47. *Aromatic Reactivity. Part XIII.*[1] *Effects of Methyl and t-Butyl Groups in Aromatic Detritiation.*

By C. Eaborn and R. Taylor.

We have measured the rates of detritiation of tritiobenzene and *o*-, *m*-, and *p*-tritio-toluene and -t-butylbenzene in one or more of the following media: aqueous sulphuric acid, acetic acid containing aqueous sulphuric acid, trifluoroacetic acid containing aqueous perchloric acid, and trifluoroacetic acid containing aqueous sulphuric acid.

The spread of rates changes markedly as the medium is varied, probably increasing as the solvating power of the media decreases. The methyl group activates the *para*-position more or less than the t-butyl group, depending on the medium, but it activates the *meta*-position less than the t-butyl group in all cases. The results are discussed in terms of hyperconjugation and solvation influences on the effects of alkyl groups in aromatic substitution.

The accuracy of some earlier reports on preparation of *m*-bromo-t-butylbenzene is questioned.

PREVIOUS studies of aromatic hydrogen-exchange reactions of alkylbenzenes have been reviewed by Lauer, Matsen, and Stedman.[2,3] We now report measurements of the rates of detritiation of monotritiated benzene, toluene, and t-butylbenzene by aqueous sulphuric acid, alone or in acetic or trifluoroacetic acid, and by aqueous perchloric acid in trifluoroacetic acid.

RESULTS

The results are listed in the Table. As we have shown,[4] when sulphuric acid is present in the reaction medium for aromatic hydrogen-exchange reactions, the extent of sulphonation must be assessed if accurate results are to be obtained, and the Table lists the observed first-order rate constants, $k_{\text{obs.}}$, in sec.$^{-1}$, the first-order rate constants, $k_{\text{sulph.}}$, separately measured for sulphonation or estimated by reasonable assumptions specified in footnotes to the Table, and the corrected first-order rate constants, $k_{\text{ex.}} = (k_{\text{obs.}} - k_{\text{sulph.}})$, for the exchange reaction, along with the rate factor, *f*, denoting the rate of exchange relative to that of [$^3H_1$]benzene. Little error would be introduced by neglecting sulphonation for benzene, *p*-tritiotoluene, and *p*-tritio-t-butylbenzene, but sulphonation is a serious competitor for the *meta*-alkylbenzenes (since the exchange is taking place at the least reactive position of the ring), and accounts for almost half of the observed rate for *m*-tritiotoluene in the trifluoroacetic acid–water–sulphuric acid medium used. Further, in this medium, sulphonation both removes an appreciable proportion of the sulphuric acid present and produces a significant amount of water, and this leads in the case of *m*-tritiotoluene to a fall-off in the integrated rate constant during a run, so that the value of $k_{\text{obs.}}$ must be obtained by extrapolation to zero reaction (cf. ref. 5). (With *m*-tritio-t-butylbenzene no fall-off is detected because of the higher $k_{\text{ex.}}/k_{\text{sulph.}}$ ratio.) Values of $k_{\text{ex.}}$ and *f* for the *meta*-compounds in this medium are thus less reliable than in the other media, but we have no reason to believe that they are more than 10% in error. Exchange in trifluoroacetic acid containing perchloric acid seems free from interfering side-reactions (see Experimental section). It should be stressed that any uncertainties introduced into values of *f* by sulphonation, or, in the case of the *para*-compounds by the large difference in rate between them and benzene, are not such as to affect the main features of the activation pattern as they are discussed below. In particular, the reactivities of *p*-tritio-toluene and -t-butylbenzene relative to one another are free from significant error.

Since the medium clearly exerts a major influence on the rate factors we cannot compare our results directly with those of previous workers. Our values of f_m^{Me} appear rather large

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[1] Part XII, Eaborn and Pande, *J.*, 1961, 297.

[2] Lauer, Matsen, and Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6433.

[3] Lauer, Matsen, and Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6437.

[4] Eaborn and Taylor, *J.*, 1960, 3301.

[5] Dallinga, Verrijn-Stuart, Smit, and Mackor, *Z. Elektrochem.*, 1957, **61**, 1019.

Detritiation of $X{\cdot}C_6H_4{\cdot}{}^3H$ *compounds in various media at* 25°.

X	71·34 wt.-% H_2SO_4		$AcOH-H_2O-H_2SO_4$ [a] (26·0)-(34·0)-(40·0)			
	$10^7k_{ex.}$	f	$10^7k_{obs.}$	$10^7k_{sulph.}$	$10^7k_{ex.}$	f
H	—	1	9·32	0·3 [b]	9·0	1
m-Me	—	5·0 [c]	63·4	18·6	44·8	5·0
m-Bu^t	—	—	95·8	12 [d]	84	9·3
o-Me	—	250 [e]	2763	18·6	2744	305
o-Bu^t	—	170 [e]	—	—	—	—
p-Me	1042	250 [c]	2835	18·6	2816	313
p-Bu^t	748	180	2079	12 [d]	2067	230

X	$CF_3{\cdot}CO_2H-H_2O-H_2SO_4$ [a] (95·31)-(2·21)-(2·48)				$CF_3{\cdot}CO_2H-H_2O-HClO_4$ [a] (92·04)-(5·45)-(2·51)	
	$10^7k_{obs.}$	$10^7k_{sulph.}$	$10^7k_{ex.}$	f	$10^7k_{ex.}$	f
H	3·74	<0·15	3·6	1	14·3	1
m-Me	59	26	33	9·2	103	7·2
m-Bu^t	131	17	114	32	339	23·7
o-Me	1974	26	1948	541	4720	330
o-Bu^t	—	—	—	—	5620	393
p-Me	2552	26	2526	702	4480	313
p-Bu^t	3125	17	3108	863	5530	387

[a] The composition of the medium is given (in parentheses) as mole-percentages. For the $AcOH-H_2O-H_2SO_4$ medium the composition is approximate, and the exact composition is specified in the Experimental section. [b] The rate of sulphonation was too low for measurement, and a value of 1/60 of that for toluene has been assumed. A value of 1/33 applies in aqueous sulphuric acid (cf. Eaborn and Taylor, *J.*, 1960, 1480), and *ca.* 1/150 in some $CF_3{\cdot}CO_2H-H_2O-H_2SO_4$ media we have used. [c] Ref. 4. [d] The value of $k_{sulph.}$ is assumed to be 2/3 of that for toluene; this ratio applies in $CF_3{\cdot}CO_2H-H_2O-H_2SO_4$. [e] From unpublished results by Mr. R. Baker for a slightly different medium.

when compared with results for deuteration in trifluoroacetic acid [2] ($f_p^{Me} = 420$; $f_m^{Me} = 4$) or for de-deuteration in trifluoroacetic acid containing sulphuric acid [6] ($f_p^{Me} = 350$; $f_m^{Me} = 3{\cdot}2$). However, the value of f_p^{Me} for the deuteration is subject to a rather large error,[2] estimated to be not more than ±25%, and a value of 5·1, calculated from figures for *p*-xylene in this medium,[2] may be more accurate. Again, the value of f_m^{Me} for the de-deuteration in trifluoroacetic–sulphuric acid was obtained, not by direct comparison of *p*-deuterotoluene and deuterobenzene in one medium, but from an extrapolation based on a dependence of rate on acidity function,[6] while with *m*-deuterotoluene, sulphonation (which, from our experience with somewhat similar media, we believe must have been extensive) was admitted to have caused difficulties, which were not defined. Stock and H. C. Brown [7] have recently shown that, for a large variety of electrophilic aromatic substitutions for which reliable partial rate factors are available, the value of the ratio $(\log f_p^{Me})/(\log f_m^{Me})$ lies between 3·18 and 4·72. Our figures give values of 3·43 ($H_2O-H_2SO_4$), 3·57 ($AcOH-H_2O-H_2SO_4$), 2·95 ($CF_3{\cdot}CO_2H-H_2O-H_2SO_4$), and 2·91 ($CF_3{\cdot}CO_2H-H_2O-HClO_4$) for this ratio; the data for deuteration in trifluoroacetic acid give a ratio of 3·60 if f_m^{Me} is taken as 5·1 (but a ratio of 5·04 if f_m^{Me} is taken as 3·2—see above).

The ratio $(\log f_p^{Bu^t})/(\log f_m^{Bu^t})$ has the values 2·44 ($AcOH-H_2O-H_2SO_4$), 1·95 ($CF_3{\cdot}CO_2H-H_2O-H_2SO_4$), and 1·88 ($CF_3{\cdot}CO_2H-H_2O-HClO_4$). For a range of electrophilic aromatic substitutions for which data were previously available [8] the ratio lay between 2·27 and 3·82.

DISCUSSION

The main features of our results which require detailed discussion are as follows: (i) The spread of rates varies markedly with the medium. (ii) The activating influence of *p*-methyl and *p*-t-butyl groups can follow either the Baker–Nathan order, Me > Bu^t, or the inductive order, Bu^t > Me, depending on the medium. (For deuteration in trifluoroacetic acid [2] and for de-deuteration in trifluoroacetic–sulphuric acid,[6] the effects of the two groups were identical within experimental error.) Reversal of the order on

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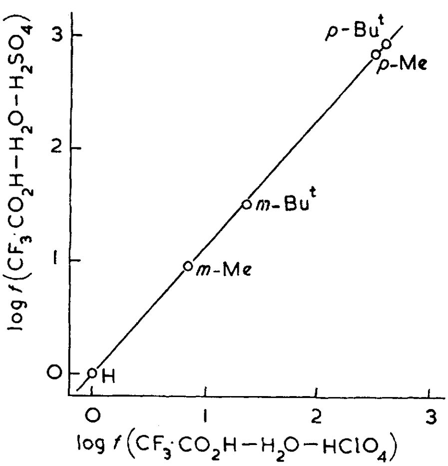
[6] Mackor, Smit, and Van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.
[7] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3323.
[8] Brown and Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 5621.

changing the medium has not, so far as we are aware, been observed previously either for ring substitutions or for side-chain reactions which involve rate-determining formation of a carbonium-ion centre adjacent to the ring (though such a dependence has been observed for *meta*-alkyl groups in some reactions of the latter type [9,10]). The only electrophilic aromatic substitution for which an inductive order has previously been reported is nitration in acetic acid containing 10% of water.[11] (iii) For *meta*-substituents the activation order in all the media is clearly $Bu^t > Me$. This order operates in all of the relatively few electrophilic aromatic substitutions for which it has been measured.[8]

We cannot interpret completely the variation in the spread of rates and in the detailed pattern of rate factors as the medium is changed within the range we have used, because so many factors vary together. We can, however, indicate what results we should expect if one property of the medium could be changed independently of the others. These would be as follows: (*a*) If the concentration of the catalysing acidic species could be increased while the solvating power of the medium were kept constant, the rates would increase but the rate factors would remain constant. (Approximation to this state of affairs is probably realised in aqueous sulphuric acid over a small range of acid concentration; cf. ref. 4). (*b*) If the nature of the acidic species could be changed while the solvating power of the medium remained constant, then as the acidity of the catalysing species decreased (and the rates also decreased) so the partial rate factors would increase, because the less electrophilic acidic species would be more selective between the different aromatic compounds (or, in other words, the π-electrons of the ring would be more involved in forming the Ar–HA bond, and the electron-deficiency on the ring in the transition state would be greater). But a linear free-energy relation could be expected between the effects of the substituents in the two media. Change from $CF_3{\cdot}CO_2H{-}H_2O{-}HClO_4$ to $CF_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$, at the compositions specified in the Table, may approximate to this state of affairs; the rate factors are larger in the latter medium, but a linear free-energy relation exists between the rate factors in the two media (see Figure). (*c*) If the nature of the acidic species could be kept constant while the solvating power of the medium were decreased, the spread of rates would increase. (As the excess of positive charge on the ring in the transition state is less effectively stabilized by solvation, so stabilization of the charge by electron-release from the substituents will increase in importance.) A linear free-energy relation might not hold between the substituent effects in the two media, since (i) the electrical effects of the substituents may be modified internally by specific solvent effects (cf. ref. 9), (ii) polar influences which operate through the medium will be modified as its dielectric constant is changed, and (iii) any steric hindrance to solvation will become less important. (The increase in the spread of rates on changing the medium in the series $H_2O{-}H_2SO_4$, $AcOH{-}H_2O{-}H_2SO_4$, $CF_3{\cdot}CO_2H{-}H_2O{-}HClO_4$, $CF_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$, probably arises mainly from a fall in the solvating power of the media. The relatively small amount of aqueous sulphuric acid in the trifluoroacetic acid makes the last medium less solvating than the $AcOH{-}H_2O{-}H_2SO_4$ mixture.)



There is considerable controversy about the origin of the activating effects of alkyl

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[9] Shiner and Verbanic, *J. Amer. Chem. Soc.*, 1957, **79**, 369.

[10] Schubert, Craven, Minton, and Murphy, *Tetrahedron*, 1959, **5**, 194.

[11] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **162**, 291.

groups in electrophilic aromatic substitution and related reactions.[12-16] The relative effects of methyl and t-butyl groups in electrophilic aromatic substitutions are most often explained by assuming that release of electrons by the inductive effect is in the order $Bu^t > Me$ but that when the C–H bonds of the methyl group are conjugated with a centre of excess positive charge in the ring or in a side chain, hyperconjugation from these bonds can lead to the overall order $Me > Bu^t$ for electron-release.* The activating power for *meta*-groups will then normally be in the order $Bu^t > Me$, but for *para*-groups in the reverse order, though the extent to which hyperconjugation operates may, the argument runs, depend on the electron-demand.[13-15] Thus, in molecular bromination, the pronounced Baker–Nathan order ($f_p^{Me} = 2420$, $f_p^{Bu^t} = 752$, in 85% acetic acid [17]) may result from a large demand for electrons from the alkyl groups to assist polarization and ultimate ionization of the attacking bromine molecule, an electron-demand which shows up in the large f_p^{Me} factor. In nitration in 90% acetic acid,[11] on the other hand, the electron-demand on the substituents is smaller because the highly reactive nitronium ion makes use of the permanent polarization of the substituted ring, and the inductive order of activation results ($f_p^{Me} = 58$, $f_p^{Bu^t} = 75$); [14] the smallness of the electron-demand when compared with that in molecular bromination is reflected in the relatively small value of f_p^{Me}. There are difficulties in this simple picture; for example, in ionic bromination by Br^+ or a related species in aqueous dioxan,[18] the Baker–Nathan order applies, although the electron-demand as measured by f_p^{Me} (*i.e.*, 59) is similar to that in nitration, and it seems that the value of f_p^{Me}, while, by definition, a guide to the overall electron-demand of any reaction, may not necessarily indicate the demand on the time-variable effects of substituents (cf. ref. 19).

Our results within themselves can be nicely explained by use of the concept of hyperconjugation. The greater inductive effect of the t-butyl group results in an inductive order for the *meta*-groups, but hyperconjugation from the methyl group brings the overall effects of the *para*-groups near to equality, and allows the *p*-methyl group to have a greater activating effect than *p*-t-butyl in some media. The change from a Baker–Nathan order to an inductive order as the dielectric constant of the medium is lowered may simply reflect the increase in the direct-field component of the inductive effect.†

The principal objection to relying on C–H hyperconjugation to explain Baker–Nathan orders is that physical measurements, particularly of spectral transition energies, indicate that electron-release by t-butyl groups is about equal to or rather greater than that by the methyl group,[10,20,21] and this has led to suggestions that the Baker–Nathan order in chemical reactions results from steric hindrance by the t-butyl group to solvation of electron-deficient centres in the transition state.[10,20-22] The most compelling single item of evidence is Kosower and Skorcz's observation that methyl and t-butyl groups in the

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* For simplicity we neglect consideration of C–C hyperconjugation but it will be appreciated that any observed effect of hyperconjugation must be the difference between C–H hyperconjugation in the methyl, and C–C hyperconjugation in the t-butyl group.

† The medium effect could also be interpreted, less simply, along lines indicated by Shiner and Verbanic [9] in discussing *meta*-alkyl groups.

[12] " Conference on Hyperconjugation " (Co-Chairmen: V. J. Shiner and E. Campaigne), Pergamon Press Ltd., London, 1959; de la Mare, *J. Roy. Inst. Chem.*, 1959, **83**, 634.

[13] Berliner, *Tetrahedron*, 1959, **5**, 202; Berliner and Chen, *J. Amer. Chem. Soc.*, 1958, **80**, 343.

[14] Berliner and Berliner, *J. Amer. Chem. Soc.*, 1954, **76**, 6179.

[15] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782; de la Mare and Robertson, *J.*, 1948, 100; de la Mare, *J.*, 1949, 2871.

[16] Burawoy and Spinner, *J.*, 1954, 3752; 1955, 2085; Spinner, *J.*, 1956, 1590.

[17] Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421.

[18] de la Mare and Harvey, *J.*, (*a*) 1956, 36; (*b*) 1957, 131.

[19] Yukawa, *Bull. Chem. Soc. Japan*, 1959, **32**, 971; Bekhum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[20] Schubert and Sweeney, *J. Org. Chem.*, 1956, **21**, 119.

[21] Kosower and Skorcz, *J. Amer. Chem. Soc.*, 1960, **82**, 2195.

[22] Clement and Naghizadeh, *J. Amer. Chem. Soc.*, 1959, **81**, 3154.

4-position have identical effects on the position of the charge-transfer band of 1-methylpyridinium iodides in chloroform.[21] The transition involved is to a state in which the pyridinium ring is essentially uncharged from a ground state in which the nitrogen atom carries a unit positive charge; if C–H hyperconjugation operated, the 4-methyl group would be expected to stabilize this ground state relative to the excited state markedly more than the 4-t-butyl group does, and thus increase the transition energy to a greater extent. (The electron-demand, as measured by the effect of substituents on the transition energy, is very large.) Kosower and Skorcz suggest, as the simplest interpretation of their results, that the electrical effects of alkyl groups are the same and largely depend on the nature of the bond by which they are attached to a given molecule. They further suggest that any deviations from equality of effect, as in chemical reactions, must be explained in other terms, such as steric hindrance to solvation.

In view of the markedly greater activation of the *meta*-position by a t-butyl than by a methyl group in detritiation, as in some other electrophilic reactions, it is unsatisfactory when considering chemical reactivities to regard these groups as having similar electron-releasing properties. To explain our results in terms of steric hindrance to solvation, excluding hyperconjugation from consideration, we should have to assume that the inherent electron-release is clearly in the order $\mathrm{Bu^t} > \mathrm{Me}$, and that there is negligible steric hindrance to solvation by the *m*- but considerable hindrance by the *p*-t-butyl group. The change in the activation order p-Me $>$ p-$\mathrm{Bu^t}$ to p-Me $<$ p-$\mathrm{Bu^t}$ could then follow as the medium is changed in the direction of decreasing solvating power.* We are not satisfied with this interpretation, partly because the ratio $f_o^{\mathrm{Me}}/f_p^{\mathrm{Me}}$ is very similar to the ratio $f_o^{\mathrm{Bu^t}}/f_p^{\mathrm{Bu^t}}$, both in trifluoroacetic acid containing sulphuric acid and in aqueous sulphuric acid.[23] If steric hindrance to solvation were as important as it would have to be to explain the large reduction in the relative activation by t-butyl and methyl groups on changing from the *meta*- to the *para*-position, then the latter ratio would be expected to be markedly smaller than the former, since the *o*-t-butyl group, in addition to hindering solvent approach to the ring carbon to which it is attached, should also directly hinder solvation at the reaction centre, near which a large proportion of the excess of positive charge must lie in the transition state.

It seems to us most likely that both hyperconjugation and steric effects operate to determine the effects of *p*-methyl and *p*-t-butyl groups in detritiation. Certainly we feel that hyperconjugation must be invoked in interpreting the influence of alkyl groups on reaction rates, in spite of the difficulty of reconciling this with the influence of the groups on spectral transition energies. One source of difference between effects of substituents on reaction rates and on transition energies is that in a reaction nuclei can move to minimise the free energy at every stage of the progress from reactants to transition state, but the positions of the nuclei cannot change in the time of a spectral transition.† If a transition occurs from a ground state in which hyperconjugation would not be expected, to an excited state in which it would, bond lengths and bond angles cannot adjust to those which are most appropriate for operation of hyperconjugation, and this will act as a restriction on the ease of the electron migrations involved, even though these are not themselves forbidden by the Franck–Condon principle. Conversely, if hyperconjugation is present in the ground state, as would be expected in the case of alkylpyridinium methiodides, then the nuclear positions cannot readjust to conform with disappearance of hyperconjugation in the excited state, and the hyperconjugation is to some extent frozen into the excited state,

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* Nothing of significance emerges from attempts to attribute the observed variations to a particular group by analysis of various log *f* ratios. For example, if the steric effect of the *p*-t-butyl group were the only important variant, the ratio $(\log f_p^{\mathrm{Bu^t}})/(\log f_m^{\mathrm{Bu^t}})$ would be expected to vary more than $(\log f_p^{\mathrm{Me}})/(\log f_m^{\mathrm{Me}})$, while the reverse should be true if the hyperconjugative effect of the *p*-methyl group were the only important variant. In fact both ratios vary to much the same extent as the medium is changed.

† The effect of this on solvation has frequently been discussed (see, *e.g.*, refs. 20 and 21).

[23] Baker and Eaborn, unpublished work.

and its existence in the ground state will thus be hidden. The apparent discordance between effects of alkyl groups in reaction rates and spectral transitions may in part originate in this freezing. The energy involved in the freezing will be small,[24] but the differences between methyl and t-butyl groups which we seek to explain, are themselves small.

EXPERIMENTAL

m-*Bromo-t-butylbenzene*.—Bromine (48 g., 0·3 mole) was added dropwise during 2 hr. to a stirred, refluxing solution of *p*-t-butylacetanilide [25] (53 g., 0·27 mole) in glacial acetic acid (500 ml.). The mixture was refluxed for 6 hr. more and set aside for 18 hr. It was then added to water, and the suspension was decolorised with sodium hydrogen sulphite. The solid was filtered off, washed with water, and recrystallised from aqueous ethanol to give 2-bromo-4-t-butylacetanilide (68·5 g., 91·5%), m. p. 159·5°.

de la Mare and Harvey report m. p. 158° for 2-bromo-4-t-butylacetanilide.[18b] Previous workers have reported 153°,[26] 138·5°,[27] and 138°,[28] and it seems that they were actually dealing with a mixture of the 2-bromo-derivative with unchanged *p*-t-butylacetanilide. Thus on deacetylation and deamination of their product, Cadogan, Hey, and Williams [28] obtained t-butylbenzene as well as *m*-bromo-t-butylbenzene, and assumed that the former product arose from a removal of the bromine atom *ortho* to the diazonium group; from our 4-amino-2-bromo-t-butylbenzene we obtained no t-butylbenzene. We made a few mixtures of *p*-t-butylacetanilide and its 2-bromo-derivative and found them to melt fairly sharply between 135° and 155°.

The 2-bromo-4-t-butylacetanilide was converted into 2-bromo-4-t-butylaniline,[26] b. p. 151°/17 mm., and this was deaminated to give *m*-bromo-t-butylbenzene [28] (89%), b. p. 113°/23·5 mm.

Preparation of Tritiated Compounds.—The preparations of some of the tritiated aromatic compounds have been described; [4] the three tritiated t-butylbenzenes (all *ca.* 5 mc./g.) and *o*-tritiotoluene (*ca.* 5 mc./g.) were made similarly from the aryl bromides. The activities given are maximum values, which may be up to five times too large (cf. ref. 4).

Reaction Media.—" Reagent Grade " acetic acid (May and Baker Ltd.) was purified by Orton and Bradfield's method [29] and fractionally distilled, to give material of m. p. 15·00° calculated [30] to contain 0·8% of water. This acid (631 g.) was mixed with 86·74 wt.-% aqueous sulphuric acid (4828 g.) to give the stock mixture A. For kinetic work 50 ml. portions of this acid were mixed with 10 ml. of 99·2% acetic acid (see below). (The composition of the resulting medium is completely specified by the description we have given of its preparation; we did not measure the density of the medium A, and to calculate the *approximate* molar composition given in the Table we have assumed volume additivity on mixing acetic acid and aqueous sulphuric acid in preparing medium A.)

Anhydrous trifluoroacetic acid was prepared by fractionally distilling the Eastman " White Label " acid (1000 g.) from sulphuric acid (50 g.). The fraction of b. p. 71°/755 mm. was found by titration against alkali to be 100·0% pure. For the kinetics, either (i) the acid (169·51 g.) was mixed with 97·60 wt.-% aqueous sulphuric acid (3·89 g.) and water (0·53 g.) (to give a medium of molar composition, $CF_3{\cdot}CO_2H$, 95·31; H_2O, 2·21; H_2SO_4, 2·48%), or (ii) the acid (194·40 g.) was mixed with 72·02 wt.-% aqueous perchloric acid (6·48 g.) (to give a medium of molar composition, $CF_3{\cdot}CO_2H$, 92·04; H_2O, 5·45; $HClO_4$, 2·51%).

Exchange-rate Measurements.—The general procedures have been described.[4, 31]

For reactions in $CH_3{\cdot}CO_2H$–H_2O–H_2SO_4, 50 ml. of medium A (see above) was added (a pipette drainage time of 2½ min. being necessary for reproducibility) to 10 ml. of a solution of the tritiated aromatic compound (*ca.* 1 ml./500 ml.) in 99·2% acetic acid in a tube of 62—63 ml.

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[24] Mulliken, *Tetrahedron*, 1959, **6**, 68.
[25] Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, **16**, 608
[26] Gelzer, *Ber.*, 1888, **21**, 2944.
[27] Crawford and Stewart, *J.*, 1952, 4443.
[28] Cadogan, Hey, and Williams, *J.*, 1954, 3352.
[29] Orton and Bradfield, *J.*, 1927, 963.
[30] de Visser, *Rec. Trav. chim.*, 1893, **12**, 101.
[31] Eaborn and Taylor, *J.*, 1960, 1480.

capacity. (With a larger vapour space first-order rate coefficients were not satisfactorily constant during a run.) The tube was closed with a Teflon-sleeved standard-taper stopper and placed in a thermostat at 25·0°. Five such tubes were used for each run. Subsequent procedure was as previously described,[4] toluene being used for the extractions. (Initially benzene and t-butylbenzene were used for extraction in reactions involving [$^3H_1$]benzene and [*x*-^{3}H]-t-butylbenzene, but it was later found that use of toluene gave the same results.) Sometimes the extract was slightly yellow, and it was then decolorised with a small amount of activated charcoal; when the extraction solvent was the same as the compound under study, distillation was sometimes used, with identical results.

For runs in trifluoroacetic acid containing sulphuric acid or perchloric acid, a weighed amount (*ca.* 0·1 ml.) of the tritiated aromatic compound was dissolved in a weighed amount (*ca.* 5·5 ml.) of the medium described above. Aliquot parts (1 ml.) were pipetted into drawn-out glass tubes of *ca.* 1·2 ml. capacity, and the tubes were sealed and placed in the thermostat together. The residue of the solution was then weighed so that the weight per aliquot part was known. On removal from the thermostat each tube was broken under 10 ml. of toluene and 100 ml. of 3% aqueous sodium hydroxide. Subsequent procedure was as before,[4] except that, since the mole-ratio of aromatic compound to solvent was larger than in the other media, it could not be assumed that a negligible amount of tritium would remain in the aromatic compound at equilibrium. It was assumed that in benzene all six positions were available for the tritium at equilibrium, and that in runs on *m*-tritiotoluene, and *m*-tritio-t-butylbenzene five positions were available, but that for the other tritiated toluenes and t-butylbenzenes only three positions were available (since tritiation of the *meta*-positions will not be appreciable in ten times the half-life of the detritiation). The error in neglecting isotope effects on the equilibrium is insignificant.

The method is exemplified by the following run involving [$^3H_1$]benzene in $CF_3{\cdot}CO_2H{-}H_2O{-}HClO_4$ of the composition specified above. Five 1 ml. portions were taken from a solution of 0·0645 g. of [$^3H_1$]benzene in 7·4306 g. of the medium, and the residue weighed 0·192 g., so that there was *ca.* 0·0126 g. of [$^3H_1$]benzene in each of the reaction tubes. Separate measurement showed that this amount of [$^3H_1$]benzene dissolved in 10 ml. of toluene gave a deflection of 228 mm. On the assumption that one position of trifluoroacetic acid, one of perchloric acid, two of water, and six of benzene are equally available for tritium, the benzene hydrogen atoms represent 6·5% of the total available, and at equilibrium the titriated benzene in each sample will give rise to a deflection, D_∞, of 7·3 mm. for each 4·365 g. of the toluene extract (this being the weight used for each activity measurement). The first-order rate coefficient, $k_{obs.}$, is given by $tk_{obs.} = 2{\cdot}303 \log [(D_0 - D_\infty)/(D_t - D_\infty)]$, where D_0 is the deflection (for 4·365 g. of extract) at an arbitrary zero time and D_t the deflection at time t.

Time (hr.)	0	35·75	86·80	155·50	182·0
D_t (mm.)	92·8	78·4	62·1	46·7	40·7
$10^7k_{obs.}$ (sec.$^{-1}$)	—	14·3	14·3	14·3	14·3

The following run illustrates the effect of sulphonation on the $CF_3{\cdot}CO_2H{-}H_2O{-}H_2SO_4$ medium. [The value of D_∞ used (4 mm.) is an approximation derived by reducing the value (7 mm.) which would result after 10 half-lives of the exchange alone, by 40% to allow for concurrent sulphonation (see below).] The deflection, D_t, refers to 4·40 g. of extract.

Time (hr.)	0	9·10	21·70	43·40	72·90
D_t (mm.)	194	161	126	90·5	62·0
$10^7k_{obs.}$ (sec.$^{-1}$)	—	57·8	56·7	50·6	45·4

A value of 59×10^{-7} sec.$^{-1}$ for $k_{obs.}$ was derived by extrapolation of the log $(D_t - D_\infty)$–t plot to zero time.

The following run refers to sulphonation of α-tritiated toluene in the same medium as the preceding run. In this case $D_\infty = 0$.

Time (hr.)	0	12·10	34·50	61·00	115·8
D_t (mm.)	157	141	118	100	75
$10^7k_{sulph.}$ (sec.$^{-1}$)	—	24·9	23·0	20·6	17·7

By extrapolation, $k_{sulph.}$ at zero time = 26×10^{-7} sec.$^{-1}$.

Rates of Sulphonation.[*]—Sulphonation of toluene was studied by measuring the loss of α-tritiated toluene as previously described.[31]

Sulphonation of t-butylbenzene was studied by using n-heptane in place of toluene in the extraction process and measuring the optical density, E, of the extract at 247, 252, 258, and 264 mμ. Since the sulphonic acid is removed in the extraction process, the optical densities give a direct measure of the residual concentration of t-butylbenzene, provided no absorbing impurities are present, and the first-order rate constant, $k_{\text{sulph.}}$, is given by $tk_{\text{sulph.}} = 2{\cdot}303 \log (E_0/E_t)$. The following results refer to *t*-butylbenzene (*ca.* 0·18 g.) in $CF_3{\cdot}CO_2H–H_2O–H_2SO_4$ (*ca.* 7·5 g.), figures for only two-wavelengths being quoted:

Time (hr.)	0	116·0	135·8	233·0	305·0
E (247 mμ)	0·267	0·150	0·147	0·116	0·104
E (258 mμ)	0·485	0·276	0·268	0·208	0·190
10^7k (247 mμ) (sec.$^{-1}$)	—	13·8	11·8	9·9	8·6
10^7k (258 mμ) (sec.$^{-1}$)	—	13·5	12·1	10·1	8·6

Extrapolation of the log E_t–t plot to zero time for all four wavelengths gave, on averaging, a value of 17×10^{-7} sec.$^{-1}$ for the initial rate.

With benzene, the same procedure was followed, wavelengths of 243, 248·7, 254·5, and 261 mμ being used.

With t-butylbenzene in the $CH_3{\cdot}CO_2H–H_2O–H_2SO_4$ medium, formation of a yellow colour, some of which persisted into the n-heptane, prevented measurement of the sulphonation rate.

Absence of Side Reactions in Trifluoroacetic acid–Water–Perchloric Acid.—When α-tritiated toluene was used under the conditions of the detritiation of the ring-tritiated toluene in the $CF_3{\cdot}CO_2H–H_2O–HClO_4$ medium used, loss of activity was negligible (first-order rate constant $<1 \times 10^{-7}$ sec.$^{-1}$ for $k_{\text{obs.}}$ in the case of [3-$^3H_1$]toluene). This means that (i) no oxidation of the methyl group occurs, and (ii) no other reaction occurs to give either alkali-soluble products, or alkali-insoluble products which influence the tritium measurement. (A substance such as perchloryltoluene, for example, would probably act as an apparent scintillation-quencher relative to toluene.)

Sometimes in longer runs the reaction mixture developed a colour, but this disappeared when the mixture was added to aqueous alkali, and we believe it arises from traces of impurity. First-order rate coefficients were most satisfactorily constant during a run, and mean rate constants could be duplicated to within ±1%.

Of the media we have used for detritiation, we believe the $CF_3{\cdot}CO_2H–H_2O–HClO_4$ mixture to be most free from troublesome side-reactions.

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[*] The media in which we reported $10^6k_{\text{sulph.}}$ values for toluene of 955, 18·8, and 2·58 sec.$^{-1}$ had the following respective compositions (mole percentages in parentheses): $CF_3{\cdot}CO_2H$ (83·40)–H_2O (1·98)–H_2SO_4 (14·62); $CF_3{\cdot}CO_2H$ (85·08)–H_2O (6·42)–H_2SO_4 (8·50); $CF_3{\cdot}CO_2H$ (95·31)–H_2O (2·21)–H_2SO_4 (2·48). The slightly different values given before [31] were calculated in the belief that 99·7% trifluoroacetic acid was used, whereas it was later found to be 100·0%.