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Influence of Hydrostatic Pressure on Orientation in Electrophilic Aromatic Substitutions

M. G. GONIKBERG *et al.*[1–3] have recently found that at high pressures the attack of phenyl radicals on tertiary butyl benzene yields an appreciably higher proportion of the sterically strained 2-phenyl isomer than it does at atmospheric pressure.

We have observed a similar effect in the electrophilic nitration of 1,3-xylene by nitronium ions, NO_2^+. The nitrations were carried out under the same conditions and by the same methods that we had previously used in reaction rate measurements[4]. The initial composition of the reaction mixtures, expressed in mole fractions, was: nitric acid, 0·618; acetic acid, 0·369; 1,3-xylene, 0·013. We analysed the products by gas chromatography at several stages during the course of each reaction and found that the isomer ratios were independent of the extent of reaction. Table 1 lists the results.

It will be seen that between 1 and 2,000 atmospheres the proportion of substitution at the sterically hindered 2-position increased by 60 per cent. The change is larger than that observed by Gonikberg[1–3] presumably because in 1,3-xylene there are two adjacent groups tending to obstruct attack on the 2-position. Our result supports Gonikberg's general thesis that an increase in pressure tends to favour the formation of sterically compressed isomers.

However, some other experiments have shown that the steric factor is not the only important one in nitrations. Under the same experimental conditions that applied in the nitration of 1,3-xylene, we found that toluene and chlorobenzene yielded decreasing proportions of the 2-nitro isomers as the pressure was increased. The results are given in Table 2.

Although the shift of isomer ratio in these cases was relatively small, there was a consistent trend with increasing pressure and its direction was the same whether the groups already present on the benzene ring had electron

Table 1. MOLE FRACTIONS OF ISOMERS FORMED IN THE NITRATION OF 1,3-XYLENE BY NITRIC ACID IN ACETIC ACID SOLUTION AT 0° C

	Nitro isomer:		
Pressure (atm.)	2-	4-	5-
1	0·107	0·880	0·013
800	0·150	0·833	0·017
1,200	0·164	0·816	0·020
2,000	0·171	0·829	

Table 2. MOLE FRACTIONS OF ISOMERS FORMED IN THE NITRATION OF TOLUENE AND CHLOROBENZENE BY NITRIC ACID IN ACETIC ACID SOLUTION AT 0° C

Pressure (atm.)	Toluene			Chlorobenzene		
	Nitro isomer:			Nitro isomer:		
	2-	3-	4-	2-	3-	4-
1	0·560	0·020	0·420	0·247	—	0·753
1,200	0·550	0·022	0·428			
2,000	0·543	0·024	0·433	0·204	—	0·796

donating (activating) or electron accepting (de-activating) properties.

Experiments at atmospheric pressure[5] have established that a change of solvent alters the ratios of isomers formed in the nitration of alkyl benzenes by nitronium salts. The effect almost certainly arises from changes of dielectric constant and solvation. Presumably similar factors operate when the dielectric properties of the nitrating solution are altered by an applied pressure, and they are supplementary to the simple steric effect. Moreover, it is possible that compression may alter the distribution of electrical charge around the benzene rings. We hope to distinguish these factors more clearly in future work.

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[1] Gonikberg, M. G., Prokhorova, N. I., and Litvin, E., *Izv. Akad. Nauk. S.S.S.R.* (Otd. Khim. Nauk.), No. 8, 1495 (1962).

[2] Gonikberg, M. G., Prokhorova, N. I., and Litvin, E., *Doklady Akad. Nauk. S.S.S.R.*, **148**, 105 (1963).

[3] Gonikberg, M. G., *Zhur. Fiz. Khim.*, **37**, 477 (1963).

[4] Coillet, D. W., and Hamann, S. D., *Trans. Farad. Soc.*, **57**, 2231 (1961).

[5] Olah, G. A., and Kuhn, S. J., *J. Amer. Chem. Soc.*, **84**, 3684 (1962).

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