

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,

$$k = \frac{d}{dt}[\text{ArNO}_2] = -\frac{d}{dt}[\text{HNO}_3],$$

and the first-order constants from the relation

$$k = \frac{1}{[\text{ArH}]} \frac{d}{dt}[\text{ArNO}_2] = \frac{d}{dt} \ln \frac{[\text{ArH}]_0}{[\text{ArH}]}$$

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

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

The data show that the rate of nitration of toluene increases rather steeply with the mole fraction of nitric acid and Hughes, Ingold and Reed² have suggested that this effect arises from the increased polarity of the medium. But

TABLE 1.—THE NITRATION OF AROMATIC COMPOUNDS (ArH) BY HNO₃ IN NITROMETHANE AT 20°C

[ArH]₀ (mole fraction) = 0.025

ArH	[HNO ₃] (mole fraction)	pressure (atm)	reaction order	rate constant <i>k</i> , mole frac. min ⁻¹	$\Delta \bar{V}^\ddagger$ (cm ³ /mole)
C ₆ H ₅ CH ₃	0.220	1	zeroth	2.8 × 10 ⁻⁴	-9.1(-9.8) *
	0.220	2000	"	5.9 × 10 ⁻⁴	
	0.155	1	"	1.1 × 10 ⁻⁴	-9.3(-8.9) *
	0.155	2000	"	2.3 × 10 ⁻⁴	
	0.108	1	"	2.5 × 10 ⁻⁵	-10.1
	0.108	2000	"	5.8 × 10 ⁻⁵	
<i>p</i> -Cl ₂ C ₆ H ₄	0.178	1	first	9.7 × 10 ⁻⁴	-20.5
	0.178	2000	"	5.2 × 10 ⁻³	

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

despite the large differences in *k* at different values of [HNO₃], the influence of pressure is quite uniform and the values of $\Delta \bar{V}^\ddagger$ agree within the experimental errors (about ±1 cm³/mole).

We obtained only a single value of $\Delta \bar{V}^\ddagger$ 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 N₂O₄. 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 Happe¹⁰ (a free-radical decomposition would almost certainly be retarded

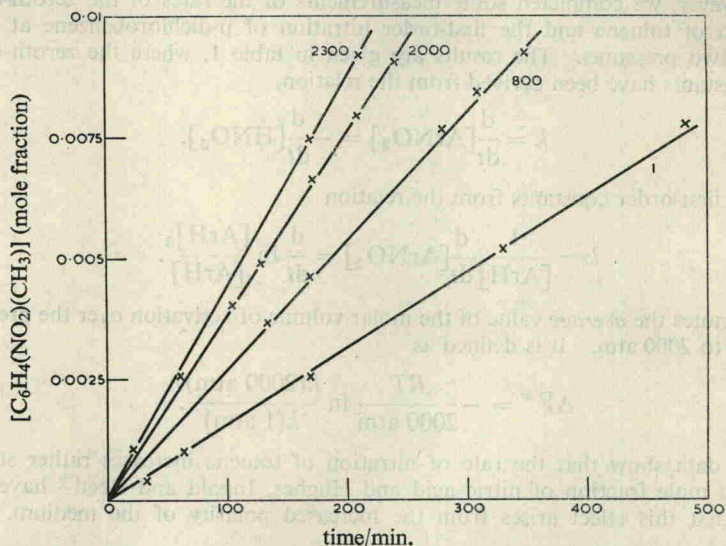


FIG. 1.—Zeroth-order rate plots for the nitration of toluene in acetic acid at 0°C ($[\text{HNO}_3] = 0.374$; $[\text{C}_6\text{H}_5\text{CH}_3]_0 = 0.0131$ mole fraction). The number on each line indicates the pressure in atm.

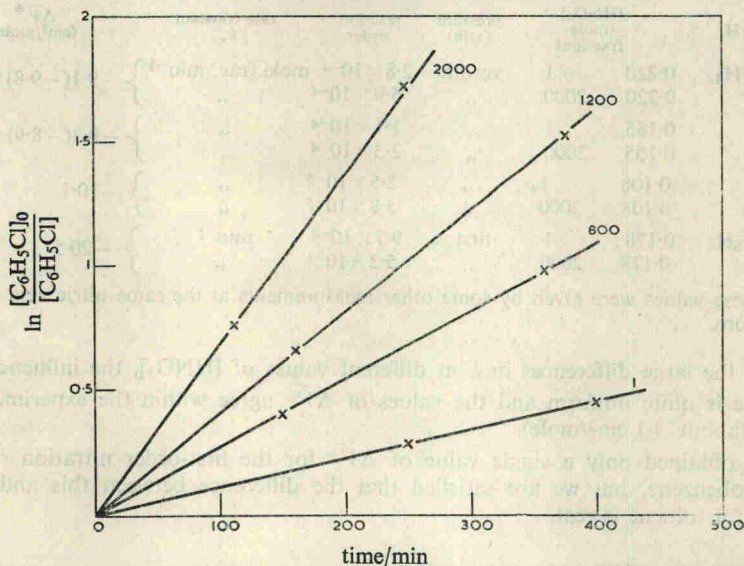


FIG. 2.—First-order rate plots for the nitration of chlorobenzene in acetic acid at 0°C ($[\text{HNO}_3] = 0.418$; $[\text{C}_6\text{H}_5\text{Cl}]_0 = 0.0128$ mole fraction). The number on each line indicates the pressure in atm.

by an increase in pressure¹¹). 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.