# The Kinetics of Hydrogen Isotope Exchange Reactions. Part III.* The Reaction between [²H₁]Benzene and Aqueous Sulphuric Acid.

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The rate of loss of deuterium from [²H₁]benzene in aqueous sulphuric acid solutions depends on the acidity of the solvent in a similar way to that for the analogous reactions of *ortho*-deuterated phenols. It is concluded that the exchange reactions of all those compounds proceed by a similar mechanism and involve a reaction intermediate in which the entering proton is more loosely attached to the aromatic nucleus than the departing deuteron. This conclusion is discussed with reference to related observations on the hydration of olefins, the basicity of aromatic hydrocarbons towards hydrochloric acid, and the general theory of aromatic substitution reactions.

THE dependence of exchange velocity on solvent acidity in the reaction between deuterated phenols and sulphuric acid has been interpreted by us (Part II*) as requiring the postulation of an intermediate, the formula of which was that of a conjugate acid of the phenol. The structure of this intermediate was left undecided as a result of that work, the only kinetic requirement being a positional non-equivalence of the protium and deuterium nuclei which are involved in the exchange, *i.e.*, structure (I) was ruled out, but either (II) or (III) would be satisfactory as intermediates. In formula (II) the proton is attached to the phenolic oxygen
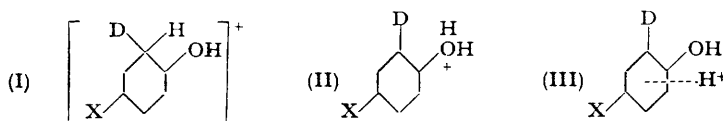
atom whereas the proton attachment in (III) is of a less definite character. We need not consider attachment of the proton to the group X as a separate possibility, since this is inherently improbable for the case of *p*-cresol (X = Me) which was one of the compounds studied by us. In order to decide whether the conclusions drawn by us from the previous work were to be restricted to molecules with a lone-pair donor atom adjacent to the ring, or whether they were of more general validity, it was necessary to examine the kinetic behaviour of a compound for which the formulation (II) was impossible, the somewhat different behaviour of phenols, amines, and similar compounds in aromatic nitration as compared with that of other aromatic molecules (cf. Bunton, Hughes, Ingold, Jacobs, Jones, Minkoff, and Reed, *J.*, 1950, 2628; Blackall, Hughes, and Ingold, *J.*, 1952, 29) being borne in mind.

For these reasons the exchange behaviour of benzene was studied as a function of solvent acidity. The difficulties involved in separating a small quantity of this compound from a large amount of aqueous acid were overcome by the application of an isotope dilution technique, which also permitted low concentrations of benzene ($\sim$0·007M) to be used. Although several earlier investigations have dealt with the exchange behaviour of benzene, the present work is believed to be the first quantitative study of this reaction under homogeneous conditions.

EXPERIMENTAL

(a) *Preparation of Monodeuterobenzene* ([²H₁]*Benzene*).—The method of preparation has been described by Bryce-Smith, Gold, and Satchell (*J.*, 1954, 2743). Isotopic analysis (method described by *idem, loc. cit.*) showed the product to contain : C₆H₅D, 89·5; C₆H₆, 10·5 mol.%.

(b) *Procedure for Kinetic Experiments.*—The rate of loss of deuterium from the prepared deuterobenzene to six different sulphuric acid–water mixtures was studied. The acids had H_0 (Hammett's acidity function) values varying from $-5\cdot08$ to $-7\cdot34$. For each acid accurately measured samples ($\sim$0·15 ml.) of the prepared benzene were dissolved in samples (220 ml.) of the acid contained in flasks (250 ml.) fitted with ground-glass stoppers and having an additional

* Part II, preceding paper.

sealing of Apiezon " Q compound." The flasks were kept in a thermostat at 25°, for suitable known times. On removal from the bath a flask was opened, and a measured amount (~1·3 ml.) of " AnalaR " benzene added to its contents, which, after resealing of the flask, were agitated for 15 min. Previous experiments had shown that equilibration between dissolved and added benzene was essentially complete well within such a period. The benzene and acid phases were now separated, and the benzene washed with water and stored over a little barium carbonate and calcium chloride in a sealed flask. Isotopic analysis of such samples (together with the assumption that there is no isotopic fractionation in the equilibration) allows the composition of the dissolved benzene to be determined, and hence the exchange rate to be calculated.

(c) *Method of Isotopic Analysis.*—The infrared spectrum of liquid monodeuterobenzene possesses bands at 11·6 and 12·8 μ (cf. Bailey, Gordon, Hale, Herzfeld, Ingold, and Poole, *J.*, 1946, 299), absent from the spectrum of ordinary benzene, which permit quantitative analysis of mixtures of these two compounds. On using a Grubb-Parsons S4 double-beam spectrometer with rock-salt optics and fixed rock-salt cells of ~0·003 cm. thickness, calibration with a series of mixtures of known composition showed Beer's law to be approximately obeyed (see Fig. 1). The cells were always recalibrated at the time of each series of measurements to obviate any error which might otherwise be introduced owing to deterioration of the rock-salt surfaces with time,
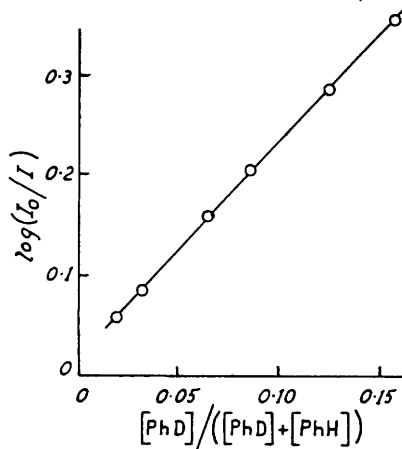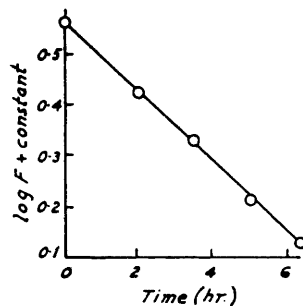
FIG. 1. *Cell calibration at 12·8 μ.*

FIG. 2. *Example of first-order exchange reaction.*

etc. Trial experiments using the isotopic dilution method described above showed that it was possible to determine the isotopic composition of an unknown, dissolved sample to ±1·0 mol.% of C_6H_5D over the range 0—90 mol.%.

The proportion of deuterium in the exchanging system being very small, the kinetics would be expected to be of the first order (Harris, *Trans. Faraday Soc.*, 1951, **47**, 716; Melander, *Arkiv Kemi*, 1954, **7**, 287). A specimen first-order plot is shown in Fig. 2. The first-order rate constants, λ, are tabulated together with the corresponding H_0 values in Table 1, and plotted against them in Fig. 3, the slope of the line being 1·36.

TABLE 1. *Dependence of the exchange rate on acidity.*

H_2SO_4 (wt. %)	66·5	68·7	73·5	75·8	79·2	83·2
$-H_0$	5·08	5·40	5·99	6·27	6·72	7·34
$10^7\lambda$ (sec.⁻¹)	2·68	5·75	35·2	115·0	453	3450

(d) *Sulphonation.*—The method of analysis, involving as it does, isotopic dilution of the sample undergoing exchange, obviously requires that there be no loss of benzene from the reaction flasks. Any sulphonation or evaporation from the flask would mean such a loss. It was possible to estimate the extent of sulphonation by reversing the dilution procedure used for studying the exchange rate. Accurately measured samples (~0·15 ml.) of " AnalaR " benzene were dissolved in samples (220 ml.) of the strongest acid used for exchange and, after various time intervals, the solutions were equilibrated with a suitable C_6H_6–C_6H_5D mixture. Isotopic analysis of the resulting samples showed sulphonation and other losses to be slight during the period occupied by the exchange experiments involving this acid. Such a situation

was assumed to hold for the other (weaker) acids also (cf. Ingold, Raisin, and Wilson, *J.*, 1936, 915). A more detailed investigation of the rates of sulphonation is now in progress.

DISCUSSION

The dependence of reaction velocity upon acidity is shown in Fig. 3, and is of the same general form as for the substituted phenols (Part II, *loc. cit.*). There is a quantitative difference between the slopes found for the different aromatic compounds but it is thought that this is a secondary effect (see Part IV, following paper) and that it does not point to any abnormal behaviour of benzene compared with that of the substituted phenols. It is therefore concluded that the mechanism of hydrogen isotope exchange is the same in all these cases.

This view is reinforced by the actual magnitudes of the rates of exchange for the various compounds. For the exchange reaction we have found that benzene and *p*-nitrophenol are about equally reactive. It has been shown that at high concentrations of nitric acid (10M) in glacial acetic acid and low concentrations of nitrous acid the mechanisms of nitration of these two compounds are identical and involve attack by the NO_2^+ ion. A rough comparison of the velocities is possible from the rate constants given by Bunton *et al.* (*loc. cit.*, Table X) and by Hughes, Ingold, and Reed (*J.*, 1950, 2400, Table IV). Such a comparison reveals approximately the same relative reactivity (per nuclear position) as we have found for exchange.

The mechanism for benzene being the same as that for the substituted phenols, it follows that a conjugate acid of benzene of a type which we formulate non-committally as (IV), must be involved as an intermediate in the exchange reaction of benzene. By analogy, the result also indicates that (III) is more likely than (II) to be the formula for the intermediate in the case of the exchange reaction with phenols. The complete mechanism for benzene is (cf. Part II, *loc. cit.*) illustrated in the annexed scheme. The existence of (V) [analogous to (I)] as a stable intermediate is not essential to the kinetics, but the possible scheme involving it is presented in order to show how the exchange mechanism is related to those of the other electrophilic aromatic substitution reactions, such as nitration, which are widely thought to involve similar intermediates, and because there is some other evidence that such structures do exist (see below).
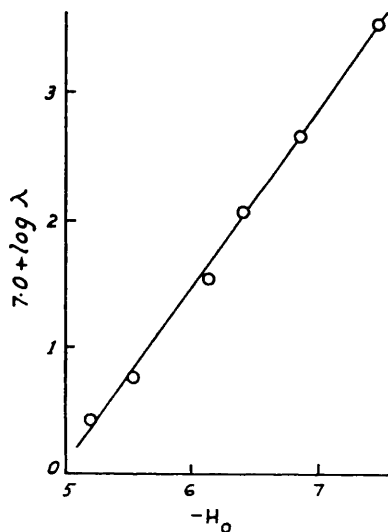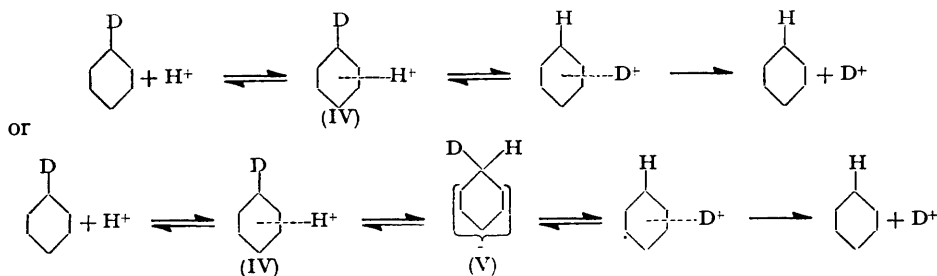
FIG. 3.

Dependence of exchange rate on acidity.

The formulation of (III) and (IV) clearly requires some non-classical concept of chemical interaction. It seems convenient to apply to the structures (I), (III), (IV), and (V) the terminology proposed by Mulliken (*J. Phys. Chem.*, 1952, **56**, 801, 821), referring to (I) and (V), where the entering and leaving substituents occupy equivalent positions, as

" inner complexes " and to (III) and (IV) as " outer complexes." Structures of this type have also been considered by Brown and Brady (*J. Amer. Chem. Soc.*, 1952, **74**, 3570) who termed them σ- and π-complexes respectively but, in view of the different interpretations placed on the term " π-complex " by different authors (cf. *idem, ibid.*), it seems preferable to avoid the name.

Two other investigations dealing with the interaction between acids and aromatic or unsaturated systems have led to conclusions very similar to those outlined in the present paper. Brown and Brady (*loc. cit.*), investigating the equilibria between hydrochloric acid and aromatic hydrocarbons, with and without added aluminium trichloride, suggested that the conjugate acid of benzene formed in the first case was an inner complex and in the second an outer complex. Only the interaction which leads to an inner complex can result in hydrogen isotope exchange between deuterium chloride and benzene (Klit and Langseth, *Z. phys. Chem.*, 1936, **176**, 65). Again, a mechanism essentially identical with ours, involving the slow interconversion of two distinct conjugate acids of the same hydrocarbon, was first proposed by Taft (*J. Amer. Chem. Soc.*, 1952, **74**, 5372) in order to explain the observation that the rate of hydration of *iso*butene appeared to follow Hammett's acidity function, rather than the concentration of hydrogen ions (see also Taft, Purlee, Riesz, and DeFazio, *ibid.*, 1955, **77**, 1584). A more general formulation of Taft's results has been advanced by de la Mare, Hughes, Ingold, and Pocker (*J.*, 1954, 2930). This formulation has, however, been discussed in Part II (*loc. cit.*), and in the light of that discussion we regard Taft's original specific representation of the mechanism of olefinic hydration as probably justified.

Mulliken (*loc. cit.*) advanced theoretical reasons for the existence of inner and outer complexes and pointed out that there may or may not be an energy barrier between them. Our results indicate that if an inner complex is, in fact, involved (cf. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334), then the transition from an outer complex to it *is* an activated process for the case of interaction between a proton and an aromatic structure.

The type of mechanism considered in this paper is different from that suggested for aromatic substitution by Dewar (" Electronic Theory of Organic Chemistry," Oxford, 1949) in that he seems to regard the formation of an outer or π-complex as the probable slow step. How far the mechanism postulated by us for the simplest electrophilic aromatic substitution—namely, isotope exchange—is applicable in other cases is, at present, speculation.

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