Tetrahedron Letters No.46, pp. 4777-4781, 1968. Pergamon Press. Printed in Great Britain.

ORGANIC REACTIONS UNDER HIGH PRESSURE III

EFFECT OF PRESSURE ON THE COMPETITIVE NITRATION OF BENZENE AND MONO-SUBSTITUTED BENZENES

Tsutomu Asano, Akira Sera and Ryozo Goto
Department of Chemistry, Faculty of Science, Kyoto University,
Kyoto, Japan

(Received in Japan 23 July 1968; received in UK for publication 13 August 1968)

On the basis of the electrostriction theory (1), Ellis et al (2) predicted that for a reaction between an ion and a neutral molecule, pressure changes should have little effect on a reaction constant, ρ, of the Hammett equation. In such a reaction, they considered, $\Delta_2V^{\ddagger}$, which represents the volume change of the solvent during the activation process (3), should be small because the charge is the same for the reactant and the transition state. Therefore, $\Delta V^{\ddagger}$ should not change with substituents.

In a previous communication (4), however, the authors reported the effect of pressure on the competitive nitration of benzene and t-butylbenzene by nitric-sulfuric acid in acetic acid and suggested that the ρ value of nitration (a reaction between an ion and a neutral molecule) should change with pressure. In the present paper the authors will show that our prediction is correct, since a change of substituent changes $\Delta V^{\ddagger}$ appreciably.

Table 1 shows the effect of pressure on the rates of nitration of toluene.

TABLE 1

Effect of Pressure on the Competitive Nitration of Benzene and Toluene in Acetic Acid at 45°C

P (kg/cm^2)	k_{Me}/k_H a)	o- (%)	m- (%)	p- (%)	f_o^{Me}	f_m^{Me}	f_p^{Me} b)
1	27.2	55.9	2.7	41.4	45.6	2.2	67.6
1000	25.0	56.4	2.8	40.9	42.1	2.1	61.1
2000	23.1	56.4	2.9	40.7	39.1	2.0	56.4

a) k_X/k_H denotes the relative reactivity[*1] of C_6H_5X to C_6H_6 .

b) f_p^{Me} denotes the partial rate factor of para position to methyl group .

TABLE 2

Effect of Pressure on the Competitive Nitration of Benzene and Halobenzenes in Acetic acid at 45°C

Bromobenzene

P (kg/cm^2)	k_{Br}/k_H	o- (%)	m- (%)	p- (%)	f_o^{Br}	$f_m^{Br} x\ 10^3$	f_p^{Br}
1	0.0337	27.3	0.91	71.8	0.0277	0.92	0.145
1000	0.0354	27.8	1.03	71.2	0.0295	1.09	0.151
2000	0.0365	28.0	1.12	70.8	0.0306	1.23	0.155

Chlorobenzene

P (kg/cm^2)	k_{Cl}/k_H	o- (%)	m- (%)	p- (%)	f_o^{Cl}	$f_m^{Cl} x\ 10^3$	f_p^{Cl}
1	0.0400	23.1	0.669	76.2	0.0277	0.80	0.183
1000	0.0409	23.6	0.768	75.7	0.0290	0.94	0.186
2000	0.0409	23.6	0.844	75.6	0.0289	1.03	0.185

[*1] Relative reactivities were calculated by the following equation (5).

$$k_X/k_H = \frac{\log [C_6H_5X]_0 - \log [C_6H_5X]_t}{\log [C_6H_6]_0 - \log [C_6H_6]_t}$$

Although change in isomer ratio in this case is relatively small compared with in the case of t-butylbenzene, there is a consistent trend with increasing pressure, and the decrease in the relative reactivity is as large as in t-butylbenzene, i.e., the partial rate factor of para position clearly decreases with increasing pressre, although the reactivity of meta position is not seriously affected.

The effects of pressure on the reaction of bromobenzene and chlorobenzene are shown in Table 2. In these cases, changes in isomer ratios are in the same direction as in the alkylbenzenes (4), but the relative reactivities increase with increasing pressure. The increase in f_m is remarkable.

Values of log f were plotted against σ^+ to give a straight line, and values calculated by the method of least squares increased with increase in pressure. (ρ=-7.12 at 1kg/cm^2, r=0.995; ρ=-6.81 at 2000kg/cm^2, r=0.995)

If ρ is a function of pressure, then $\delta_\Delta V^{\ddagger}$*2 is a linear function of σ^+ at constant temperature and pressure. Thus, a plot of $\delta_\Delta V^{\ddagger}$ against σ^+ should reveal a linear relationship (6). Zero slope indicates that ρ remains constant at different pressure. The values of $\delta_\Delta V_1^{\ddagger}$*3 (of $\delta_\Delta \overline{V}_{1000}^{\ddagger}$*4 for meta position of alkylbenzene and para position of halobenzene) given in Table 3 are plotted in Fig. 1 against σ^+. Apparently it reveals a linearity between $\delta_\Delta V_1^{\ddagger}$ and σ^+.

TABLE 3

$\delta_\Delta V_1^{\ddagger}$ or $\delta_\Delta \overline{V}_{1000}^{\ddagger}$ Values of the Nitration in Acetic Acid at 45°C (ml/mole)

substituents	$\delta_\Delta V_1^{\ddagger}$ or $\delta_\Delta \overline{V}_{1000}^{\ddagger}$	substituents	$\delta_\Delta V_1^{\ddagger}$ or $\delta_\Delta \overline{V}_{1000}^{\ddagger}$
m-methyl*	1.2	m-chloro	-5.0
p-methyl	3.2	p-chloro*	-0.5
m-t-butyl*	1.9	m-bromo	-5.2
p-t-butyl	3.5	p-bromo*	-1.1

*; $\delta_\Delta \overline{V}_{1000}^{\ddagger}$

---

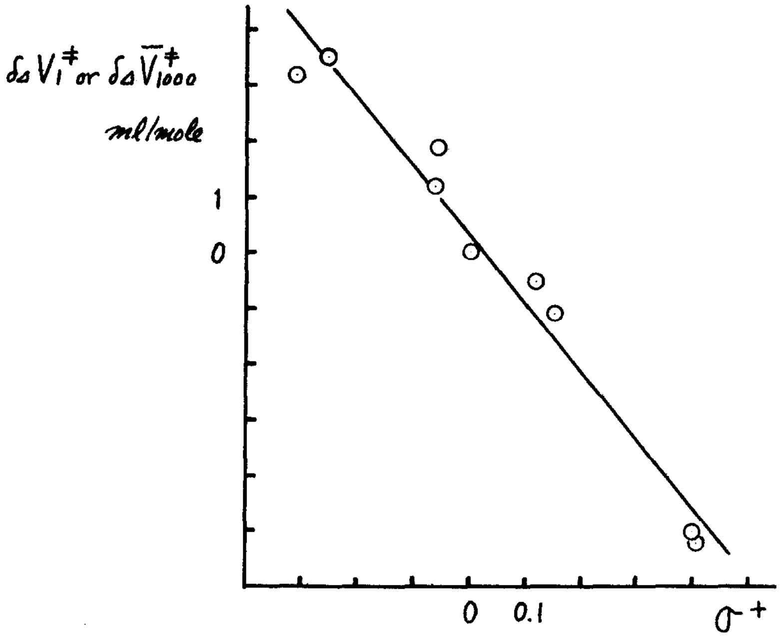
*2 $\delta_\Delta V^{\ddagger}=-RT\left(\frac{\partial \ln f}{\partial P}\right)_T$

*3 $\delta_\Delta V^{\ddagger}$ value at 1kg/cm^2 estimated graphically from log f -P curve

*4 $\delta_\Delta \overline{V}_{1000}^{\ddagger}=-RT\,(\ln f_{1000}-\ln f_1)\frac{1}{1000}$ Numerals indicate pressure.

FIG. 1

Plot of $\delta_{\Delta}V_1^{\ddagger}$ (or $\delta_{\Delta}\bar{V}_{1000}^{\ddagger}$) against σ^+



The results shown in Fig. 1 indicate that the extent of solvation in the transition states should change with substituents even for a reaction between an ion and a neutral molecule as well.

High pressure technique had been described previously (7). Reactions were carried out by adding a nitric-sulfuric acid solution to a solution of two substrates (benzene and a substituted benzene) and an internal standard at room temperature. The mixture was transferred to a reaction vessel (sealed tube or glass syringe) and maintained at 45°C at desired pressure. Reaction was stopped by adding water and products were extracted with methylene chloride and analyzed by gas chromatography.

The effect of pressure on the competitive nitration of benzene derivatives is being investigated and a detailed discussion of those data will be presented elsewhere in the terms of substituents effect.

REFERENCES

(1) S. D. Hamann, "Physico-Chemical Effects of Pressure", Butterworths Scientifi Publications, London, 1957, Chapters 8 and 9.

(2) A. J. Ellis, W. S. Fyfe, R. I. Rutherford, A. Fischer, and J. Vaughan, J. Chem. Phys., 31 176 (1959)

(3) S. D. Hamann, "High Pressure Physics and Chemistry" edited by R. S. Bradley, Academic Press, London, 1963, vol 2 chapter 8.

(4) T. Asano, R. Goto, and A. Sera, Bull. Chem. Soc. Japan, 40 2208 (1967)

(5) M. J. S. Dewar, T. Mole, and E. W. T. Warford, J. Chem. Soc., 3576 (1956)

(6) A. Fischer, B. R. Mann, and J. Vaughan, ibid., 1093 (1961)

(7) R. Goto, T. Asano, K. Matsumoto, and A. Sera, Rev. Phys. Chem. Japan, 37 16 (1967)