1956, **9**, 54. <sup>20</sup> ref.(11), p. 177.

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