Organic Reactions under High Pressure. II. Effect of Pressure on the Competitive Nitration of Benzene and *t*-Butylbenzene

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Ellis *et al.*[1] considered the effect of pressure on the ρ value of Hammett equation and predicted that pressure changes have little effect on the value of ρ for a reaction between an ion and a neutral molecule on the basis of electrostriction theory by Hamann. However, no experimental evidence of this prediction was given in their report. Recently, Imoto *et al.*[2] reported the effect of pressure on the rate of saponification of ethyl benzoates in aqueous dioxane. The values of $\Delta V^{\neq}$ were equal within experimental error and they supported Ellis's prediction.

We examined competitive nitration of benzene and *t*-butylbenzene in acetic acid at 45°C under ordinary and high pressures. Reactions were carried out by adding a mixed (nitric-sulfuric) acid solution to a solution of two substrates and *p*-nitrotoluene as internal standard at room temperature. The mixture was transferred to a reaction vessel (sealed tube or glass syringe) and maintained at 45°C and desired pressure. Reaction was stopped by adding water after a few hours depending on pressure. Reaction products were extracted with methylene chloride and analysed by gas chromatography. The results are shown in Table 1 and Fig. 1.

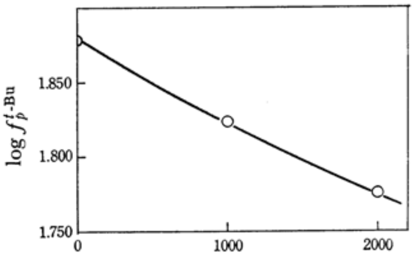

Fig. 1. $\log f_p^{t\text{-Bu}}$ - P plot for nitration in acetic acid at 45°C.

The partial rate factor*[1] of para position clearly decreases with increasing pressure. From Fig. 1, $\delta\Delta V^{\neq}=-\boldsymbol{R}T(\partial\ ln\ f_p^{t\text{-Bu}}/\partial P)_T$ is estimated at about 3.5 m*l*/mol at 1 atm. This result suggests that the ρ value of nitration should change with pressure. On the other hand, the partial rate factors of ortho and meta position are not seriously affected by pressure. ortho : para ratio increases under high pressures as expected but it is due to the decreasing reactivity of para position and not due to the increasing reactivity of ortho position.

Nitrations of other monosubstituted benzenes are now being investigated.

TABLE 1. EFFECT OF PRESSURE ON THE COMPETITIVE NITRATION OF BENZENE AND *t*-BUTYLBENZENE IN ACETIC ACID AT 45°C

P, kg/cm^2	$k_{t\text{-Bu}}/k_H$[a)]	*o*- (%)	*m*- (%)	*p*- (%)	$f_o^{t\text{-Bu}}$	$f_m^{t\text{-Bu}}$	$f_p^{t\text{-Bu}}$
1	15.2	9.7	7.4	82.9	4.4	3.4	75.6
1000	13.6	10.4	7.7	81.8	4.2	3.1	66.7
2000	12.3	11.0	8.1	80.9	4.1	3.0	59.7

a) Relative reactivity of *t*-butylbenzene to benzene.

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

2) T. Imoto, Y. Ogo and H. Oka, presented at 8th High Pressure Symposium, Kobe, Oct., 1966; Abstracts, p. 104.

*1 The rate of substitution at a selected position in the substituted benzene relative to a single position in benzene itself.