

THE NITRATION OF BIPHENYL BY THE NITRONIUM ION

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We have previously reported¹ a high ortho:para ratio of ca. 3.5 for the nitration of biphenyl by nitric acid in aqueous sulphuric acid at 25^o and have attributed this ratio to nitration by the nitronium ion. This ratio is at variance with some theoretical considerations² and with the concept of a special mechanism of ortho-substitution in acetonitrile and acetic anhydride.^{3,4} We suggested that in earlier work where low ortho:para ratios (v 0.6) were observed,^{3,4} the most consistent of which involved nitration by mixtures containing nitric and sulphuric acids, nitration via nitrosation was a possibility.

Taylor was able to show⁵ that this latter was indeed so and was responsible for some earlier low values. However, even when nitrosation was apparently excluded, the ortho:para ratio only became 1.4. One should note that the reaction medium in these experiments was heterogeneous and consisted of two phases one containing mainly nitric acid in about 68% aqueous sulphuric and the other containing mainly biphenyl in nitrobenzene.

Taylor also attempted to repeat our experiments and confirmed the high ortho:para ratio. However, there was doubt that these results related to homogeneous nitration, as he was unable to dissolve the appropriate amount of biphenyl to form a 4×10^{-5} mole dm^{-3} solution even after stirring for 24 h.⁺ This was the only evidence presented to support his conclusion that the high ortho:para ratio did not reflect normal nitration by the nitronium ion. We can see no reason why our results might be 'vitiating by problems of encounter control', even

⁺ In fact as reported below our solutions were ca 2×10^{-5} mole dm^{-3} and not ca 4×10^{-5} mole dm^{-3} as we had estimated.¹ We show below that the latter is at the limit of solubility in 68% H_2SO_4 .

if the rate of reaction were encounter controlled (see below). Another factor is the possibility that ipso attack on the molecule and subsequent rearrangement to the ortho position⁶ might result in a high ortho:para ratio.

In our original experiments¹ the substrate solution was prepared by shaking ca 0.3 g biphenyl with ca 30 cm³ sulphuric acid for ca 1 h and then filtering to yield a solution which was ca 2×10^{-5} mole dm⁻³.^{*} In the present experiments the biphenyl was added as a 3.3×10^{-2} mole dm⁻³ solution in acetic acid to 25 cm³ of 68% sulphuric acid and the solution was shaken for 5 min. A Beer's law plot was constructed of the absorbance at 250 nm ($\epsilon = 1.1 \times 10^4$ dm³ mole⁻¹ cm⁻¹) by adding different amounts of the substrate solution in acetic acid. This plot was linear up to 4.0×10^{-5} mole dm⁻³ and in the region $4-5 \times 10^{-5}$ mole dm⁻³ the substrate began to fail to dissolve. In the region $> 5 \times 10^{-5}$ mole dm³ the solution became misty as

TABLE 1

Second-order rate coefficients for nitration of biphenyl at $25.0 \pm 0.2^\circ$

H ₂ SO ₄ (%) ^a	[HNO ₃] /10 ⁻² mole dm ⁻³	k ₂ (obs) /dm ³ mole ⁻¹ s ⁻¹	log ₁₀ k ₂ (obs) log ₁₀ k ₂ (obs) (Benzene) ^b	log ₁₀ k ₂ (obs) (Mesitylene) ^{b,c} -log ₁₀ k ₂ (obs)
56.0 ^{d,e}	5.5	3.1×10^{-3}	-	-
60.3 ^b	5.5	2.2×10^{-3}	-	0.88
61.0 ^e	5.5	4.1×10^{-3}	-	0.77
62.5 ^f	5.5	7.4×10^{-3}	0.97	0.88
63.1 ^b	5.5	1.4×10^{-2}	1.08	0.75
63.7 ^e	5.5	2.0×10^{-2}	1.04	0.76
65.7 ^e	2,0.3	9.4×10^{-2}	1.10	0.64
65.9 ^f	5.5	0.114	1.13	0.60
68.3 ^b	0.2	0.93)		
68.3 ^c	0.09	0.92)	1.20	0.39
68.7 ^e	0.17	1.18	1.18	0.41
70.6 ^f	0.09	5.7	1.16	0.29
70.8 ^e	0.09	5.6	1.07	0.37
72.6 ^e	0.05	24	1.01	0.28
HClO ₄ (%) ^a				
60.0 ^e	0.09	0.45	1.17	-
62.2 ^e	0.09	3.9	1.09	-

a) [Urea] ca. 3×10^{-2} mole dm⁻³. Measurements at 250 nm; an isosbestic point for dinitration.

b) Ref. 1.

c) Ref.7.

d) at 60^o.

e) [Biphenyl] = 1.9×10^{-5} mole dm⁻³. f) [Biphenyl] = 3.3×10^{-5} mole dm⁻³.

* The value of ϵ reported below leads to this revised estimate of the concentration of biphenyl.

observed by absorbance readings at 350 nm. Kinetic measurements were therefore carried out at substrate concentrations of 1.9×10^{-5} mole dm^{-3} and 3.3×10^{-5} mole dm^{-3} and product determinations at 3.3×10^{-5} mole dm^{-3} .

Rate coefficients measured by the usual technique⁷ are given in Table 1 together with some values for nitration in aqueous perchloric acid. The rate profile constructed from these data is much more closely parallel to that for benzene ($k_2(\text{obs})\text{Biphenyl}/k_2(\text{obs})\text{Benzene} = 12$) than to that for mesitylene where the ratio $k_2(\text{obs})\text{Mesitylene}/k_2(\text{obs})\text{Biphenyl}$ varies from 8 to 2 over the range 60-73% sulphuric acid. This parallelism, the fact that the relative rate of nitration of biphenyl : benzene by nitric acid in aqueous perchloric acid is 14, and that the ratio for nitration by nitric acid in sulpholan⁸ is 16 suggest that the rate of reaction is not much affected by encounter control in this region of acidity. The behaviour is that expected for nitration by the nitronium ion⁷. Isosbestic points were again observed at 240 nm and 276 nm. The linearity of the Beer's law plot in this region, the isosbestic points and the excellent kinetic behaviour¹ offer incontrovertible evidence that these data refer to homogeneous solutions of biphenyl.

Product studies were carried out in the usual way⁹ and the results are detailed in Table 2**

TABLE 2
Products of nitration of biphenyl^{a,b,c} in sulphuric acid at $25.0 \pm 0.2^\circ$

H_2SO_4 (%)	<u>o</u> -nitrobiphenyl (%)	<u>p</u> -nitrobiphenyl (%)	Mass ^{d,e} Balance (%)	Ortho : para ratio
44.6 ^f	22	7	87 ^g	3.2
56.1 ^f	70	21	91	3.2
61.0	61	17	79	3.4
63.7	70	20	90	3.5
65.7	64	21	86	3.1
68.7	68	18	86	3.7
70.8	70	19	88	3.7
72.6	70	23	93	3.3
74.7	68	19	87	3.5

a) [Biphenyl] = 3.3×10^{-5} mole dm^{-3} . b) [Urea] ca. 3×10^{-2} mole dm^{-3} .

c) [HNO_3] ca. 6×10^{-5} → 6×10^{-2} mole dm^{-3} .

d) 95% of a mixture of nitrobiphenyls of appropriate concentration could be recovered in unchanged ratio from a typical reaction medium. In all cases 1 dm^3 of reactant solution was used.

e) Except for that in 44.6% H_2SO_4 reactions were allowed to proceed for 3 half lives and mass balances are calculated from a possible total yield of 87%.

f) At 60^o

g) 59% biphenyl recovered.

** The minor products noted previously¹ were not observed and were presumably the result of soluble impurities dissolved from the excess of biphenyl on shaking with sulphuric acid.

Reactions were only allowed to proceed to the extent of 87% to avoid complications due to dinitration (for rates see ref. 1). The ortho : para ratio is high (3.1 - 3.7) over the whole range 44-75% sulphuric acid. The total yield is good in all cases. These two factors mean that if ipso-substitution is important rearrangement must compete favourably with nucleophilic capture of the ipso-substituted Wheland intermediate even in 45% sulphuric acid. We feel that this fact taken together with the fact that the ipso position is not expected to be activated to electrophilic attack make this route most unlikely.

We therefore reiterate our view that, anomalous though this is, nitration of biphenyl by the nitronium ion in aqueous sulphuric acid leads to an ortho:para ratio for mono substitution of ~ 3.5 and add that an explanation involving ipso-substitution seems most unlikely. It may be that the apparent discrepancy between this value and that of 1.4 obtained by Taylor in the reaction medium described above lies in the heterogeneity of the latter. The method has in our hands led to values of 1.4 - 2.0.

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