

The Partial Rate Factor for Nitration *ipso* to a Methyl Group

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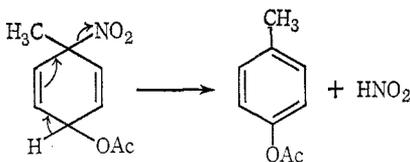
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Abstract

The partial rate factor for nitration *ipso* to a methyl group is *c.* three times that for substitution at the *meta* position.

Electrophilic aromatic substitution of groups other than hydrogen is now recognized to be a normal reaction of many aromatic derivatives. However, little data are yet available relating to substituent effects on the rate of electrophilic attack at the substituted (*ipso*) position, although there is much current interest in this topic.¹⁻⁴ The *ipso* factors for the methyl group are difficult to measure directly, since the methyl group is rarely displaced in aromatic substitution. We have been able to derive the partial rate factor for nitration *ipso* to a methyl group from results of previous studies^{5,6} of nitration reactions of methylbenzenes. In reactions carried out in acetic anhydride, aryl acetates were obtained as well as the expected nitro substitution products.^{5,6} We have subsequently shown that the acetates are formed from the 1,4 acetyl nitrate adducts.⁷ The adducts themselves are formed by attack of nitronium



ion (or incipient nitronium ion) at a position *ipso* to a methyl group followed by addition of acetate to the phenonium ion so obtained. In the case of those adducts which contain a secondary acetate, as in the example shown above, elimination of nitrous acid to form the aryl acetate occurs cleanly on heating. The yields of these aryl acetates thus provide a measure of the extent of *ipso* nitration at the methyl group

¹ Baciocchi, E., and Illuminati, G., *J. Am. chem. Soc.*, 1967, **89**, 4017.

² Perrin, C. L., and Skinner, G. A., *J. Am. chem. Soc.*, 1971, **93**, 3389.

³ Berwin, H. J., *Chem. Commun.*, 1971, 237.

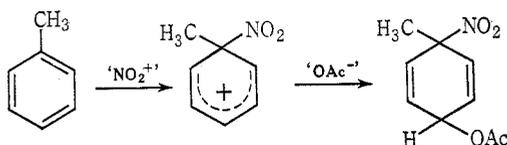
⁴ Fischer, P. B., and Zollinger, H., *Helv. chim. Acta*, 1972, **55**, 2139.

⁵ Fischer, A., Packer, J., Vaughan, J., and Wright, G. J., *Proc. chem. Soc.*, 1961, 369.

⁶ Fischer, A., Vaughan, J., and Wright, G. J., *J. chem. Soc. (B)*, 1967, 368.

⁷ Blackstock, D. J., Fischer, A., Richards, K. E., Vaughan, J., and Wright, G. J., *Chem. Commun.*, 1970, 641; Blackstock, D. J., Cretney, J., Fischer, A., Hartshorn, M. P., Richards, K. E., Vaughan, J., and Wright, G. J., *Tetrahedron Lett.*, 1970, 2793.

para to the acetate. In this communication we report the partial rate factor for nitration *ipso* to a methyl group calculated in this way and its application in the prediction of the relative yields of products obtained in nitration of polymethylbenzenes.^{6,8}



Nitration of toluene in acetic anhydride gave⁶ 58.2 mole % *o*-nitrotoluene, 2.8 mole % *m*-nitrotoluene, 35.9 mole % *p*-nitrotoluene and 3.1 mole % *p*-tolyl acetate.* The ratio of the nitro substitution products is in excellent agreement with other literature values for acetic anhydride solution^{10,11} and is in fact close to the mean of these. The ratio is also in good agreement with values determined in other solvents.^{6,10} The ratio of partial rate factors is given by the product ratio as $2o_f : 2m_f : p_f : i_f$ 58.2 : 2.8 : 35.9 : 3.1, from which we obtain $o_f : m_f : p_f : i_f$ 20.8 : 1.0 : 25.6 : 2.2. In order to obtain the absolute values of the partial rate factors the rate for toluene relative to benzene is required. The accepted value¹² for acetic anhydride solution is *c.* 25, but more recent and more precisely determined values¹¹ are 50 (kinetics) and 38 (competition) with a mean of 44. The first (25) value, which is appropriate to nitration in other solvents, if not to acetic anhydride, leads to the factors o_f 44, m_f 2.1, p_f 54 and i_f 4.7 whereas the higher (44) value gives o_f 77, m_f 3.7, p_f 95, i_f 8.2. Regardless of which set of values is taken a methyl group activates the *ipso* position and is twice as activating there as at the *meta* position.

The ratio of partial rate factors given above (or, with slightly lesser convenience, the partial rate factors themselves) may be used to calculate the product distribution expected on nitration of the polymethylbenzenes, assuming additivity of substituent effects, i.e., a product rule¹³ of partial rate factors for the effect of two (or more) substituents on the relative rate of substitution at a particular position in a di(poly)-substituted benzene. Thus, the 1 position of *o*-xylene is *ipso* to one methyl and *ortho* to another and its relative rate of attack is $2i_f o_f$; for the 3 position the relative rate is $2o_f m_f$; and for the 4 position $2m_f p_f$ (the factor of 2 in each case allows for the two identical such sites in the substrate). The predicted product ratio is $i_f o_f : o_f m_f : m_f p_f$ 50 : 23 : 28 (%). The product distribution observed, i.e., the ratio of 3,4-dimethylphenylacetate : 3-nitro-*o*-xylene : 4-nitro-*o*-xylene from g.l.c. is 59 : 14 : 28 (%).

* Integration of the diene and aromatic regions of the n.m.r. spectrum of the crude product mixture indicated that diene adduct was present to the extent of 3–4%, in agreement with the g.l.c. analysis for the acetate obtained on decomposition.⁹

⁸ Blackstock, D. J., Fischer, A., Richards, K. E., and Wright, G. J., *Aust. J. Chem.*, 1973, **26**, 775.

⁹ Fischer, A., and Ramsay, J. N., *J. chem. Soc. Perkin II*, 1973, 237.

¹⁰ Hoggett, J. G., Moodie, R. B., Penton, J. R., and Schofield, K., 'Nitration and Aromatic Reactivity' pp. 64, 83 (Cambridge University Press: London 1971).

¹¹ Harshorn, S. R., Moodie, R. B., and Schofield, K., *J. chem. Soc. (B)*, 1971, 1256.

¹² Ridd, J. H., 'Studies on Chemical Structure and Reactivity' (Ed. J. H. Ridd) p. 136 (Methuen: London 1966).

¹³ Holleman, A. F., *Chem. Rev.*, 1924, **1**, 187.

Predicted and observed product distributions for all of the polymethylbenzenes are given in Table 1. In the cases of *p*-xylene, pseudocumene, the tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene, at least one adduct has a tertiary acetate function and elimination to aryl acetate cannot occur without rearrangement. In this circumstance other rearomatization reactions intervene⁹ and thus g.l.c. studies of the nitration product mixtures do not provide a simple measure of the amount of adduct formed. However, integration of the n.m.r. spectrum, with appropriate allowance for any decomposition of the adducts which has occurred, does give an estimate of the rate of adduct : nitro substitution products, i.e. of *ipso* : non-*ipso* attack. 'Best values' of

Table 1. Product distributions (%) for nitration of methylbenzenes in nitric acid-acetic anhydride

Hydro-carbon	Predicted subst. or addition at						Observed subst. or addition at					
	1	2	3	4	5	6	1	2	3	4	5	6
<i>o</i> -Xylene	50		23		28		59 ^A		14		28	
<i>m</i> -Xylene	0.3	29		71	0.1		0.7 ^A	15		85	0	
<i>p</i> -Xylene	58	42					75 ^B	25				
Hemimellitene	4	45		50	1		11 ^A	35		46	8	
Pseudocumene	52	2	19	2	24	1						
Mesitylene	0.0	100					0 ^A	100				
Prehnitene	44	36			20							
Isodurene	0.2	52		48	0.1							
Durene	84		16				> 75 ^B		< 25			
Pentamethylbenzene	4	77	2			18						

^A G.l.c. analysis.

^B N.m.r. analysis.

^C (1+2+4) : (3+5+6) 60 : 40 by n.m.r.

^D (1+2) : 5 80 : 20 by n.m.r.

the partial rate factor ratio were obtained by treating the partial rate factors as parameters and varying them to minimize the sum of the deviations between calculated and observed values of the product distributions for toluene, *o*-xylene, *m*-xylene, hemimellitene and mesitylene. The ratio of partial rate factors obtained in this way is $o_f : m_f : p_f : i_f$ 15.5 : 1.1 : 25.6 : 3.4. Compared to the values derived from toluene alone these values indicated a lower *ortho* activating effect, probably a consequence of steric hindrance in the polysubstituted benzenes, and an increased *ipso* activating effect.

The *ipso* factors for methyl (0.29) and *t*-butyl (0.25) groups have been obtained by Baciocchi and Illuminati from bromination of 4-substituted 2,6-di-*t*-butylphenols in 98% acetic acid.¹ Our value indicates that the methyl group activates the *ipso* position, as would be expected for an electron-donating group. It is possible that steric effects, which would make attack at a position *ipso* to an acetyl group slower than one *ipso* to hydrogen, are more important in the bromination reaction studied by Baciocchi and Illuminati. However, whatever the reason for the difference, our value is consistent with data from the nitration reactions of all of the polymethylbenzenes.