597. *Homolytic Aromatic Substitution. Part XXV.* The Determination of the Total and Partial Rate Factors for the Phenylation of Naphthalene.*

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Benzoyl peroxide is shown to be unsuitable for the determination of the rate ratio in a competitive reaction with nitrobenzene and naphthalene. The rate of phenylation of naphthalene relative to that of nitrobenzene has been determined with phenyl radicals derived from *N*-nitrosoacetanilide. A value for ${}^{\mathrm{C_{10}H_8}}_{\mathrm{C_6H_6}}K$ has been derived, as also have the partial rate factors for phenylation at the 1- and the 2-position. The values thus obtained are discussed and compared with those derived from earlier work and from theoretical calculations.

The first attempt to determine the relative rate of the phenylation of naphthalene ${}^{\mathrm{C_{10}H_8}}_{\mathrm{C_6H_6}}K$ was reported by Huisgen and Sorge,[1] who used a competitive reaction in which the solvent was a mixture of benzene and naphthalene with *N*-nitrosoacetanilide as the source of the phenyl radical. They reported values ranging from 31 to 17·7 but, on account of the difficulty in eliminating or estimating losses of biphenyl during the removal of the excess of benzene and naphthalene these values are probably high. Hey and Williams subsequently reported [2] a value of 23·9, which was based on work carried out by Augood,[3] who used a competitive reaction between naphthalene and nitrobenzene with benzoyl peroxide as the source of the phenyl radical. This result cannot now be accepted because it has since been established [4] that the reaction between benzoyl peroxide and naphthalene is complicated by the formation of binaphthyls and appreciable quantities of esters. It was also reported [3] that aniline was isolated after hydrolysis of the product from the naphthalene–nitrobenzene reaction. A redetermination of ${}^{\mathrm{C_{10}H_8}}_{\mathrm{C_6H_6}}K$ was reported by Huisgen and Grashey [5] who used a competitive reaction with naphthalene and pyridine, *N*-nitrosoacetanilide again being used as the source of the phenyl radical. The values reported ranged from 13 to 8·3. More recently, Huisgen, Jakob, and Grashey [6] have reported competitive reactions with benzene and naphthalene, using phenylazotriphenylmethane, *N*-nitrosoacetanilide, and benzoyl peroxide as radical sources. In these determinations a more refined analytical technique was used which involved the use of isotopically labelled carbon. With phenylazotriphenylmethane and with *N*-nitrosoacetanilide values ranging from 13·5 to 14·7 were obtained, whereas with benzoyl peroxide the values were 10·5 and 11·5. The values 10·5 and 11·5 must again be distrusted because the reaction with benzoyl peroxide and naphthalene leads also to binaphthyls.

Experiments are now reported on competitive reactions with mixtures of naphthalene and nitrobenzene, in which *N*-nitrosoacetanilide was the source of the phenyl radical. These reactions gave a value of 9·9 for ${}^{\mathrm{C_{10}H_8}}_{\mathrm{C_6H_6}}K$. The formation of aniline in the hydrolysis products obtained in this reaction is also confirmed and discussed. These results have been reported briefly elsewhere.[7]

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* Part XXIV, preceding paper.

[1] Huisgen and Sorge, *Annalen*, 1950, **566**, 162.
[2] Hey and Williams, *Discuss. Faraday Soc.*, 1952, **14**, 216.
[3] Augood, Ph.D. Thesis, University of London, 1952.
[4] Davies, Hey, and Williams, *J.*, 1958, 1878.
[5] Huisgen and Grashey, *Annalen*, 1957, **607**, 46.
[6] Huisgen, Jakob, and Grashey, *Ber.*, 1959, **92**, 2206.
[7] Hey, Kekulé Symp., " Theoretical Organic Chemistry," Butterworths Scientific Publ., London, 1959, 250.

EXPERIMENTAL

Reagents.—Benzoyl peroxide and nitrobenzene were purified as described in Part II [8] and naphthalene as described in Part XIII.[4] *N*-Nitrosoacetanilide was prepared by France, Heilbron, and Hey's method.[9]

Decomposition of Benzoyl Peroxide in a Mixture of Nitrobenzene and Naphthalene—Benzoyl peroxide (6 g.) was allowed to decompose in an equimolar mixture of nitrobenzene (97·9 g.) and naphthalene (102·1 g.) kept at 80° in a thermostat for 72 hr. The reaction was carried out in duplicate (Expts. 1 and 2). The resulting dark solutions, which partially solidified on standing, were worked up as in the benzoyl peroxide–naphthalene reactions described in Part XIII [4] except that benzene–light petroleum (b. p. 60—80°) (1 : 1) was used as eluent in the chromatographic stage in place of benzene. In addition, the benzene solution containing the biaryls, obtained after the hydrolysis of the esters, was repeatedly shaken with concentrated hydrochloric acid, which gave a deep purple extract. Neutralisation of this extract with aqueous sodium hydroxide gave an orange-coloured cloudy solution which was extracted with methylene chloride (3 × 40 ml.) and then with ether (40 ml.). The combined dark red extracts were dried (Na_2SO_4) and removal of the solvents by distillation at atmospheric pressure left a residue from which aniline distilled at 80°/20 mm. Its identity was established by infrared spectroscopy and preparation of its benzoyl derivative (m. p. and mixed m. p. 163°). The non-volatile red residue probably contained azobenzene. The main products isolated from these reactions are shown in Table 1.

TABLE 1. *Products from the decomposition of benzoyl peroxide in nitrobenzene–naphthalene.*

Expt. No.	1	2
Free benzoic acid (g.)	3·35	3·38
Benzoic acid from hydrolysis of esters and benzanilide (g.)	2·26	2·22
Biaryl fraction, b. p. 108—140°/0·1 mm. (g.)	1·14	1·17
Biaryl fraction, b. p. 150—180°/0·1 mm. (g.)	0·61	0·57
Residue after distillation of biaryls (g.)	0·08	0·06
Aniline (after hydrolysis) (g.)	0·49	0·52
Residue after distillation of aniline (g.)	0·15	0·21
Peroxide accounted for, calculated on the weights of free and ester acid (%)	92·7	92·6

The biaryl fraction, b. p. 108—140°/0·1 mm., contained 4·15% of nitrogen. If this fraction contains only nitrobiphenyls and phenylnaphthalenes its composition must be 59% of the former and 41% of the latter, but this would account for more than 100% of the peroxide. The fraction is most likely to contain, in addition, nitrophenylnaphthalenes because naphthyl radicals, generated by abstraction of hydrogen from naphthalene by benzoyloxy-radicals, can attack nitrobenzene (as well as naphthalene). Attempts to isolate single compounds from this fraction were unsuccessful. The second biaryl fraction (b. p. 150—180°/0·1 mm.) was dissolved in hot light petroleum (b. p. 80—100°) (20 ml.); when the solution was cold, 2,2′-binaphthyl (0·029 g.) separated in plates, m. p. and mixed m. p. 183—184°. Concentration of the mother-liquor gave crystals, m. p. 130—135°, the infrared spectrum of which was consistent with that required for a mixture of 1,1′- and 1,2′-binaphthyl.

In a third experiment it was found that after removal of the free acid from the benzene solution of the product by extraction with saturated aqueous sodium hydrogen carbonate, subsequent extraction with concentrated hydrochloric acid gave no aniline, which is therefore not a final product of the reaction.

Determination of ${}^{C_{10}H_8}_{PhNO_2}K$.—*N*-Nitrosoacetanilide (5 g.) was added slowly during 1 hr. to a mixture of nitrobenzene (158·7 g.) and naphthalene (41·3 g.) (molar ratio 4 : 1) in a thermostat at 20°. The reaction was carried out in quadruplicate (Expts. 3—6). Nitrogen was steadily evolved and the colour of the solutions changed from yellow to red and finally to dark red. After 3 days the acetic acid and excess of nitrobenzene and naphthalene were removed by distillation at 20 mm. with a helix-packed column. The residue (*ca.* 25 ml.) was boiled under reflux for 4 hr. with a 1 : 1 mixture (100 ml.) of ethanol and concentrated hydrochloric acid.

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[8] Augood, Hey, and Williams, *J.*, 1952, 2094.

[9] France, Heilbron, and Hey, *J.*, 1940, 369.

The ethanol was then distilled off and the mixture was extracted with benzene (4 × 40 ml.). The benzene solution was successively washed with (*a*) concentrated hydrochloric acid (10 × 50 ml.), (*b*) 2N-aqueous sodium hydroxide (3 × 50 ml.), and (*c*) water (2 × 50 ml.). After the resulting solution had been dried ($CaCl_2$), most of the benzene was removed from it by distillation, and the residue (*ca.* 30 ml.) was subjected to chromatography on alumina (35 × 1·5 cm.). Elution was effected with a 1 : 1 mixture (500 ml.) of benzene and light petroleum (b. p. 60—80°). The pale orange-yellow eluate gave, on distillation, the biaryl fraction which was collected at 0·1 mm. The weights of the biaryls and non-volatile residues are shown in Table 2.

The biaryl fractions were estimated for nitro-group content by reduction with titanous sulphate by the method described in Part XVIII.[10] In the distillation of the biaryls a small forerun was rejected in order to ensure that the fraction submitted for analysis contains no nitrobenzene or naphthalene. The analytical results are also included in Table 2.

TABLE 2. *Weights of biaryls and residues obtained in the reaction of* N-*nitrosoacetanilide with nitrobenzene–naphthalene.*

Expt. No.	3	4	5	6
Biaryls (g.)	2·85	3·03	3·13	2·97
Residue (g.)	0·73	0·70	0·66	0·62
Nitrobiphenyls in biaryl fraction (%)	53·4	53·2	54·5	53·8
N-Nitrosoacetanilide accounted for in the biaryl fraction (%)	46·45	49·35	51·0	48·4

The mean nitrobiphenyl content of the biaryl fraction is thus 53·7% and hence, after allowance for the fact that a 4 : 1 molar mixture of nitrobenzene and naphthalene was used, ${}^{C_{10}H_8}_{Ph\cdot NO_2}K = 3{\cdot}36$.

DISCUSSION

It is clear that benzoyl peroxide is unsuitable for use in competitive phenylation experiments with mixtures of nitrobenzene and naphthalene, because whereas with naphthalene the predominant reaction is with the benzoyloxy-radical by substitution and hydrogen abstraction, the main reaction with nitrobenzene is with the phenyl radical by substitution. In addition it can be shown that in a competitive reaction with benzoyl peroxide more than 100% of the peroxide can be accounted for on the basis of the quantities of the free acid, the acid formed after hydrolysis and the biaryl fraction formed if this fraction is considered to consist solely of nitrobiphenyls and phenylnaphthalenes. It is likely that this anomaly is due, at least in part, to the formation of nitrophenylnaphthalenes resulting from the attack on nitrobenzene by naphthyl radicals produced by hydrogen-abstraction from naphthalene.

The identification of aniline after the hydrolysis stage in the working up of the product of the reaction of benzoyl peroxide with a mixture of nitrobenzene and naphthalene provides evidence of the fate of some of the hydrogen which is removed from the intermediate resulting from the attack on naphthalene by a free radical. The high reactivity of naphthalene towards free radicals results in an insufficiency of radicals (or benzoyl peroxide molecules) to dehydrogenate all the intermediate complexes and it is suggested that some of these are oxidised by nitrobenzene to give aniline which undergoes rapid reaction with benzoyl peroxide to give benzanilide. Nozaki and Bartlett[11] have drawn attention to the reactivity of aniline towards benzoyl peroxide, and other workers[12,13] have shown that benzanilide is in fact a major product of the reaction of benzoyl peroxide with aniline. These observations are in agreement with the fact that aniline is found only after the reaction product has been subjected to alkaline hydrolysis.

Partial Rate Factor for the Phenylation of Naphthalene.—The relative rate of the phenylation of naphthalene ${}^{C_{10}H_8}_{C_6H_6}K$ may be calculated from ${}^{C_{10}H_8}_{Ph\cdot NO_2}K$ and ${}^{Ph\cdot NO_2}_{C_6H_6}K$, the value for

[10] Hey, Moulden, and Williams, *J.*, 1960, 3769.

[11] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

[12] De Paolini, *Gazzetta*, 1930, **60**, 589.

[13] Horner and Schwenk, *Annalen*, 1950, **566**, 69.

which has been reported in Part XXIII[14] to be 2·94. Thus ${}^{C_{10}H_8}_{C_6H_6}K = {}^{C_{10}H_8}_{Ph\cdot NO_2}K \times {}^{Ph\cdot NO_2}_{C_6H_6}K = 3{\cdot}36 \times 2{\cdot}94 = 9{\cdot}9$. The value, ${}^{Ph\cdot NO_2}_{C_6H_6}K = 2{\cdot}94$, refers to a temperature of 80° but the variation with temperature is not considered to be serious. Huisgen and Grashey[5] have recorded a figure of 3·1 for ${}^{Ph\cdot NO_2}_{C_6H_6}K$ for a competitive phenylation reaction carried out at 25°. If F_1 and F_2 represent the partial rate factors for the phenylation of naphthalene at positions 1 and 2 respectively, then:

$$6\,{}^{C_{10}H_8}_{C_6H_6}K = 4F_1 + 4F_2$$

By using the isomer ratio 79·1 : 20·9 for the phenylation of naphthalene in positions 1 and 2 with *N*-nitrosoacetanilide at 25°, due to Huisgen and Grashey,[5] the following values are obtained for the partial rate factors: $F_1 = 11{\cdot}7$; $F_2 = 3{\cdot}1$. These results are considerably lower than those reported by Augood,[3] and Hey and Williams[2] for the benzoyl peroxide reaction now distrusted, but they are in reasonable agreement with the more recent results reported by Huisgen, Jakob, and Grashey[6] who used an entirely different experimental technique.

Some values derived from theoretical calculations for the total and partial rate factors for the phenylation of naphthalene are given in Table 3. The calculations based on free valence numbers agree well with experiment but those based on atom localisation energies are far too large. Williams[15] has suggested that this gross overestimate may be due to the inappropriate use of the carbon–carbon resonance integral (β) in the calculation of the localisation energies. For instance, Dewar, Mole, and Warford[16] have shown that, for substitution of polycyclic hydrocarbons with reagents of high intrinsic reactivity, such as methyl radicals, agreement between experimentally determined and calculated relative rates of reactions is obtained only when parameters β'_x which have much lower numerical values than β, are used in the calculations. This arises from the circumstance that the σ-complexes which were originally considered by Wheland[17] to approximate closely to the transition states for reaction at the various sites are, in fact, true intermediates representing minima in the potential energy curves, and that the actual transition states are closer to the parent aromatic system than to the Wheland structures. The hybridisation of the carbon atom *r* at which substitution occurs is therefore intermediate between sp^2 and sp^3, and not sp^3 as in the Wheland structure. Some allowance must, therefore, be made for the incomplete removal of carbon atom *r* from the system over which delocalisation occurs, and β should be replaced, for substitution by the reagent X, by β'_x, which is given by $\beta'_x = \beta - \beta_x$, where β_x is the value of the resonance integral between atom *r* and the adjacent carbon atoms in the transition state for substitution by X. Since the intrinsic reactivity of the phenyl radical is probably comparable with that of the methyl radical, these considerations probably also apply to phenylation, and if this is so the discrepancy between the experimental and calculated reactivities is readily understood.

TABLE 3. *Calculated total and partial rate factors for the phenylation of naphthalene.*[a]

Method	F_1	F_2	${}^{C_{10}H_8}_{C_6H_6}K$
Free valence numbers	11·29	1·10	8·26
,, ,, ...	13·71	1·34	10·03
Atom localisation energies	$87{\cdot}79 \times 10^3$	19·71	$4{\cdot}39 \times 10^4$

[a] See Augood and Williams, *Chem. Rev.*, 1957, **57**, 123.

The partial and total rate factors for the phenylation of naphthalene are the largest yet reported for an aromatic compound, but the increased reactivity of naphthalene relative to benzene is very much smaller for phenylation than for nitration. The partial rate factors for the nitration of naphthalene are $F_1 = 470$ and $F_2 = 50$,[16] which indicates

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[14] Hey, Orman, and Williams, *J.*, 1961, 565.

[15] Williams, " Homolytic Aromatic Substitution," Pergamon Press Ltd., London, 1960, p. 22.

[16] Dewar, Mole, and Warford, *J.*. 1956, 3581.

[17] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

that the phenyl radical is much less sensitive than the nitronium ion towards increased electron availability at the site of substitution. The decreased importance of electronic effects in radical substitution is also emphasised by the fact that $F_1/F_2 = 9{\cdot}4$ for nitration but only 3·8 for phenylation. Smid and Szwarc [18] recently determined the relative methyl, ethyl, and propyl affinities of naphthalene relative to benzene and found them to be 30, 34·5, and 34·2 respectively.

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[18] Smid and Szwarc, *J. Amer. Chem. Soc.*, 1957, **79**, 1534.