540. *The Kinetics of Hydrogen Isotope Exchange Reactions. Part V.** *Partial Rate Factors for the Hydrogen Isotope Exchange Reaction between Toluene and Sulphuric Acid.*

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For protium–deuterium exchange the partial rate factors referring to the *ortho-*, *meta-*, and *para*-positions in toluene have been found to be 83, 1·9, and 83, respectively, in 68% aqueous sulphuric acid at 25°. These values are compared with the corresponding factors found for other electrophilic substitution reactions.

VARIOUS investigations have established that hydrogen isotope exchange between aromatic compounds and mineral acids is an electrophilic substitution reaction.[1] A recent kinetic study of the reaction [2] indicated that its mechanism may be somewhat more complex than that which at present suffices to explain the results obtained in other cases.[3] It was felt, therefore, that a comparison between partial rate factors † referring to exchange and those referring to other substitutions would be interesting. The rate of loss of deuterium from monodeuterobenzene to sulphuric acid under homogeneous conditions being known,[2] it was only necessary to study the relevant exchange rates of those benzene derivatives for which data concerning other reactions were available for comparison. Toluene was chosen first because from this point of view it is the most thoroughly studied benzene derivative. In addition, it was expected to offer convenient exchange rates.

Results for toluene, analogous to those now reported for homogeneous exchange, have recently been obtained in heterogeneous exchange experiments with tritium.[1c,4] These are discussed later.

EXPERIMENTAL

Preparation of [p-^{2}H]*Toluene.*—It was unnecessary to obtain a sample completely free from light toluene and therefore no special modification of the standard Grignard procedure was used. The product from the reaction of ethereal *p*-tolylmagnesium bromide with deuterium oxide was treated with solid carbon dioxide to destroy excess of Grignard reagent. The solid products were decomposed with ammonium chloride, and the ether layer was separated, washed with water, and dried ($CaCl_2$). Deuterotoluene was obtained in 60% yield by fractional distillation. No isotope analysis was performed but, as judged from previous experience and that of other workers, the product probably contained less than 20 mole % of C_7H_8. [*o*-$^2H_1$]Toluene and [*m*-$^2H_1$] toluene were prepared similarly from the appropriate Grignard reagents.

Procedure for Kinetic Experiments.—The rate of loss of deuterium from the prepared toluenes was studied as a homogeneous reaction.

[*p*-^{2}H]Toluene was allowed to react with five different sulphuric acid–water mixtures having H_0 (Hammett's acidity function) values varying from $-3{\cdot}57$ to $-5{\cdot}96$. The *ortho-* and *meta*-isomers were studied with only one acid ($H_0 = -5{\cdot}28$) but the runs were duplicated. The

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* Part IV, *J.*, 1955, 3622.

† A partial rate factor for any reaction is the relative rate of attack at a particular nuclear position in an aromatic compound, the rate for one position in benzene being taken as unity.

[1] (*a*) Ingold, Raisin, and Wilson, *J.*, 1936, 1637; (*b*) Best and Wilson, *J.*, 1938, 28; (*c*) Olsson and Melander, *Acta Chem. Scand.*, 1954, **8**, 523; (*d*) Lauer and Day, *J. Amer. Chem. Soc.*, 1955, **77**, 1904.

[2] Gold and Satchell, *J.*, 1955, 3609, 3619, 3622.

[3] See Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Son, Ltd., London, 1953.

[4] Melander, *Svensk Kem. Tidskr.*, 1955, **67**, 51.

experimental procedure was similar to that used for benzene [2] but, since toluene is less soluble in aqueous mineral acids, it was necessary to use ~0·1 ml. samples dissolved in ~400 ml. of acid.

Method of Isotopic Analysis.—Under the conditions used, the exchange reaction is a first-order process.[5] For kinetic purposes it is only necessary to determine how the isotopic content of the toluene changes with time: a knowledge of the absolute abundances is not essential. The method of analysis was therefore identical with that used for benzene, the *o*-, *m*-, and *p*-deutero-isomers of toluene having characteristic infrared bands at 12·90 μ, 12·55 μ, and 11·95 μ, respectively, which can be used for the analysis of mixtures of these compounds with light toluene. The bands are also sufficiently free from mutual overlap to exclude significant errors in the rate constants for a given isomer arising from the presence of isomeric impurities, introduced at the first stage of the synthesis as isomeric bromotoluenes. Such errors would not be excluded by a technique in which total isotope abundance is determined. They would be most serious for the *meta*-compound since it is the least reactive isomer.

Sulphonation.—It was shown in the experiments with benzene that interference from sulphonation was negligible. Towards sulphonation toluene is known [6] to be about five times more reactive than benzene, whereas for exchange the relative reactivity found in the present work is of the order of 40. Hence a change from benzene to toluene, at a given acidity, should decrease any chance of interference from sulphonation. Further, it is known [7] that the rate of sulphonation of benzene in aqueous sulphuric acid decreases with decreasing acidity much more rapidly than does the rate of isotope exchange. Since the most concentrated kinetically useful acid for toluene was necessarily more dilute than the most concentrated acid usable with benzene, interference from sulphonation should have been absent from the experiments with toluene as well as from those with benzene. These arguments are supported by the experimental findings of Olsson and Melander.[1c]

DISCUSSION

The measured first-order rate constants (λ) for the loss of deuterium from the three deuterotoluenes to the various acids are tabulated below, together with the corresponding H_0 values.

Dependence of exchange rate on acidity at 25°.

	[p-^{2}H]*toluene*			[m-^{2}H]*toluene*	
H_2SO_4 (wt. %)	$-H_0$	$10^7\lambda$ (sec.$^{-1}$)	H_2SO_4 (wt. %)	$-H_0$	$10^7\lambda$ (sec.$^{-1}$)
53·0	3·57	1·36	68·0	5·28	8·21
58·5	4·16	9·40			
63·9	4·76	56·6		[o-^{2}H]*toluene*	
68·9	5·39	498	68·0	5·28	356
73·4	5·96	4250			

Fig. 1 contains the plots of the logarithms of the rate constants against $-H_0$ for benzene [2] and [*p*-^{2}H]toluene. Both plots are straight lines, that for benzene having a slope of about 1·36, that for the toluene about 1·40. This result is in agreement with all previous kinetic findings, the mechanistic implications of which have been discussed in Parts II—IV. The two sets of results permit the partial rate factor at the *para*-position in toluene to be evaluated over a range of acid concentrations. The two slopes being very nearly equal, the value obtained does not depend greatly on the particular acid composition chosen. (This is by no means the case for the substituted phenols, the data concerning which are contained in Parts II and IV.) The rate constants for the *ortho*- and *meta*-isomers were obtained by using an acid of H_0 value −5·28. At this composition the partial rate factor for the *para*-position is estimated from Fig. 1 to be 83. Those for the *ortho*- and *meta*-positions are likewise found to be 83 and 1·9, respectively. (These values are all regarded as being subject to maximum errors of about ±5%).

Olsson and Melander [1c, 4] have recently reported the partial rate factors for exchange between the three isomeric nuclear-tritiated toluenes and aqueous sulphuric acid under heterogeneous conditions (the two components were shaken together). Spectroscopic

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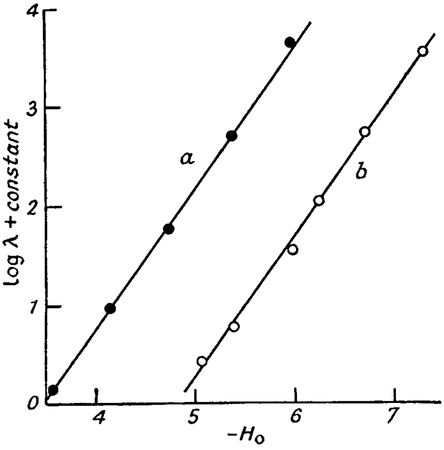
[5] Gold and Satchell, *Quart. Rev.*, 1955, **9**, 51.

[6] See Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

[7] Ingold, Raisin, Wilson, Bailey, and Topley, *J.*, 1936, 915; Gold and Satchell, *J.*, 1956, 1635.

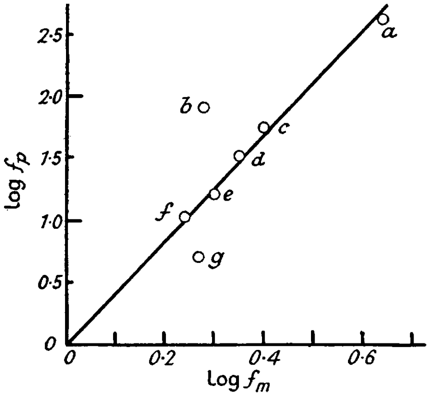
investigations[8,9] indicate that the characteristic frequencies of the C–D bonds in the *o*-, *m*-, and *p*-monodeuterotoluenes are not very different. Hence the magnitude of any isotope effect on substitution rates, produced by the replacement of deuterium by tritium, would be expected to be very similar at each position. Therefore the relative reactivities of the three positions towards any particular substitution would be similar regardless of whether they all carry deuterium or they all carry tritium. That the exchange process in Olsson and Melander's experiments took place in the sulphuric acid phase is probable by analogy with other work and also because a conversion factor, based on the volumes of the phases used by Olsson and Melander and an approximate result of ours for the solubility of toluene in aqueous sulphuric acid, will turn our rates into theirs within an order of magnitude. These considerations imply that Olsson and Melander's results should be fairly directly comparable with ours. Melander[4] reports the partial rate factors at the *ortho*-, *meta*-, and *para*-positions as 70, 2·2, and 63, respectively, at 25°. These values are only in qualitative agreement with ours, but we understand from Dr. Melander[10] that more recent experiments in his laboratory indicate that the factors for the *ortho*- and *para*-positions quoted above are too low. A final comparison between the two sets of data is therefore not yet possible. However, Dr. Melander also informs us[10] that, in recent experiments with Mr. S. Olsson, he finds the relative reactivities of the three monodeuterotoluenes, with 78% sulphuric acid under heterogeneous conditions, to be $o : m : p = 51 \pm 2 : 1 \pm 0{\cdot}04 : 46 \pm 3$. These values agree well with our findings of $o : m : p = 44 : 1 : 44$, under homogeneous conditions. It is clear that, towards hydrogen isotope exchange, the *ortho*- and *para*-positions of toluene are about equally reactive, and that the *meta*-position is about twice as reactive as a position in benzene.

FIG. 1. *Dependence of exchange rate on acidity*



(*a*) *Toluene.* (*b*) *Benzene.*

FIG. 2. *Relation between the partial rate factors for various reactions of toluene.*



(*a*) *Chloromethylation* (60°).[6]
(*b*) *Deuterium exchange* (25°).
(*c*) *Nitration* (45°)[6] *and bromination* (25°).[17]
(*d*) *Mercuration* (25°).[11a]
(*e*) *Detrimethylsilylation* (25°).[11c]
(*f*) *Methylation with methyl iodide* (0°).[11c]
(*g*) *Methylation with methyl bromide* (28°).[11c]

It is of interest to compare the partial rate factors found for exchange with those found for other electrophilic substitutions of toluene. Brown and his collaborators[6,11] have directed attention to the theoretical implications of such comparisons by showing that the partial rate factors for various substitution reactions of toluene may be discussed in terms

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[8] Smith, Choppin, and Nance, *J. Amer. Chem. Soc.*, 1950, **72**, 3260.

[9] Cf. Turkevich, McKenzie, Friedman, and Spurr, *ibid.*, 1949, **71**, 4045.

[10] Melander, personal communication.

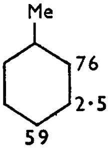
[11] (*a*) Brown and McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2300; (*b*) McGary, Okamoto, and Brown, *ibid.*, p. 3037; (*c*) Brown and Jungk, *ibid.*, p. 5584.

of Hammett's $\rho\sigma$-rule.[12] If the rule is applicable to substituent effects on aromatic substitution it follows that the partial rate factors for *meta*- and *para*-substitution (f_m and f_p) for different reactions of a given substituted benzene should be related through the equation :

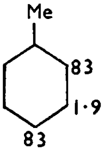
$$\log f_p = (\sigma_p/\sigma_m) \log f_m$$

where σ_p and σ_m are the substituent constants referring to the *para*- and the *meta*-position respectively. By obtaining a reasonably good straight-line plot of $\log f_p$ against $\log (f_p/f_m)$, Brown *et al.* have shown that, for toluene, σ_p/σ_m for various reactions is, in fact, fairly constant. Some of the data recorded by Brown *et al.* are reproduced in Fig. 2 where $\log f_p$ is plotted against $\log f_m$—this being a more sensitive plot than that used by the above authors. The data recorded by Brown but omitted from Fig. 2 are those which we regard as untrustworthy. For instance, to derive the partial basicity factors [13] it is necessary to ignore the experimental fact that hexamethylbenzene is more basic than any other methylated benzene. Again, the factor for *meta*-chlorination quoted by Brown is an estimated value and not an experimental one.[14] However, even after eliminations of this kind and in spite of the use of the more sensitive plot, the remaining points fall on a surprisingly good straight line, that for isotope exchange being a notable exception. The amount of correlation which exists is surprising because, as has been mentioned, it implies that for a considerable variety of aromatic substitution reactions σ_p/σ_m has a constant value and this is surely not necessarily to be expected. In general, if a substituent is capable of giving rise to time-variable (electromeric or inductomeric) effects then these are likely to operate differently at different positions, so that σ_p/σ_m would be liable to change somewhat from one reaction to another, depending on the importance of the time-variable component in determining the total rate. On these theoretical grounds the Hammett $\rho\sigma$-rule would not be expected to hold rigorously for aromatic substitution.[15] In the case of toluene, it is known that the methyl substituent is indeed capable of giving rise to important time-variable effects [16] and this makes the linearity of the plot in Fig. 2 more noteworthy than the fact that every point does not fall on the line. The reactions represented by those which do, probably do not involve important time-variable effects.

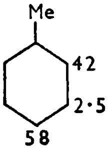
A further point of interest concerns the *ortho*/*para* ratio. The diagrams show the partial rate factors obtained for bromination involving attack by Br^+ or $BrOH_2^+$, for nitration involving attack by NO_2^+, and for deuterium exchange.



Bromination



Exchange



Nitration

The higher *ortho*/*para* ratio for bromination compared with nitration has recently been attributed by de la Mare and Harvey [17] to a decreased steric effect, the positive halogen being a smaller attacking agent than the nitronium ion. If steric effects are indeed important in this context, as seems reasonable, then the fact that the *ortho*/*para* ratio for hydrogen isotope exchange lies between those for bromination and nitration, implies that the attacking species involved in exchange is probably larger than a bromine cation.

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[*Received, October 6th*, 1955;
augmented, March 1st, 1956.]

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[12] Hammett, " Physical Organic Chemistry," McGraw Hill Book Co. Inc., New York, 1940.

[13] Condon, *J. Amer. Chem. Soc.*, 1952, **74**, 2528.

[14] *Idem, ibid.*, 1948, **70**, 1963.

[15] Cf. de la Mare, *J.*, 1954, 4450; Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525; Jaffe, *Chem. Rev.*, 1953, **53**, 191.

[16] de la Mare and Robertson, *J.*, 1943, 279.

[17] de la Mare and Harvey, *J.*, 1956, 36.