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.

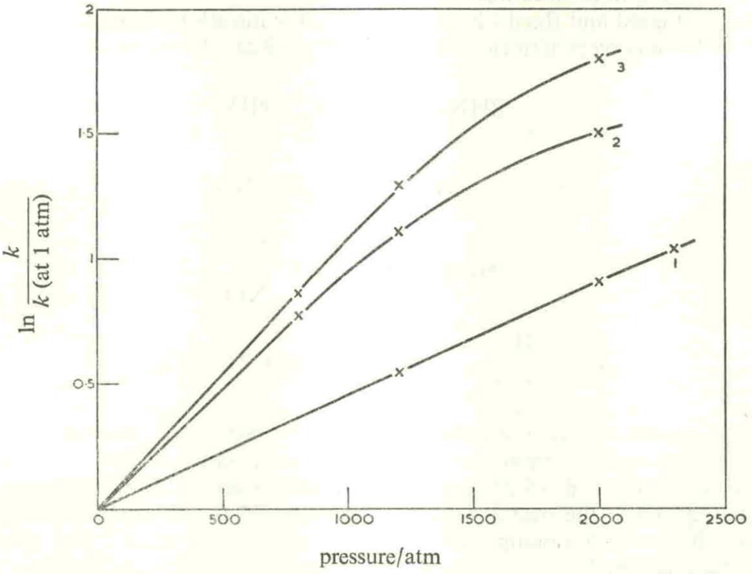


FIG. 3.—The influence of pressure on rate constants for nitration in acetic acid. Curve 1: the zeroth-order reaction of toluene; curve 2: the first-order reaction of benzene: curve 3: the first-order reaction of chlorobenzene.

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	,,	$6{\cdot}6\times10^{-3}$	,,	

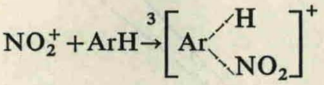
DISCUSSION

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.

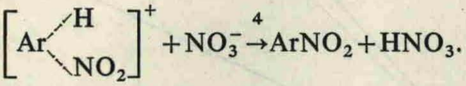
Hughes, Ingold and Reed [2] have shown that the nitration of an aromatic compound ArH by an excess of nitric acid in an inert medium follows the general scheme,

$$2HNO_3 \underset{-1}{\overset{1}{\rightleftharpoons}} H_2NO_3^+ + NO_3^- \qquad (1)$$

$$H_2NO_3^+ \underset{-2}{\overset{2}{\rightleftharpoons}} H_2O + NO_2^+ \qquad (2)$$



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



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

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:

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

where

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

and the rate of nitration is given by

$$\frac{d[ArNO_2]}{dt} = \frac{d[NO_2^+]}{dt} = k_2 K_1^{\frac{1}{2}}[HNO_3]. \qquad (7)$$

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

$$k_{\text{zeroth}} = d[ArNO_2]/dt \quad \propto \quad k_2 K_1^{\frac{1}{2}}. \qquad (8)$$

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

* 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]