969. *Aromatic Reactivity. Part XIX.*[1] *Detritiation of* [o- *and* p-³H₁]-*Toluene and* -t-*Butylbenzene.*

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The reactivity of *o*- relative to that of *p*-tritiotoluene in detritiation varies markedly with the medium (*e.g.*, the reactivity ratio is 1·05 in 74·8% sulphuric acid at 25°, 0·49 in anhydrous trifluoroacetic acid at 70°, and 0·39 in anhydrous heptafluorobutyric acid at 70°). The relative reactivities of *o*- and *p*-tritio-t-butylbenzene vary in a closely similar way, and so the effect cannot originate in steric hindrance by the *o*-alkyl groups. It is suggested that in this and other electrophilic substitutions, activation of an *ortho*- relative to that of a *para*-position by an alkyl group may depend upon the nature of the electrophile, possibly increasing with increasing reactivity of the latter.

THE relative reactivities of the *ortho*- and *para*-positions of toluene in hydrogen-exchange seem to vary considerably as the medium is varied. Thus the following ratios, f_o/f_p, of the rate factors applying to these positions have been reported: 1·11 for tritiation in 80·8% aqueous sulphuric acid,[2] 1·09 for dedeuteration in 70·8% aqueous perchloric acid,[3] 1·00 for dedeuteration in 68% aqueous sulphuric acid,[4] 0·95 for deuteration in 50 mole-% sulphuric acid,[5] 0·70 for deuteration in trifluoroacetic acid containing a little sulphuric acid,[6] 0·60 for deuteration in *ca.* 95 vol.-% aqueous trifluoroacetic acid,[5] 0·41 for dedeuteration in anhydrous heptafluorobutyric acid,[3] and 0·17 for deuteration in liquid deuterium bromide.[7]

It is usual to explain f_o/f_p ratios for electrophilic substitution in toluene in terms of steric hindrance, and Tiers suggested as a possible explanation of the smallness of the ratio in hydrogen-exchange in heptafluorobutyric acid the larger steric requirements of the proton donor compared with those in aqueous perchloric acid.[3] As an alternative, Lauer, Matson, and Stedman [5] suggested that steric hindrance to solvation for reaction at the *ortho*- relative to that at the *para*-position might be smaller in sulphuric acid than in trifluoroacetic or heptafluorobutyric acid, although it is more likely that steric hindrance to solvation by the *o*-methyl group would be relatively *less* important in the more weakly solvating media (cf. ref. 8).

Again, from the magnitude of the f_o/f_p ratio in dedeuteration in 68% aqueous sulphuric

[1] Part XVIII, Eaborn and Sperry, preceding paper.
[2] Melander and Olsson, *Acta Chem. Scand.*, 1956, **10**, 879.
[3] Tiers, *J. Amer. Chem. Soc.*, 1956, **78**, 4165.
[4] Gold and Satchell, *J.*, 1956, 2743.
[5] Lauer, Matson, and Stedman, *J. Amer. Chem. Soc.*, 1958, **80**, 6433.
[6] Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.
[7] Shatenshtein, Kalenachenko, and Varshavskii, *Zhur. fiz. Khim.*, 1956, **30**, 2098.
[8] Eaborn and Taylor, *J.*, 1961, 247.

acid compared with the ratios in ionic bromination [9] and nitronium-ion nitration [10] (*viz.*, 1·29 and 0·72, respectively), Gold and Satchell inferred that the attacking species in the dedeuteration is larger than that in the bromination,[4] although such an inference is, in our opinion, inconsistent with their mechanism for the exchange process. In this " unorthodox " mechanism,* a fast proton-transfer from the acid to the aromatic compound gives an " outer " complex, and the hydrogen exchange occurs in a slow rearrangement of this complex.[4,11] The rate-determining transition state contains only the aromatic species and a proton, free from solvent, and it is difficult to believe that the steric requirements of this proton would be larger than that of the bromonium ion. Any evidence of marked variation in steric hindrance by an *o*-methyl group with change in the catalysing acid, HA, would argue strongly against the mechanism, since the conjugate base A is absent in the rate-determining transition state and cannot exercise any direct influence on it.

To throw light on the importance of steric effects in hydrogen-exchange we have measured the rates of detritiation of [*o*- and *p*-$^3H_1$]-toluene and -t-butylbenzene in several media; if variation in the f_o/f_p ratio in toluene arises from steric hindrance, either by compression between the methyl group and the incoming and outgoing groups at the reaction centre, or by interference with solvation, then the effect should be much greater in t-butylbenzene. The results, listed in the Table, show that the f_o/f_p ratio varies in precisely the same way for toluene and t-butylbenzene, being slightly lower for the latter throughout. The variations must thus arise from the polar influences of the alkyl groups.

Detritiation of X·C_6H_4·^3H compounds.

(i) Medium: H_2SO_4–H_2O.   Temperature: 24·84°.

[H_2SO_4]ᵃ	10⁷k (sec.⁻¹)ᵇ		f_o/f_p	[H_2SO_4]ᵃ	10⁷k (sec.⁻¹)ᵇ		f_o/f_p
	X = *o*-Me	*p*-Me			X = *o*-Me	*p*-Me	
74·85	5185	4915	1·055	69·00	316	320	0·99
73·25	2800	2710	1·04	64·50	49·6	50·7	0·98
70·70	753	753	1·00		X = *o*-Buᵗ	*p*-Buᵗ	
				71·41	768	805	0·955

(ii) Temperature: 70·11°.

Medium	10⁷k (sec.⁻¹)				f_o^{Me}/f_p^{Me}	$f_o^{Bu^t}/f_p^{Bu^t}$
	X = *o*-Me	*p*-Me	*o*-Buᵗ	*p*-Buᵗ		
CF₃·CO₂H–H₂O–HClO₄ᶜ,ᵈ (92·04)–(5·45)–(2·51)	330	313	393	387	1·05	1·02
CF₃·CO₂H–H₂O–H₂SO₄ᶜ,ᵈ (93·00)–(5·12)–(1·88)	1295	1770	1565	2180	0·73	0·72
CF₃·CO₂H	20·8	42·7	23·0	50·9	0·49	0·45
n-C₃F₇·CO₂H	2·79	7·08	3·34	8·94	0·39	0·37

ᵃ Wt.-%.   ᵇ No corrections for sulphonation have been applied since they would be small, and identical for *ortho*- and *para*-isomers.   ᶜ These results are from Eaborn and Taylor, *J.*, 1961, 247.   ᵈ Figures in parentheses denote mole-%.

The fall in the f_o/f_p ratio parallels the fall in the dielectric constant of the medium. Electrostatic repulsion between the partial positive charges on the hydrogen atoms of the alkyl group and the positive charge at the reaction centre will be greater in media of low dielectric constant, and might be expected to contribute to the smallness of the f_o/f_p ratios, but if this were a major effect it would be much more marked with the t-butyl than with

* For the meaning of the descriptions " orthodox " and " unorthodox " in this context see refs. 8 and 12.

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

[10] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291; cf. Knowles, Norman, and Radda, *J.*, 1960, 4885.

[11] Gold and Satchell, *J.*, 1955, 3609, 3619, 3622; Gold, Lambert, and Satchell, *Chem. and Ind.*, 1959, 1312.

[12] Kresge and Chiang, *Proc. Chem. Soc.*, 1961, 81.

the methyl group. The most likely explanation of the variations is that the polar effect of an o- relative to that of a p-alkyl group varies with the electron-demand of the attacking electrophile, and our results are consistent with associating the decrease in the f_o/f_p ratios with decreasing acidity and reactivity of the attacking acid. It is reasonable to assume that inductive effects of alkyl groups reach *ortho*- more effectively than *para*-positions, but that their tautomeric effects (or polarizability effects, in general) reach the *para*-position more easily (just as the $+T$ effects of OR and NR_2 groups activate *para*- more than *ortho*-positions [13]). A decrease in the reactivity of the attacking acid will be accompanied by increasing demand on polarizability effects, and thus the f_o/f_p ratio can be expected to fall.* Alternatively the high f_o/f_p ratios may be associated with positively charged, and the low ratios with neutral, attacking species (*e.g.*, the un-ionized acids, $CF_3 \cdot CO_2H$, $C_3F_7 \cdot CO_2H$, and DBr), and it is noteworthy that, in chlorination, for example, the ratio is higher for attack by the chloronium ion or related species ($f_o/f_p = 1 \cdot 63$) than for attack by molecular chlorine ($f_o/f_p = 0 \cdot 75$).[16] (Steric factors probably play some part in molecular chlorination, however, but possibly not a large one in the case of toluene, since the $f_o{}^{But}/f_p{}^{But}$ ratio is only five times smaller than the $f_o{}^{Me}/f_p{}^{Me}$ ratio.[16]) However, the greater electron-demand usually shown by neutral than by positively charged electrophiles is probably itself a result of the greater reactivity of the positively charged species.

It will be realised that whatever the explanation of our results they have a general significance for interpretation of f_o/f_p ratios in electrophilic substitutions in alkylbenzenes, since these can no longer necessarily be attributed wholly or even mainly to steric effects. Thus it is no longer justifiable to use the f_o/f_p ratios in ionic chlorination and bromination of toluene ($1 \cdot 63$ and $1 \cdot 29$, respectively) to conclude that the steric requirements of the former reaction are smaller [16] (although they probably are), for it is likely that the steric effect is small in both bases and that the lower ratio in bromination is associated with the greater stability, and thus lower reactivity, of the bromonium ion. Similarly, it cannot be concluded from the f_o/f_p ratios in toluene that the steric requirements of hydrogen exchange in aqueous sulphuric acid are intermediate between those in ionic bromination and nitration, as has been suggested.[4] We suggest that only when a low f_o/f_p ratio for toluene is accompanied by a markedly smaller ratio for t-butylbenzene is it reasonable to conclude that steric hindrance to *ortho*-substitution is probably important in t-butylbenzene, and possibly of significance also in toluene.

Our results are, we believe, more easily reconciled with the " orthodox " than with the " unorthodox " mechanism of hydrogen exchange. In the former the conjugate base A of the catalysing acid HA is covalently involved in the highest-energy transition state(s) and thus can influence the electron demand directly, so that the variations in the f_o/f_p ratio become understandable in terms of the chemical properties of the acid HA, as we have indicated above. In the " unorthodox " mechanism, the residue A is not covalently involved in the highest-energy transition state(s), and the effect on the f_o/f_p ratios of changing the acid would have to be explained either in terms of general solvent effects (which would be difficult) or by introducing the complication of postulating changes in mechanism with changes of acid.

The increase in the f_o/f_p ratio for toluene with increasing concentration of aqueous

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* From medium to medium the value of $f_p{}^{Me}$ in hydrogen exchange is not a wholly reliable measure of the demand on polarizability effects,[8, 14] but the highest values of the f_o/f_p ratio for toluene, those in trifluoroacetic acid containing perchloric acid and those in aqueous sulphuric acid, are associated with the smallest values of $f_p{}^{Me}$ (*viz.*, 313 [8] and 250,[15] respectively) while the intermediate values of the ratio correspond with intermediate values of $f_p{}^{Me}$ (in anhydrous trifluoroacetic acid, $f_p{}^{Me} = 450$), and the lowest value of the ratio, that in anhydrous deuterium bromide, is associated with an exceptionally large value of $f_p{}^{Me}$ (*viz.*, 6000).[7]

[13] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, pp. 145—146.
[14] Eaborn and Taylor, *J.*, 1961, 2388.
[15] Eaborn and Taylor, *J.*, 1960, 3301.
[16] Ref. 13, pp. 142—144.

sulphuric acid is probably real, and this would agree with the few results previously reported separately for particular concentrations.[2-5] It is noteworthy that, while the hyperconjugative order of activation, o-Me $>$ o-Bu^t, applies in aqueous sulphuric acid, the inductive order, o-Bu^t $>$ o-Me applies in trifluoroacetic acid, alone or containing aqueous sulphuric or perchloric acid, the type and magnitude of the change being very similar to those noted previously for the p-alkyl groups. As one possible explanation in the case of the *para*-substituents it was suggested that the direct-field component of the inductive effect might be larger in media of low dielectric constant, so that the inductive order might apply.[8] Such an effect would, however, be much larger with the *ortho*-groups; and, since it is not, the suggestion is invalid.

EXPERIMENTAL

Materials.—Preparation of the tritiated aromatic compounds has been described.[8,15]

Anhydrous trifluoroacetic acid was prepared by fractionally distilling the Eastman " White Label " acid first from sulphuric acid and then from silver trifluoroacetate. Alkali titration showed it to be 100·0% pure, and Karl Fischer titration, in presence of excess of pyridine, showed it to contain $<0·01\%$ of water.

Anhydrous heptafluorobutyric acid was prepared analogously.

Rate Measurements.—The techniques were as previously described.[8,14,15]

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