371. *Homolytic Aromatic Substitution. Part XVII.* The Phenylation of Tritiobenzene.*

By Chang Shih, D. H. Hey, and Gareth H. Williams.

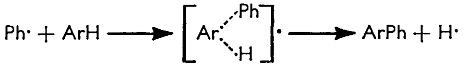
Phenylation of tritiated benzene with benzoyl peroxide has been shown not to involve a kinetic isotope effect. The substitution stage of this reaction is therefore considered to proceed by slow formation of an addition complex between the phenyl radical and the substrate, followed by loss of a hydrogen atom, probably as a result of interaction of the complex with another radical or other oxidising agent in a fast, kinetically insignificant, stage.

THREE mechanisms may be suggested for the substitution step in homolytic arylation. These are:

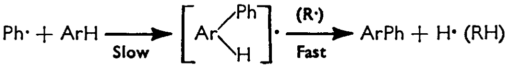
(*a*) Removal of a hydrogen atom from a substrate molecule by the attacking phenyl radical, leaving an aryl radical, which eventually combines with another aryl radical to yield a diaryl:

$$\mathrm{ArH} + \mathrm{Ph}\cdot \longrightarrow \mathrm{Ar}\cdot + \mathrm{PhH}$$
$$\mathrm{Ar}\cdot + \mathrm{Ar}\cdot\ (\text{or } \mathrm{Ph}\cdot) \longrightarrow \mathrm{Ar_2}\ (\text{or } \mathrm{ArPh})$$

(*b*) Synchronous approach of the attacking phenyl radical and recession of the ejected hydrogen atom:



(*c*) Slow formation of an addition complex between the phenyl radical and substrate, followed by the loss of a hydrogen atom, probably by interaction with another radical or other oxidising agent, in a fast, kinetically insignificant stage:



The first mechanism has been discussed by Grieve and Hey [1] and by Hey and Waters [2] and, more recently, by Augood, Hey, and Williams [3] and by Augood and Williams,[4] and was considered unlikely. The second and the third mechanism differ from mechanism (*a*) in that they represent reactions of hydrogen replacement rather than of hydrogen abstraction. These two mechanisms (*b*) and (*c*) were discussed by Augood and Williams [4] who concluded that mechanism (*c*) was the more likely, a view which had been previously put forward by Price [5] and by Hey, Nechvatal, and Robinson.[6] This mechanism can involve, as a non-kinetically significant stage, either the ejection of a free hydrogen atom or its removal by another radical. The latter alternative has always been favoured in preference to the former (see, for example, Hey, Nechvatal, and Robinson [6]), and this view was accepted by Augood and Williams.[4] However, this conclusion has been misinterpreted by Lewis and Symons [7] who, in a brief and incomplete discussion of the subject, attributed the opposite view to Augood and Williams, and themselves restated the actual views of those authors. The confusion has arisen from the quotation by Lewis and Symons of

---

* Part XVI, *J.*, 1958, 4403.

[1] Grieve and Hey, *J.*, 1934, 1797.

[2] Hey and Waters, *Chem. Rev.*, 1937, **21**, 169.

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

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

[5] Price, " Reactions at the Carbon–Carbon Double Bond," Interscience Publ. Inc., New York, 1946.

[6] Hey, Nechvatal, and Robinson, *J.*, 1951, 2892.

[7] Lewis and Symons, *Quart. Rev.*, 1958, **12**, 230.

equation (1) from Augood and Williams's review [4] as an expression of the reaction mechanism, whereas it was employed by Augood and Williams merely as a means of distinguishing the stoicheiometry of hydrogen replacement by mechanisms (*b*) and (*c*) from that of hydrogen abstraction by mechanism (*a*).

$$C_6H_5X + C_6H_5\cdot \longrightarrow C_6H_5\cdot C_6H_4X + H\cdot \quad \ldots \ldots \ldots \quad (1)$$

Of mechanisms (*b*) and (*c*), only (*b*) should be subject to a kinetic isotope effect. This test has been applied by Milyutinskaya, Bagdasaryan, and Izrailevich [8] to the arylation of some deuterated aromatic compounds by measurement of the deuterium content of the diaryls, and by Convery and Price [9] to the phenylation of 2 : 4-dinitrotritiobenzene. No isotope effect was found in either investigation. However, it appears desirable to apply this test to the simplest possible arylation, namely, the phenylation of benzene, using the conditions most favourable to the exhibition of an isotope effect of appreciable magnitude.

The radical R•, which is responsible for bringing about the second stage of mechanism (*c*), is usually the benzoyloxy-radical. However, it has been shown that under certain circumstances the radical R• can be a second aryl*cyclo*hexadienyl radical (the addition complex formed in the first stage). The interaction of two such radicals may then give rise by disproportionation to the formation of one molecule of a diaryl and one molecule of a dihydrodiaryl, which may subsequently become oxidised to a diaryl. De Tar and Long [10] have thus isolated a dihydrodiphenyl after decomposition of benzoyl peroxide in very dilute solution in benzene under nitrogen. If some of the diaryl is formed in this way, even under less extreme conditions, its isotopic composition can clearly not be independent of the relative rates of removal of hydrogen and tritium from the addition complex, and the measurement of the isotopic composition of the diaryl is not strictly diagnostic of the existence or non-existence of an isotope effect in the formation of the complex. However, the isotopic composition of the unchanged aromatic substrate is dependent only on the formation of addition complexes, and should be different from the isotopic composition of the starting material only if the formation of the complex, or transition state, involves partial cleavage of the C–H bond [mechanism (*b*) above]. The magnitude of the expected change in isotopic composition can be appreciable provided the initial concentration of benzoyl peroxide in tritiobenzene is high.

Our results show that the isotopic composition of the substrate is unchanged within experimental error. The maximum possible error in the determinations was estimated to be ±3%, since a number of specimens of tritiated benzene were assayed to this degree of accuracy. The actual error is probably smaller than this. Thus, the ratio of the final to the initial activity must be less than 1·03, and calculations show that the ratio of the rates of reaction at carbon atoms carrying hydrogen and tritium respectively (k_H/k_T) cannot therefore be greater than 1·2. Isotope effects with tritium, if they operate at all, are expected to be much greater (cf. Bigeleisen [11]). Hence one may conclude that the contribution of energy associated with the partial cleavage of the C–H or C–T bond can make, at most, only a very small contribution to the activation energy for the substitution reaction, and that therefore mechanism (*c*) is a much more accurate picture of the process than mechanism (*b*).

EXPERIMENTAL

Tritiated benzene was prepared by the exchange reaction of benzene with tritiated aqueous sulphuric acid.[12] Benzene (24 ml.) was shaken at room temperature for 4 days with tritiated 83% w/w sulphuric acid (10 ml.). After separation from the acid, the benzene was washed twice with water, then with aqueous sodium carbonate, and with water again. After being

[8] Milyutinskaya, Bagdasaryan, and Izrailevich, *Zhur. fiz. Khim.*, 1957, **31**, 1019

[9] Convery and Price, *J. Amer. Chem. Soc.*, 1958, **80**, 4101.

[10] De Tar and Long, *ibid.*, p. 4742.

[11] Bigeleisen, Brookhaven Conference Report, Isotopic Exchange Reactions and Chemical Kinetics, 1948, p. 53.

[12] Ingold and Wilson, *J.*, 1936, 915.

dried ($CaCl_2$) it was twice distilled through an 8″ helix-packed column (b. p. 79·5°, n_D^{20} 1·5008). It was diluted with inactive benzene to the required activity. At the tracer level of activity, at which it was prepared, the mole fraction of C_6H_5T is of the order of 10^{-6}, so that the concentration of doubly tritiated molecules ($C_6H_4T_2$) is quite negligible.

Reaction of Benzoyl Peroxide with Tritiated Benzene.—In experiments 1 and 2, benzoyl peroxide (6 g.) was allowed to decompose in tritiated benzene (20 ml. and 12 ml. respectively) for 24 hr. at 80° (thermostat). In experiment 3, benzoyl peroxide (30 g.) was allowed to-decompose in tritiated benzene (20 ml.) under the same conditions. The residual tritiated benzene was then collected by careful distillation through a helix-packed column at atmospheric pressure. It was redistilled once and analysed for tritium activity by gas counting. The percentage conversion of tritiated benzene was 11, 18, and 55 in the three experiments.

Assay of Tritiated Benzene.—Through a vacuum line of standard design, the tritiated benzene was introduced into a gas counter (type GA 10/M) at known pressure, together with the basic filling gas, which for the present determinations was butane.[13] The tritiated benzene formed 10—30% of the gas mixture. Under these conditions it had previously been found possible to count the tritiated benzene with a reproducibility better than ±3% in the Geiger region. The length of the plateau was about 200 v and its slope rather less than 3% per 100 v. Before each determination, the counter-tube was heated in a stream of warm air and pumped out continuously. It was then filled with pure butane for the determination of the background counting rate. After this determination, it was flushed with a mixture of the required composition and again filled for the determination of the activity of the tritiated benzene. The results of experiments 1, 2, and 3 are summarised in the Table, which shows that, within the experimental error, the activity of the tritiated benzene is unchanged after reaction with benzoyl peroxide.

Experiment no.	1	2	3
Sp. activity (c.p.m./ml.*): original benzene	499	499	1298
,, ,, ,, ,, residual ,,	496 †	505	1271

* At S.T.P. † Counted after dilution to twice its volume with inactive benzene, in order to check the results and eliminate the possibility of coincidence.

The authors acknowledge with thanks the receipt of grants from the Research Fund of the University of London and from the Distillers Company Limited.

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

[*Received, January 9th,* 1959.]

---

[13] Powell and Reid, *J. Amer. Chem. Soc.*, 1945, **67**, 1020.