

large preponderance of  $\text{NO}_2^+$  ions over  $\text{H}_2\text{NO}_3^+$  ions, as there appears to be in pure nitric acid,<sup>13</sup> then  $[\text{NO}_2^+] \approx [\text{NO}_3^-]$  and we can write

$$[\text{NO}_2^+] = (K_1 K_2)^{\frac{1}{2}} [\text{HNO}_3] / [\text{H}_2\text{O}]^{\frac{1}{2}}, \quad (9)$$

where

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

The rate of nitration is thus

$$\begin{aligned} \frac{d[\text{ArNO}_2]}{dt} &= k_3 [\text{NO}_2^+] [\text{ArH}] \\ &= k_3 (K_1 K_2)^{\frac{1}{2}} [\text{HNO}_3] [\text{ArH}] / [\text{H}_2\text{O}]^{\frac{1}{2}}. \end{aligned} \quad (11)$$

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  $[\text{HNO}_3]$  and  $[\text{H}_2\text{O}]$  are effectively unchanged during the reaction, and that the first-order rate constant is

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

In our present experiments we have measured the quantities

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

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

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

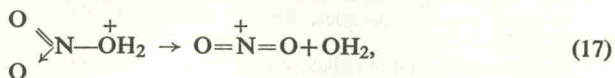
$$\Delta V_{\text{zeroth}}^* = \Delta V_2^* + \frac{1}{2} \Delta V_1, \quad (15)$$

$$\Delta V_{\text{first}}^* = \Delta V_3^* + \frac{1}{2} \Delta V_1 + \frac{1}{2} \Delta V_2, \quad (16)$$

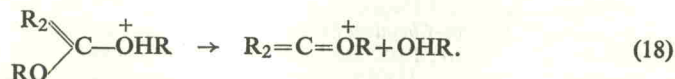
where the  $\Delta V^*$  are volumes of activation\* and the  $\Delta V$  are total volume changes for complete reaction. To interpret the results adequately, we need to separate these terms.

#### ZERO-ORDER REACTIONS

There is no way of measuring  $\Delta V_2^*$  or  $\Delta V_1$  directly, but we can make a fair estimate of the magnitude of  $\Delta V_2^*$  by considering an analogous reaction. Reaction 2 probably occurs by way of a heterolytic fission:<sup>2</sup>



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



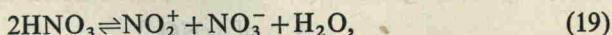
\* In the transition-state theory, certain approximations are involved in deriving the relationship  $\Delta V^* = -RT (\partial \ln k / \partial P)$ . These have been discussed by Benson<sup>14</sup> and Hamann.<sup>15</sup>

Koskikallio and Whalley<sup>6</sup> have found that pressure has only a small influence on the rates of these hydrolyses,  $\Delta V^\ddagger$  being either zero or slightly positive ( $\leq 2$  cm<sup>3</sup>/mole). We may safely assume that  $\Delta V_2^\ddagger$  will be similarly small and can be neglected. It follows that  $\Delta V_{\text{zerth}}^\ddagger \approx \frac{1}{2} \Delta V_1$ . From the values of  $\Delta V_{\text{zerth}}^\ddagger$  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  $-20$  cm<sup>3</sup>/mole, which is close to the value  $-23$  cm<sup>3</sup>/mole for the autoprotolysis of water.<sup>16</sup> The large contraction is undoubtedly caused by electrostriction of the liquid around the  $\text{H}_2\text{NO}_3^+$  and  $\text{NO}_3^-$  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,



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  $\text{H}_2\text{NO}_3^+$  and  $\text{NO}_2^+$  ions is analogous to that between  $\text{I}_3^-$  and  $\text{I}^-$  ions:



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

<sup>1</sup> 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.

<sup>6</sup> Koskikallio and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 809.

<sup>7</sup> Kolthoff and Robinson, *Rec. trav. chim.*, 1926, **45**, 169.

<sup>8</sup> Zambelli, *J. Chem. Soc. Abstr.*, 1887, 533.

<sup>9</sup> Bellinger, Friedman, Bauer, Eastes and Bull, *Ind. Eng. Chem.*, 1948, **40**, 1320.

<sup>10</sup> Cordes, Fetter and Happe, *J. Amer. Chem. Soc.*, 1958, **80**, 4802.

<sup>11</sup> Hamann, *Physico-Chemical Effects of Pressure* (Butterworths, London, 1957), p. 166.

<sup>12</sup> 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.