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CHEMICAL EFFECTS OF PRESSURE

PART 7.—THE RATES OF ELECTROPHILIC AROMATIC NITRATIONS IN SOLUTION

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Measurements have been made of the influence of pressure on the rates of nitration of aromatic compounds by nitric acid in inert solvents. It is found that an increase in pressure accelerates the zeroth-order nitration of toluene in acetic acid and in nitromethane by an amount corresponding to an activation volume of -10 cm^3/mole. The acceleration probably arises from an increase in the stationary concentration of nitric acidium ions ($H_2NO_3^+$).

The first-order nitrations of p-dichlorobenzene in nitromethane and of benzene and chlorobenzene in acetic acid are all accelerated by pressure in a more marked degree than the zeroth-order reaction of toluene. Their activation volumes are about -22 cm^3/mole. It is likely that, in these reactions, an increase in pressure both favours the formation of the active nitronium ions (NO_2^+) and speeds up the rate at which they attack the aromatic compounds.

This paper is the first of a series describing the influence of pressure on aromatic substitutions. The only previously reported measurements in this field are a few which Gonikberg and Gavrilova [1] made on the heterogeneous carboxylation of benzene by CO_2 in the presence of $AlCl_3$. They found indications that the reaction was accelerated by an increase in pressure. But its mechanism and kinetics are obscure and the results have little fundamental value. We have, therefore, considered it worthwhile to undertake a systematic study of the effects of pressure on both the rates and products of aromatic substitutions. For the present we have restricted ourselves to simple homogeneous reactions whose mechanisms are already known at atmospheric pressure.

In this paper we describe measurements of the rate of mononitration of aromatic compounds (ArH) by an excess of nitric acid in inert solvents:

$$HNO_3 + ArH \rightarrow ArNO_2 + H_2O.$$

Hughes, Ingold and Reed [2] have made a thorough study of the rates and mechanisms of these reactions and shown that the active agent is the nitronium ion NO_2^+ formed by the decomposition of nitric acid. If the aromatic substrate is sufficiently reactive then the formation of this ion is the slowest step in the nitration, and the rate is independent of both the nature of the substrate and its concentration. In a large excess of nitric acid the kinetics are of the zeroth order and the reaction proceeds at a constant rate until all the substrate is consumed. If, on the other hand, the substrate is relatively unreactive, the rate-determining step becomes the bimolecular attack of the NO_2^+ ion on the aromatic nucleus. Under these conditions the rate of nitration depends on the nature of the substrate and is proportional to its concentration, so that the kinetics are of the first order. In our

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present work we have measured the rates of both kinds of reactions at pressures between 1 atm and 2300 atm. In a later paper we shall describe measurements of the influence of pressure on the relative yields of the different isomers formed by nitrating substituted benzene derivatives under the same conditions as applied in the present rate measurements.

Concurrently with the experiments on nitrations, we have made a less extensive study of the influence of pressure on the Friedel-Crafts benzoylation of aromatic compounds under such conditions [3] that the reactions were homogeneous and obeyed simple second-order kinetics. The results of these experiments will be published later.

EXPERIMENTAL

MATERIALS

Benzene, toluene and chlorobenzene were dried and purified by conventional methods.[4] p-Dichlorobenzene was purified by crystallization from alcohol. The materials were analyzed by gas chromatography and shown to be at least 99·5 % pure.

Anhydrous nitric acid was prepared by distillation from sulphuric+nitric acid mixtures, and freed from dinitrogen tetroxide (which is an inhibitor in nitrations [2]) by several low-temperature sublimations under vacuum. It was stored as a solid at −80°C and dispensed into the reaction mixtures as a liquid at −15°C.

Acetic acid was prepared by refluxing the reagent-grade material with potassium permanganate for 2 h and distilling it. It was then treated with pure acetic anhydride and sulphuric acid to remove water, and fractionated. Analytical grade nitromethane was dried thoroughly and fractionated.

APPARATUS

The high-pressure nitrations were carried out in a sampling vessel similar in principle to those described by Perrin [5] and Koskikallio and Whalley.[6] There were small differences in detail, imposed by the extremely corrosive nature of the reaction mixtures. The mixtures were held in a thin-walled polyethylene capsule which could deform to transmit the pressure of the surrounding hydraulic fluid. The capsule was connected by a polyethylene tube to the seat of a stainless steel outlet valve, so that the only metal in contact with the reaction mixture was the small area of steel at the valve seat.

A number of preliminary experiments with a thermocouple immersed in the reaction mixture showed that the heat generated by the initial compression could be counterbalanced by pre-cooling the mixture. For instance, a mixture pre-cooled to −32°C reached the desired reaction temperature of 0°C after rapid (nearly adiabatic) compression to 2000 atm. In addition to preventing over-heating, the pre-cooling had the desirable effect of quenching the reaction until the pressure was applied.

The pressure vessel was immersed in a constant temperature bath and the temperature and pressure of the mixture were kept constant during the withdrawal of each sample by simultaneously pumping more hydraulic fluid into the vessel.

METHODS OF ANALYSIS

The progress of the reactions in nitromethane was followed by titrating the unchanged nitric acid with alkali under carefully controlled conditions. But this method was unsatisfactory for the reactions in acetic acid, both because the change in total acidity was much smaller and because the end-point was less well defined. For these reactions we measured the concentration of the nitrated product by titrating it with titanous chloride solution to an electrometric end-point in the presence of sodium citrate buffer.[7] The titanous chloride was standardized against pure nitrobenzene.

The amount of the inhibitor N_2O_4 in each sample was estimated colorimetrically as α-naphthol azo-sulphanilic acid.[8] It was never greater than 0·002 mole/l.

RESULTS

REACTIONS IN NITROMETHANE

We made only a few measurements in nitromethane because we found that this solvent forms extremely explosive mixtures with nitric acid. Pure nitromethane can be detonated by sudden compression to 150 atm,[9] and we found that the addition of nitric acid makes it both a more sensitive and a more powerful explosive.

However, we completed some measurements of the rates of the zeroth-order nitration of toluene and the first-order nitration of p-dichlorobenzene at 20°C and at two pressures. The results are given in table 1, where the zeroth-order rate constants have been derived from the relation,

$$k = \frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{ArNO_2}] = -\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{HNO_3}],$$

and the first-order constants from the relation

$$k = \frac{1}{[\mathrm{ArH}]}\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{ArNO_2}] = \frac{\mathrm{d}}{\mathrm{d}t}\ln\frac{[\mathrm{ArH}]_0}{[\mathrm{ArH}]}.$$

$\Delta\overline{V}^{\ddagger}$ denotes the *average* value of the molar volume of activation over the pressure range 1 to 2000 atm. It is defined as

$$\Delta\overline{V}^{\ddagger} = -\frac{RT}{2000\ \mathrm{atm}}\ln\frac{k(2000\ \mathrm{atm})}{k(1\ \mathrm{atm})}.$$

The data show that the rate of nitration of toluene increases rather steeply with the mole fraction of nitric acid and Hughes, Ingold and Reed [2] have suggested that this effect arises from the increased polarity of the medium. But despite the large differences in k at different values of $[\mathrm{HNO_3}]$, the influence of pressure is quite uniform and the values of $\Delta\overline{V}^{\ddagger}$ agree within the experimental errors (about ±1 cm³/mole).

TABLE 1.—THE NITRATION OF AROMATIC COMPOUNDS (ArH) BY $\mathrm{HNO_3}$ IN NITROMETHANE AT 20°C

$[\mathrm{ArH}]_0$ (mole fraction) = 0·025

ArH	$[\mathrm{HNO_3}]$ (mole fraction)	pressure (atm)	reaction order	rate constant k,	$\Delta\overline{V}^{\ddagger}$ (cm³/mole)
$\mathrm{C_6H_5CH_3}$	0·220	1	zeroth	$2{\cdot}8\times10^{-4}$ mole frac. min^{-1}	−9·1(−9·8) *
	0·220	2000	,,	$5{\cdot}9\times10^{-4}$,,	
	0·155	1	,,	$1{\cdot}1\times10^{-4}$,,	−9·3(−8·9) *
	0·155	2000	,,	$2{\cdot}3\times10^{-4}$,,	
	0·108	1	,,	$2{\cdot}5\times10^{-5}$,,	−10·1
	0·108	2000	,,	$5{\cdot}8\times10^{-5}$,,	
p-$\mathrm{Cl_2C_6H_4}$	0·178	1	first	$9{\cdot}7\times10^{-4}$ min^{-1}	−20·5
	0·178	2000	,,	$5{\cdot}2\times10^{-3}$,,	

* These values were given by some other measurements at the same nitric acid concentrations.

We obtained only a single value of $\Delta\overline{V}^{\ddagger}$ for the first-order nitration of p-dichlorobenzene, but we are satisfied that the difference between this and the values for toluene is real.

REACTIONS IN ACETIC ACID

To avoid the explosive hazards of the nitromethane mixtures, we employed acetic acid as the solvent in the majority of our measurements.

Initially we worked at 25°C, but it proved difficult to obtain reproducible results at that temperature, particularly in the high pressure experiments. The cause of the trouble was the thermal decomposition of nitric acid to form the inhibitor $\mathrm{N_2O_4}$. This decomposition is speeded up at high pressures, a fact which suggests that it occurs by an ionic mechanism involving electrostriction of the medium, rather than by the free-radical mechanism proposed by Cordes, Fetter and Happe [10] (a free-radical decomposition would almost certainly be retarded by an increase in pressure [11]). Apparently the decomposition has a higher activation energy than the nitration reactions and we were able to suppress it by working at 0°C, where only an insignificant amount of N_2O_4 was formed after several hours.

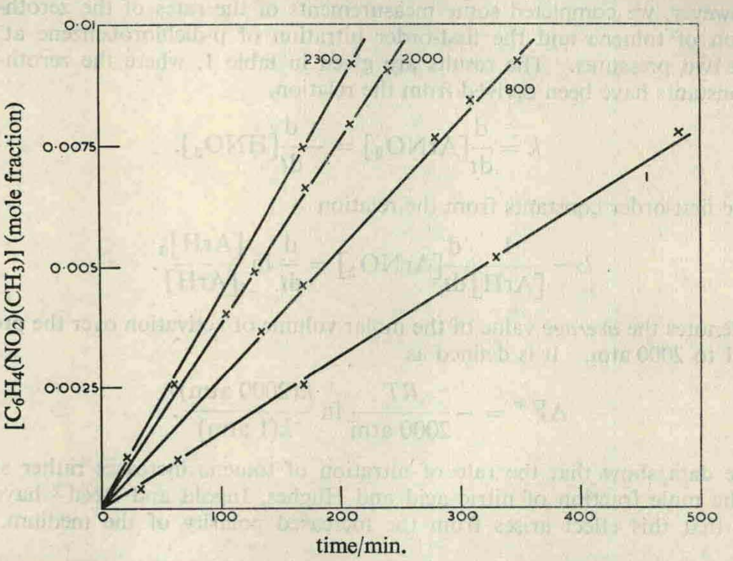


FIG. 1.—Zeroth-order rate plots for the nitration of toluene in acetic acid at 0°C ($[HNO_3] = 0{\cdot}374$; $[C_6H_5CH_3]_0 = 0{\cdot}0131$ mole fraction). The number on each line indicates the pressure in atm.

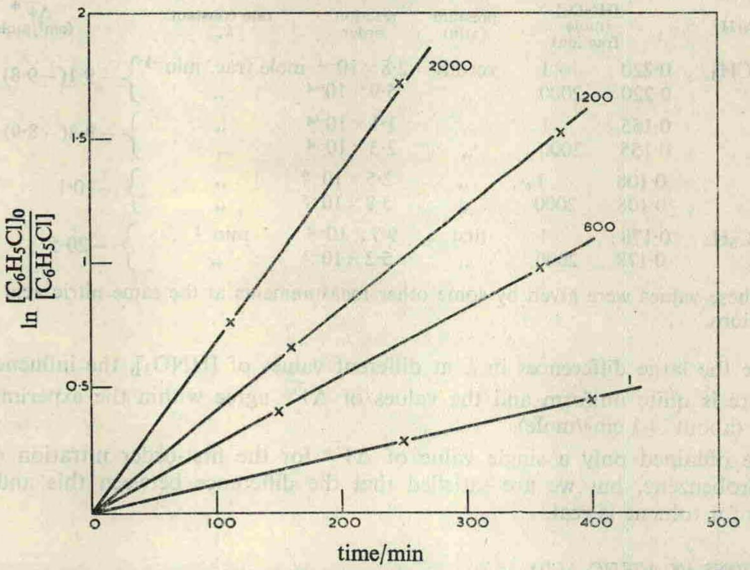


FIG. 2.—First-order rate plots for the nitration of chlorobenzene in acetic acid at 0°C ($[HNO_3] = 0{\cdot}418$; $[C_6H_5Cl]_0 = 0{\cdot}0128$ mole fraction). The number on each line indicates the pressure in atm.

Some of our results are illustrated in fig. 1 and 2. These data, along with a number of others, showed that the rate of nitration of toluene was accurately of the zeroth order whereas the nitrations of benzene and chlorobenzene were of the first order under our conditions. In no instance was there any indication that the reaction order changed with pressure.

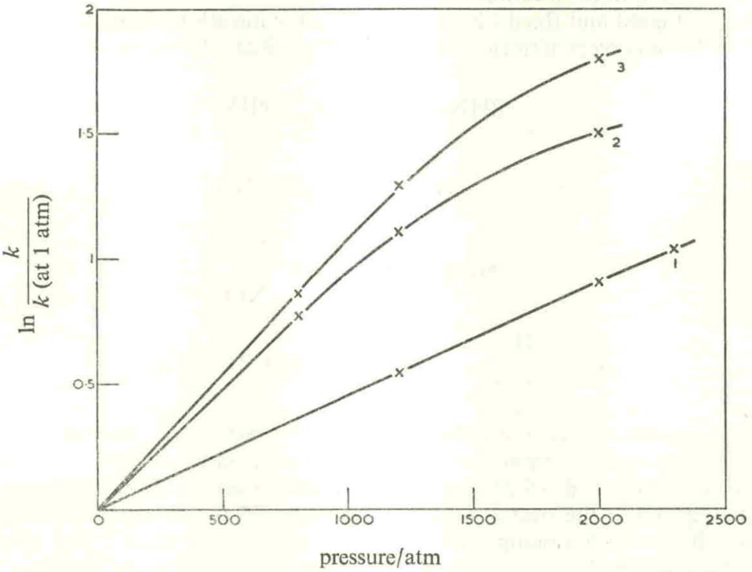


FIG. 3.—The influence of pressure on rate constants for nitration in acetic acid. Curve 1: the zeroth-order reaction of toluene; curve 2: the first-order reaction of benzene: curve 3: the first-order reaction of chlorobenzene.

Table 2 lists average values of the rate constants for the two classes of reactions. The quantity $\Delta V^{\ddagger}_{P=1}$ denotes the activation volume at atmospheric pressure, defined as

$$\Delta V^{\ddagger}_{P=1} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_{T,x} \quad \text{(at 1 atm).}$$

Its magnitude is proportional to the initial slopes of the curves in fig. 3.

TABLE 2.—THE NITRATION OF AROMATIC COMPOUNDS (ArH) BY HNO_3 IN ACETIC ACID AT 0°C

$[ArH]_0$ (mole fraction) = 0·0130

ArH	$[HNO_3]$ (mole fraction)	pressure (atm)	reaction order	rate constant k,		$\Delta V^{\ddagger}_{P=1}$ (cm³/mole)
$C_6H_5CH_3$	0·374	1	zeroth	$1{\cdot}56\times10^{-5}$	mole frac min.$^{-1}$	−10·0
	0·374	1200	,,	$2{\cdot}7\times10^{-5}$	,,	
	0·374	2000	,,	$3{\cdot}9\times10^{-5}$	,,	
	0·374	2300	,,	$4{\cdot}4\times10^{-5}$		
C_6H_6	0·396	1	first	$4{\cdot}4\times10^{-3}$	min^{-1}	−22·0
	0·396	800	,,	$9{\cdot}5\times10^{-3}$	,,	
	0·396	1200	,,	$1{\cdot}42\times10^{-2}$	,,	
	0·396	2000	,,	$2{\cdot}1\times10^{-2}$	,,	
C_6H_5Cl	0·418	1	first	$1{\cdot}17\times10^{-3}$	min^{-1}	−23·5
	0·418	800	,,	$2{\cdot}7\times10^{-3}$	,,	
	0·418	1200	,,	$4{\cdot}2\times10^{-3}$	,,	
	0·418	2000	,,	$6{\cdot}6\times10^{-3}$	,,	

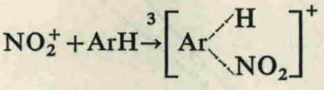
DISCUSSION

It is clear from tables 1 and 2 that an increase in pressure accelerates all the nitrations, although it has a more marked influence on the first-order reactions than on the zeroth-order ones. To explain these facts we need to consider the detailed mechanism of nitration.

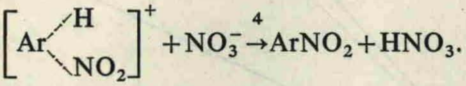
Hughes, Ingold and Reed [2] have shown that the nitration of an aromatic compound ArH by an excess of nitric acid in an inert medium follows the general scheme,

$$2HNO_3 \underset{-1}{\overset{1}{\rightleftharpoons}} H_2NO_3^+ + NO_3^- \tag{1}$$

$$H_2NO_3^+ \underset{-2}{\overset{2}{\rightleftharpoons}} H_2O + NO_2^+ \tag{2}$$



$$NO_2^+ + ArH \xrightarrow{3} \left[Ar\begin{matrix} H \\ NO_2 \end{matrix} \right]^+ \tag{3}$$



$$\left[Ar\begin{matrix} H \\ NO_2 \end{matrix} \right]^+ + NO_3^- \xrightarrow{4} ArNO_2 + HNO_3. \tag{4}$$

The first equilibrium is established very rapidly because it involves only the transference of a proton from one molecule of nitric acid to another. The second equilibrium is reached much more slowly, and reaction 2 may be the rate determining step in the overall nitration. Reaction 3 is also comparatively slow and may be rate-determining. Reaction 4 is much faster than 3 and plays no part in the kinetics.[12]

The experimental evidence shows that when reaction 2 is rate-determining, the nitronium ions NO_2^+ are removed by reaction 3 as rapidly as they are formed, and the nitration proceeds at a constant rate until all the ArH is consumed. The rate of formation of NO_2^+ is proportional to the concentration of $H_2NO_3^+$, which must be nearly the same as the concentration of NO_3^-.* We therefore have the relationship:

$$[H_2NO_3^+] = K_1^{\frac{1}{2}}[HNO_3], \tag{5}$$

where

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[H_2NO_3^+][NO_3^-]}{[HNO_3]^2}, \tag{6}$$

and the rate of nitration is given by

$$\frac{d[ArNO_2]}{dt} = \frac{d[NO_2^+]}{dt} = k_2K_1^{\frac{1}{2}}[HNO_3]. \tag{7}$$

If the nitric acid is in large excess, its concentration is effectively constant during the reaction and the kinetics are of zeroth order:

$$k_{\text{zeroth}} = d[ArNO_2]/dt \quad \propto \quad k_2K_1^{\frac{1}{2}}. \tag{8}$$

On the other hand, when reaction 3 is rate-determining, the experiments show [2] that the rate of removal of ArH is accurately of the first order (with respect to ArH), implying that there is a stationary concentration of NO_2^+ ions corresponding to almost complete establishment of the second equilibrium 2. If there is a

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* It is probably not exactly the same because the water formed in reaction 2 may have a slight influence on the concentration of NO_3^- ions.[2]

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

$$\begin{aligned}\frac{d[ArNO_2]}{dt} &= k_3[NO_2^+][ArH] \\ &= k_3(K_1K_2)^{\frac{1}{2}}[HNO_3][ArH]/[H_2O]^{\frac{1}{2}}.\end{aligned} \tag{11}$$

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

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

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:

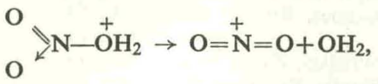
$$\Delta V^{\ddagger}_{\text{zeroth}} = \Delta V_2^{\ddagger} + \tfrac{1}{2}\Delta V_1, \tag{15}$$

$$\Delta V^{\ddagger}_{\text{first}} = \Delta V_3^{\ddagger} + \tfrac{1}{2}\Delta V_1 + \tfrac{1}{2}\Delta V_2, \tag{16}$$

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.

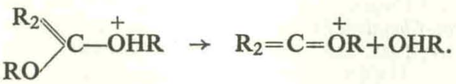
ZEROTH-ORDER REACTIONS

There is no way of measuring $\Delta V_2^{\ddagger}$ or ΔV_1 directly, but we can make a fair estimate of the magnitude of $\Delta V_2^{\ddagger}$ by considering an analogous reaction. Reaction 2 probably occurs by way of a heterolytic fission:[2]



$$O_2N\text{—}\overset{+}{O}H_2 \rightarrow O{=}\overset{+}{N}{=}O + OH_2, \tag{17}$$

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



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

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* 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, $\Delta V^{\ddagger}$ 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 $\Delta V^{\ddagger}_{\text{zeroth}} \approx \frac{1}{2}\Delta V_1$. From the values of $\Delta V^{\ddagger}_{\text{zeroth}}$ 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,

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O, \tag{19}$$

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:

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

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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