

661. *Aromatic Reactivity. Part XI.* The Influence of meta- and para-Methyl Groups in Detritiation by Aqueous Sulphuric Acid.*

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We have measured the rates of detritiation of [$^3\text{H}_1$]benzene, *m*-[$^3\text{H}_1$]toluene, and *p*-[^3H]toluene in 68—80 wt.-% sulphuric acid at 25°. In 73—75 wt.-% acid, *meta*- and *para*-methyl groups activate 5.0 and 250 times, respectively.

Possible mechanisms for aromatic hydrogen isotope exchanges are discussed.

THIS paper is the first of a series on the effects of ring substituents on the rate of detritiation of ring-tritiated aromatic compounds in acidic media under homogeneous conditions. It is concerned with the rates of detritiation of *m*- and *p*-[$^3\text{H}_1$]toluene and of [$^3\text{H}_1$]benzene in aqueous sulphuric acid, and with the dependence of these rates on the concentration of the acid.

The rate measurements involve extraction of unchanged tritiated aromatic compound and measurement of its total activity. If any sulphonation occurs at a tritiated position this will obviously result in loss of tritium, but sulphonation at a non-tritiated position also results in loss of tritium, since the sulphonation product remains in the aqueous phase during the extraction. The rate of loss of activity will thus be higher than the rate of exchange. Fortunately, the rates of sulphonation of benzene and toluene are known,^{1,2} and appropriate corrections can be applied.† The rate of sulphonation increases rather more rapidly than that of detritiation as the concentration of acid is increased, but even so it accounts for less than 0.3% of the apparent rate for *p*-[^3H]toluene in 75.3 wt.-% acid, and less than 4% for [$^3\text{H}_1$]benzene in 84.0 wt.-% acid, these acids being the most concentrated used in the two cases. With *m*-[$^3\text{H}_1$]toluene, however, in which exchange is at the least reactive aromatic position, sulphonation accounts for *ca.* 3% of the total rate in 73.2 wt.-% acid and for 17% in 81.14 wt.-% acid.

Effects of m- and p-Methyl Groups.—In the Table are listed the total observed rate constants, $k_{\text{obs.}}$, the approximate rate constants, $k_{\text{sulph.}}$, for sulphonation, and the corrected rate constants k_{T} for the detritiation, along with the factors, f , giving the rate for each toluene compound relative to that for benzene. In 73.24% acid the rate factors are $f_p^{\text{Me}} = 254$, and $f_m^{\text{Me}} = 5.0$, and in 75.30% acid they are 243 and 5.0. The rate factors can be expected to change somewhat as the ratio of water to sulphuric acid is varied, for

* Part X, *J.*, 1960, 1566.

† The rate reported for sulphonation of toluene may include a small contribution from other side reactions such as oxidation of the methyl group, which will also give rise to loss of tritium.

¹ Gold and Satchell, *J.*, 1956, 1635.

² Eaborn and Taylor, *J.*, 1960, 1480.

considerably different factors are obtained in acetic acid-sulphuric acid-water and trifluoroacetic acid-sulphuric acid-water media.³ The apparent change in f_p^{Me} is within experimental error, but the observed rise in f_m^{Me} to 5.7 on going to stronger acid seems to be real. Since the corrections for sulphonation are relatively large in the stronger acids, however, we shall at present discuss only the rate factors of $f_p^{\text{Me}} = 250$ and $f_m^{\text{Me}} = 5.0$ which apply in 73–75% acid.

These factors are different from those reported by Gold and Satchell⁴ for dedeuteration in 68% acid, *viz.*, $f_p^{\text{Me}} = 83$ and $f_m^{\text{Me}} = 1.9$, and it is important to see at what point their results diverge from ours. It should first be noted that our rate factors are based on direct comparison of [³H₁]toluenes and [³H₁]benzene in the same acids, whereas Gold and Satchell compared rates for *m*- and *p*-[²H₁]toluene with those derived for [²H₁]benzene by interpolation from their earlier results.⁵ The ratio $f_p^{\text{Me}}/f_m^{\text{Me}}$ from our results in 73–75% acid, *viz.*, 50, agrees satisfactorily with that, *viz.*, 44, reported by Gold and Satchell for 68% acid, and with those, *viz.*, 46 ± 3 and 41 ± 2 respectively, reported by Ollson and Melander⁶ for dedeuteration and detritiation in 80.8% acid under heterogeneous conditions. Furthermore, the ratio k_T/k_D , of the rate constants for detritiation and dedeuteration, has a value of 0.7 for the *p*-tolyl compounds in 68.9% acid, in reasonable agreement with the k_T/k_D ratios of 0.52 observed by Ollson and Melander in 80.8% acid under heterogeneous conditions.⁶

Detritiation of X·C₆H₄·[³H] in sulphuric acid at 25°.

H ₂ SO ₄ (wt.-%)	X	10 ⁷ <i>k</i> _{obs.} (sec. ⁻¹)	10 ⁷ <i>k</i> _{sup.} (sec. ⁻¹)	10 ⁷ <i>k</i> _T (sec. ⁻¹)	<i>k</i> _{rel.}
68.23	<i>p</i> -Me	224	—	224	—
70.08	<i>p</i> -Me	637	—	637	—
71.34	<i>p</i> -Me	1042	—	1042	—
73.24	H	11.85	(0.06) ^a	11.8	—
	<i>m</i> -Me	60.90	2.0 ^b	58.9	4.99
	<i>p</i> -Me	3000	2.0 ^b	2998	254
75.30	H	29.30	(0.57) ^a	28.7	—
	<i>m</i> -Me	161.7	17.6	144	5.02
	<i>p</i> -Me	7000	17.6	6982	243
77.67	H	104.5	2.8 ^a	102	—
	<i>m</i> -Me	640	86.8	553	5.42
79.80	H	353	11.6 ^a	341	—
	<i>m</i> -Me	2310	359	1951	5.72
81.14	H	898	25 ^c	873	—
	<i>m</i> -Me	5950	976	4974	5.70
82.82	H	3395	105 ^c	3290	—
84.03	H	6540	240 ^c	6300	—

^a Calculated by dividing by 31 the value for toluene (cf. ref. 2). ^b By extrapolation. ^c By interpolation from data in ref. 1.

The apparent disagreement between Gold and Satchell's results and ours seems to originate in the values for benzene; detritiation appears to be 3 times slower than dedeuteration in 73.5% acid, but the two reactions appear to have the same rate in 83% acid. It is theoretically possible for the large k_D/k_T ratio at low acidities and the variation of the ratio with acidity to be real, but it is much more likely that they arise from experimental error, even though the dedeuteration and detritiation experiments were very similar, the only essential differences being in the isotope analyses. The following facts encourage us to believe that our results are not at fault: (i) Because of the disagreement with the dedeuteration results, we have checked our work carefully, and have investigated all the possible sources of error that occurred to us. (ii) The dependence of the rate of detritiation of [³H₁]benzene on acid concentration, while very different from that reported

³ Eaborn and Taylor, *Chem. and Ind.*, 1959, 949.

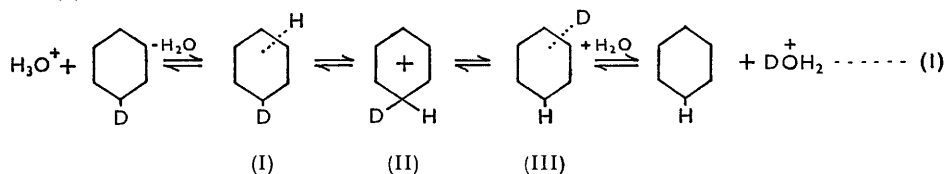
⁴ Gold and Satchell, *J.*, 1956, 2743.

⁵ Gold and Satchell, *J.*, 1955, 3619.

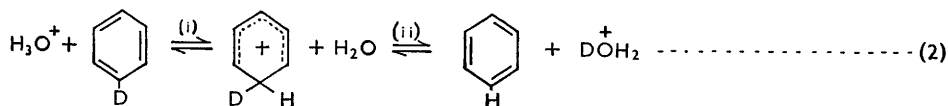
⁶ Melander and Ollson, *Acta Chem. Scand.*, 1956, **10**, 879; Ollson, *Arkiv Kemi*, 1959, **14**, 85.

by Gold and Satchell (see below), is very similar to that for m -[$^2\text{H}_1$]toluene. (iii) For the many electrophilic aromatic substitutions for which reliable rate data are available, Stock and H. C. Brown have recently noted ⁷ that the ratio $\log f_p^{\text{Me}}/\log f_m^{\text{Me}}$ lies between 3.18 and 4.72. Our figures correspond with a ratio of 3.42, and Gold and Satchell's with a ratio of 6.88. Rate factors determined for detritiation in acetic acid-water-sulphuric acid ³ correspond with a ratio of 3.65, and those for deuteration in aqueous trifluoroacetic acid ⁸ with a ratio of 4.3 ± 0.8 .

Dependence of Rate on Acid Concentration, and the Reaction Mechanism.—Gold and Satchell ^{4,5,9} suggested that aromatic hydrogen exchange involves rapid and reversible proton transfer from the catalysing acid (which is usually the oxonium ion, written here conventionally as H_3O^+ , but which could be represented generally as HA) to form a loose "outer" complex (I) of unspecified nature (cf. ref. 9*b*), and that this is then transformed in a slow step to the analogous complex (III) [possibly *via* the σ -complex (II)] as in scheme (I):



They rejected the simpler mechanism (2) (which we describe as "orthodox" since it is of the type most commonly assumed for electrophilic aromatic substitution ¹⁰) because the transition states of steps (i) and (ii) (both of which must contribute to determination of the overall rate in hydrogen exchange) would involve a solvent molecule (or entity A of the acid HA) partly bound covalently. This they held to be ruled out by their observation of a linear dependence of the logarithms of the rate constants for dedeuteration on the Hammett acidity function H_0 . Normally, only $\log k-H_0$ plots with a slope of near -1.0 are considered to be mechanistically significant, but the departures of the reported slopes for benzene (-1.4) and toluene (-1.36) from unity were accepted as reasonable salt effects.



The Figure shows some plots of $\log k_T-H_0$, the H_0 values being obtained by interpolation from those selected by Long and Paul ¹¹ from Hammett and Deyrup's original data. ¹² Gold and Satchell's results for dedeuteration of benzene can be presented either as a straight line of slope -1.5 , or as a curve of slope varying from *ca.* -1.2 to *ca.* -1.7 . Our results for detritiation lead to a curve of slope varying from *ca.* -1.5 to *ca.* -2.2 , and the plot for m -[$^3\text{H}_1$]toluene is very similar. If the values of H_0 employed are those selected by Gold and Satchell from the Hammett and Deyrup data (which allow a wide choice in this region of acidity), then for dedeuteration the plot of $\log k$ against H_0 is roughly a straight line of slope -1.4 , while for detritiation it is a curve with slope varying from *ca.* -1.5 to *ca.* -2.0 . For p -[^3H]toluene the corresponding plot (Long and Paul's values for

⁷ Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3324.

⁸ Lauer, Matson, and Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6433.

⁹ (a) Gold and Satchell, *J.*, 1955, 3609, 3622; (b) Gold, Lambert, and Satchell, *Chem. and Ind.*, 1959, 1312.

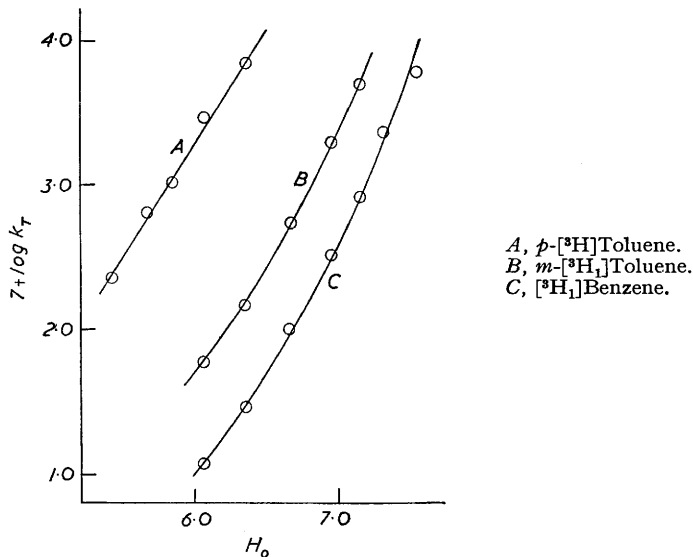
¹⁰ Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, Chap. VI.

¹¹ Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

¹² Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

H_0 again being used) approximates to a straight line of slope -1.6 ; the equivalent line for dedeuteration has a slope of -1.55 . We are unable to accept that there is any significant relation between the rate of exchange and the H_0 acidity function.

For some other aromatic compounds, particularly phenols, more satisfactory $\log k_D-H_0$ plots appear to be obtained,⁹ and in considering mechanisms it could be argued that benzene and toluene are abnormal in behaviour.* However, there is considerable uncertainty about the precise mechanistic significance of linear $\log k-H_0$ plots even when these have unit slope,¹³ and in our opinion there is no firm ground for the belief that such plots exclude the possibility of covalent participation of a solvent molecule in the rate-determining step. (We hope later to discuss the meaning of linear dependence of $\log k$



on H_0 in detail.) It has, indeed, recently been demonstrated that detritiation of 1,3,5-trimethoxy[²⁻³H]benzene by aqueous weak acids is general-acid catalysed,¹⁴ so that proton transfer from catalysing acid to substrate is involved in the rate-determining step, and it is unlikely that a different mechanism operates for less reactive aromatic compounds in concentrated strong acids. In our opinion, all the experimental features of aromatic hydrogen exchange (including the small solvent isotope effects recently reported^{9b}) can be interpreted in terms of the orthodox mechanism (2).

Recently, however, R. D. Brown has suggested a general mechanism (3) for electrophilic aromatic substitution, in which σ -complexes (Wheland intermediates) of type (VI) are not involved.¹⁵ The intermediates (IV) and (V) are charge-transfer complexes, E^+ is an electrophil (as in the original papers, only the case of a positively-charged electrophil is discussed), and B is a base.

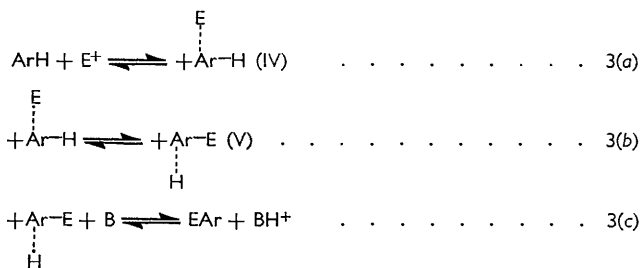
* The satisfactory $\log k_D-H_0$ plots obtained for some phenols in aqueous sulphuric acid must, however, be largely fortuitous, since protonation of diarylethylenes in this medium is not governed by H_0 (Deno, Groves, and Saines, *J. Amer. Chem. Soc.*, 1959, **81**, 5790), and this process is more closely analogous to the aromatic hydrogen exchange than is protonation of the nitrogen and oxygen bases used to measure H_0 .

¹³ Long and Paul, *Chem. Rev.*, 1957, **57**, 935; Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507; Deno and Perizzolo, *J. Amer. Chem. Soc.*, 1957, **79**, 1345.

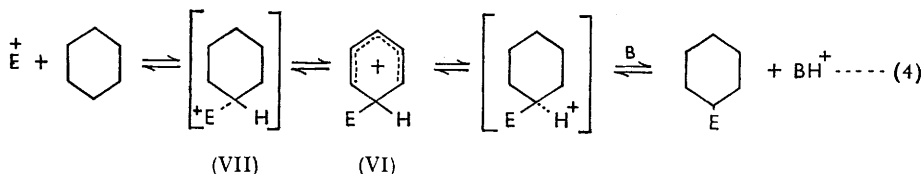
¹⁴ Kresge and Chiang, *J. Amer. Chem. Soc.*, 1959, **81**, 5509.

¹⁵ R. D. Brown, *J.*, 1959, 2224, 2232.

Any one of the steps (a), (b), and (c) may be rate-determining, and the structure (VI) is considered to represent a point of maximum potential energy between the complexes (IV) and (V).



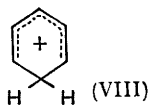
R. D. Brown lists six features of electrophilic aromatic substitutions which have to be taken into account in devising a mechanism. One of these is the conclusion^{3,9} that linear dependence of $\log k$ on H_0 rules out the possibility of a solvent molecule's being covalently involved in the transition state in aromatic hydrogen exchange, a conclusion which, as we have indicated above, is unjustified. All the other five features are, in our opinion, equally consistent with the orthodox mechanism (4) (in which the entities in



brackets are transition states). It should be stressed that the rate-determining transition state does not coincide in structure with the intermediate (VI), but is removed to a greater or lesser extent from it towards the reactants or products (compare, *e.g.*, ref. 16). The fact that calculations based on the new theory give a better fit to rate data for nitration of polynuclear aromatics than do calculations^{16a} of atom localization energies for intermediates of the type (VI) is not sound evidence in favour of the theory, since the fit results from using two disposable parameters to characterise the nature of the electrophil E and the transition state, and there is little doubt that the fit of calculations based on the assumption of an intermediate of type (VI) would also be improved by introducing two parameters to allow for displacement of the transition state from the intermediate along the reaction co-ordinate. Indeed, it is difficult to see how rate studies can distinguish between the two theories, since, to take the case in which the C-H bond is not broken in the rate-determining step, the transition state in mechanism (3) is described¹⁵ as predominantly a "resonance hybrid" of E-ArH⁺ structures in which the bond links the electrophil in turn to each carbon atom of the aromatic system, these bonds being energetically negligible except for that to the central carbon (the carbon bearing the proton to be displaced), with a small contribution also from E⁺...ArH and other structures; the bond between E and the central carbon atom is not strong enough to exclude this atom from the conjugation of the aromatic system, but the extent of conjugation with the aromatic system is reduced compared with the original aromatic compound. Now this is precisely the description of the transition state (VII) of the orthodox mechanism (4), and any difference seems to us to be merely one of terminology. To the extent that we are correct in this assertion, R. D. Brown's calculations for the transition state of mechanism (3) are equally valid for the orthodox mechanism (4).

¹⁶ (a) Dewar, *J.*, 1956, 3581; (b) Mason, *J.*, 1958, 4329; Mason, *J.*, 1959, 1233; Hammond, *J. Amer. Chem. Soc.*, 1955, 77, 334.

A real distinction between the two theories is possible in principle, not from rate studies but from structural investigation of the intermediates isolated or detected in electrophilic aromatic substitutions. R. D. Brown suggests that these have unsymmetrical structures of type (IV) in which "no loss of aromaticity occurs," rather than the usually assumed structures of type (VI). In most cases the structures have not been examined, but the complexes formed by some polynuclear hydrocarbons in strong acids have been studied in detail, and their spectra have been shown to be quantitatively in agreement with those expected for structures based on the prototype (VIII);^{17,18} in particular, proton-spin resonance has shown that the protonated carbon atom has aliphatic character.¹⁸



We conclude that there is no reason at present to discard the orthodox mechanism of electrophilic aromatic substitution in favour of a more complex one.

EXPERIMENTAL

Materials.—The tritiated aromatic compounds were prepared from the appropriate Grignard reagents, derived from carefully purified aryl bromides, by adding to the ethereal solution a molar proportion of tritiated water (20–50 mc/ml.) followed by excess of ordinary water. The usual working-up was followed by fractional distillation. The activities of the products calculated by assuming quantitative use of the tritium would be [³H₁]benzene 2.5 mc/g., *m*-[³H]toluene 5 mc/g., *p*-[³H]toluene 5 mc/g., but the actual activities must have been smaller, possibly by as much as a factor of 5.

Toluene ("sulphur-free") used for extractions and in making solutions for liquid scintillation measurements was passed through a column of activated alumina before use.

Kinetics.—To ca. 260 ml. of sulphuric acid in a 1-l. flask was added a small quantity of [³H]benzene (<0.15 ml.) or [³H]toluene (<0.065 ml.). (Preliminary experiments showed that if these quantities were much exceeded, particularly with the more aqueous acids, then first-order rate coefficients were not satisfactorily constant; this was probably mainly because the solubility limit was exceeded, even though the system appeared homogeneous to the eye.) The flask was sealed, and shaken mechanically for 5–10 min., after which 5 aliquot parts were transferred by means of a 50-ml. pipette to boiling-tubes of 51–53 ml. capacity. (Satisfactory rate coefficients were not obtained if the vapour space above the solution was too large.) The exact quantity of mixture in each tube need not be known; a pipette drainage time of 1½ min. was found by weighing to lead to delivery of equal quantities each time. The tubes were sealed with Teflon-sleeved stoppers and placed together in a thermostat at 25.0°, maintained to within ±0.02°; the first tube was removed after ca. 20 min., and others at appropriate intervals. The contents of each tube were transferred quickly at a recorded time to a 250-ml. long-necked conical flask containing a fixed amount of toluene (ca. 10.0 ml.) and ca. 100 g. of crushed ice, the last traces being washed in with water. The flask was sealed with a Teflon-sleeved glass stopper and, held upright, was shaken mechanically for 15 min. The toluene layer was then separated, washed (successively with water, aqueous 10% sodium hydroxide, and water), and dried (Na₂SO₄). Some extracts, more particularly in experiments with the [³H]toluenes, were slightly yellow, and the colour was removed with a small amount of activated charcoal. (Alternatively, in the case of experiments on [³H]toluene, the extract was distilled, the colour then being left in the residue; this led to results identical with those obtained when charcoal was used. Separate experiments showed that charcoal did not significantly change the specific activity of tritiated toluene or benzene.) A weighed amount of the extract (usually 2–5 g.) was placed in the counting vessel along with a fixed quantity (ca. 20 ml.) of a solution of 4 g. of *p*-terphenyl and 0.01 g. of 1,4-di-(5-phenyl-2-oxazolyl)benzene in 1 l. of toluene, and the activity was recorded as a galvanometer deflection, *D*_{obs}.¹⁹ The weight of extract used for each analysis

¹⁷ Gold and Tye, *J.*, 1952, 2172, 2184; Dallinga, Mackor, and Verrijn Stuart, *Mol. Phys.*, 1958, **1**, 123; Mackor, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66; Verrijn Stuart and Mackor, *J. Chem. Phys.*, 1957, **27**, 826.

¹⁸ Maclean, van der Waals, and Mackor, *Mol. Phys.*, 1958, **1**, 247; Aalsberg, Hoiijtink, Mackor, and Weijland, *J.*, 1959, 3055.

¹⁹ Eaborn, Matsukawa, and Taylor, *Rev. Sci. Instr.*, 1957, **28**, 725; Matsukawa and Eaborn, *Research (Correspondence)*, 1956, **9**, S37.

was not varied by more than a few units % throughout a run, and the deflection, D , per 1 g. of extract (the "specific deflection") was used in calculating rate constants. The amount of extract taken was such that two independent sets of measurements could be carried out on each group of extracts.

When [^3H]benzene was being used, benzene was used for extractions in the early experiments, but extractions with toluene gave identical results, and this solvent was subsequently used throughout.

The possibility was investigated that by-products of the reaction might be such as to affect scintillation measurements (most probably as quenchers), and, by surviving the extraction process, give rise to false results. A sample of ordinary benzene was treated with 84.3% sulphuric acid under conditions used for the kinetic studies, and after 30 min. (in which time more than 85% of exchange would have occurred, and sulphonation would be more serious than in any of the runs with benzene) was recovered by the usual toluene-extraction procedure. A quantity of this extract (5 ml.) had an effect identical (within 1%) with that of an equal quantity of pure toluene on the deflection caused by a fixed amount of tritiated toluene.

Rate constants were calculated from the equation $k_T t = 2.303 \log D_0 / (D_0 - D_t)$, where D_0 is the specific deflection for the first sample removed, and D_t that for a sample removed at time t . (The assumption that the deflection would ultimately fall to zero, as expected from the small ratio of aromatic compound to hydroxylic solvent species, was checked in a few cases in which samples were kept at 25° for ten times the half-life.) Runs were normally taken to more than 70% completion. Individual rate coefficients varied from the mean by less than $\pm 3\%$ (usually $\pm 2\%$), and the mean rate coefficients (usually determined from the slope of a $\log D_T - t$ plot) could be reproduced to within $\pm 2\%$. In the following typical runs, the first involving [^3H]benzene and the second p -[^3H]toluene, D_{obs} is the deflection observed for the weight of extract taken, and D is the deflection per g. of extract.

(i) [H_2SO_4] = 81.14 wt.-%.

Time (hr.)	0	0.50	1.00	2.25	4.00
Wt. of extract (g.)	4.107	4.122	4.095	4.100	4.107
D_{obs} (mm.)	54.3	46.3	39.1	26.4	15.2
D (mm.)	13.22	11.24	9.55	1.44	3.70
$10^7 k_T$ (sec. $^{-1}$)	—	895	909	894	884

(ii) [H_2SO_4] = 73.24 wt.-%.

Time (hr.)	0	0.40	0.90	1.50	2.25
Wt. of extract (g.)	4.043	4.061	4.057	4.069	4.050
D_{obs} (mm.)	75.6	49.4	28.4	15.2	6.9
D (mm.)	18.70	12.17	7.00	3.74	1.70
$10^7 k_T$ (sec. $^{-1}$)	—	2980	3030	2990	2960

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