cule, and hence reduce the *ortho* reactivity. An effect of this type has been suggested by Tiers.[7]

A second possibility is that a mechanism of the type suggested by Gold and Satchell[4] exists in all three cases, but that for substitution at the *o*-position it is easier for solvation of the π- and σ-complexes to occur, relative to the *p*-position, in concentrated sulfuric acid than in trifluoroacetic acid or heptafluorobutyric acid due to steric effects.

MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Hydrogen Isotope Exchange Reactions. II. Monoalkylbenzenes[1]

BY WALTER M. LAUER, GALE W. MATSON[2a] AND GEOFFREY STEDMAN[2b]

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The relative rates of deuteration of a number of monoalkylbenzenes in mixtures of trifluoroacetic acid and deuterium oxide have been measured by several methods and the isomer distribution determined. All the alkyl groups studied have very similar reactivities and the *ortho–para* ratio does not decrease greatly between toluene and *t*-butylbenzene. It appears that steric effects are small in this reaction.

Recent work has led to a quantitative correlation of *meta* and *para* partial rate factors for electrophilic aromatic substitution in toluene,[3] and a proposed extension of this treatment to include *ortho* partial rate factors.[4] In a previous paper[5] the results of a study of the deuteration of benzene and toluene in mixtures of trifluoroacetic acid and deuterium oxide were reported. Some differences in the *ortho–para* ratio between these results and those for exchange in concentrated sulfuric acid were noted. This work now has been extended to other monoalkylbenzenes in order to obtain information on the magnitude of steric effects in the *o*-position and to determine, if possible, whether the reactivity in the *m*- and *p*-positions, which are free of steric effects, followed the inductive or hyperconjugative order.

Experimental Part

Materials.—Hydrocarbons were White Label Grade materials obtained from Eastman Kodak Co. or the Aldrich Chemical Co. They were purified by fractional distillation before use. Other materials used were described previously.[5]

Procedure for Kinetic Runs.—The procedure used for ordinary kinetic runs already has been described.[5] For "competition" experiments a mixture of hydrocarbons was used in place of a single compound, and at the end of a run the mixture was separated into pure components by fractional distillation on a spinning band column. Deuterium analyses always were made on successive fractions and checked well; infrared spectra were run to check the efficiency of separation. In the experiments using "low concentrations" of aromatic compounds, analyses were run on the deuterated hydrocarbon after washing and drying, omitting the distillation.

Isomer Distribution.—The same method used in the determination of the isomer distribution in deuterated toluene was used for the monoalkylbenzenes. The purity of the fractionated nitro compounds was checked by gas phase chromatography, and small corrections were made where necessary for the presence of other isomeric nitromonoalkylbenzenes.

Calculations.—Relative rates were calculated as previously described.[5] For some of the monoalkylbenzenes, relative rates were calculated as the reciprocal of the ratios of the times needed to reach a certain deuterium content.

In the competitive experiments, deuteration was followed only during the initial stages, to an average deuterium content of approximately 0.06 g. atom of deuterium per mole, and the usual form of rate equation for competitive reactions reduces to

$$k_1/k_2 = D_1/D_2$$

k_1/k_2 is the relative reactivity of 1 to 2; $D = (\mathrm{ArD}/\mathrm{ArH}_0)$; ArD = concentration of deuterated aromatic hydrocarbon calculated as the excess over normal of the monodeuterio compound; ArH_0 = initial concentration of aromatic compound.

For the "low concentration" experiments, the deuterium content of the medium did not vary significantly during reaction, and as reaction was followed only during the initial stages the concentration of undeuterated aromatic did not vary significantly, less than 3.5%. Under these conditions the ratio of the D values (excess over normal) should be almost equal to the ratio of the rate constants.

Results and Discussion

Relative Rates.—Experiments reported in paper I of this series, which utilized a high concentration of aromatic compound, showed that it was necessary to check for the size of the solvent effect on changing the nature of the aromatic hydrocarbon. This check was made by a "competition" method in which an equimolar mixture of toluene and the other hydrocarbon under investigation was deuterated at 70°, using the same total concentration of aromatic hydrocarbon, trifluoroacetic acid and deuterium oxide. Under these conditions the differences in rate of deuteration should reflect almost solely reactivity differences. An alternative approach that was used involved deuterating the hydrocarbons individually in such low concentration that changing the nature of the hydrocarbon has no effect on the solvent properties. The relative rates determined by these methods are given in Table I, together with the results obtained from the high concentration runs.

The obvious parallelism between the "competitive" and "low concentration" experiments establishes that the high concentration experiments are subject to a solvent effect. If it is assumed that the solvent effect of each extra methylene group in the side chain reduces the rate relative to some standard by an arbitrary factor of $(1.22)^n$, the high concentration experiments give very similar

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[1] Taken in part from a thesis submitted by Gale W. Matson in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[4] H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

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TABLE I

DEUTERATION OF THE MONOALKYLBENZENES C_6H_5R AT 70°

	Relative reactivities[a]				Relative reactivities		
R	a	b	c	R	a	b	c
H	6	6	6	n-C_4H_9	453	1044	1146
CH_3	765.6	934[b]	964	s-C_4H_9	422	889	1043
C_2H_5	625	970	1088	t-C_4H_9	423	893	..
n-C_3H_7	..	912	..	i-C_5H_{11}	..	1074	..
i-C_3H_7	550	1017	1145				

[a] a, high concentration experiments: CF_3COOH = 50.5, D_2O = 10.1, ArR = 39.4; b, "competitive" experiments of C_6H_5R with $C_6H_5CH_3$: [CF_3COOH] = 62.9, [D_2O] = 12.5, [C_6H_5R] = 12.3, [$C_6H_5CH_3$] = 12.3; c, low concentration experiments, [CF_3COOH] = 81.9, [D_2O] = 16.3, [ArR] = 1.8; all concentrations in mole %. [b] Value from column a corrected by factor, $(1.22)^n$, for solvent effect.

results to the "competitive" experiments. For most of the monoalkylbenzenes, the results of this correction already have been reported.[5] It is important to establish this correction, in order that it can be applied to the benzene–toluene case. *Ortho*, *meta* and *para* ratios are necessarily determined on compounds deuterated under high concentration conditions in order to obtain sufficient material, while accurate "competitive" experiments on benzene and toluene at high concentrations are not possible due to the wide differences in rate. The present results are unusual inasmuch as in chlorination,[6] nitration,[7] mercuration[8] and isopropylation[9] of these compounds there is a steady decrease in rate with increasing size of the alkyl group, partly due to steric effects in the *o*-position.

Isomer Distribution.—The relative amounts of *o*- and *p*-substitution were determined by the same method used for toluene and described previously.[5] From these results and the competitive relative rates, partial rate factors were calculated, making a small correction for the *m*-position which was assumed to be as reactive as in toluene. This assumes that there is no difference in the isomer distribution for the deuteration of aromatic compounds individually, and competitively with toluene.

TABLE II

PARTIAL RATE FACTORS FOR THE MONOALKYLBENZENES

R	o_f	m_f	p_f	R	o_f	m_f	p_f
H	1	1	1	i-C_3H_7	259	..	493
CH_3	253	3.5[a]	421	n-C_3H_7	..	6.8[a]	..
..	..	*ca.* 4[b]	..	s-C_4H_9	202[d]	8.4[a]	478[d]
C_2H_5	257	6.9[b]	449	t-C_4H_9	198	*ca.* 7[e]	490
		ca. 5[c]					

[a] Obtained by analysis of tribromoaniline, which resulted from the following reaction sequence: deuterated hydrocarbon → carboxylic acid → aniline → tribromoaniline. [b] Obtained by conversion to 2,4,6-trinitrotoluene. [c] Calculated from reactivities of *o*- and *p*-diethylbenzenes. [d] Approximate value; deuterium contents of *o*- and *p*-positions did not check with directly determined total deuterium content of the hydrocarbon. [e] Determined from reactivity of *p*-*t*-butyltoluene.

The *para* partial rate factor shows a slight increase from toluene to *t*-butylbenzene. This is a rather small difference in view of the possible errors in the determination of relative rates and isomer ratios. To check on this value the exchange of *p*-*d*-toluene and *p*-*d*-*t*-butylbenzene at 70°, [ArH] = 1.8 mole %, [H_2O] = 16.3 mole %, [CF_3COOH] = 81.9 mole %, was investigated. Under these conditions, exchange is first order in deuterioaromatic: for *p*-*d*-toluene k_1 = 0.0276 hr.$^{-1}$, for *p*-*d*-*t*-butylbenzene k_1 = 0.0295 hr.$^{-1}$. We therefore conclude that in hydrogen exchange under our conditions the *para* partial rate factor for *t*-butylbenzene is equal to or perhaps slightly greater than that for toluene. Mackor, Smit and van der Waals[10] have recently reported that both rate constants and activation energies for H–D exchange at the *p*-positions in toluene, ethylbenzene and *t*-butylbenzene are equal within the experimental error. These and our results are in contrast to the results obtained for most other aromatic substitutions[8,11,12] and are of interest because nitration is the only well established case in which the *para* partial rate factor for *t*-butylbenzene is not markedly less than for toluene.

***ortho* Partial Rate Factors.**—While the *meta* and *para* partial rate factors perhaps increase slightly from toluene to *t*-butylbenzene, the *ortho* partial rate factors decrease slightly. Such a decrease is reasonably ascribed to steric hindrance. A comparison of the present results with those of other aromatic substitution reactions indicates that the steric effect for deuteration in trifluoroacetic acid is much less than for other aromatic substitutions. Relevant data has been collected and summarized in ref. 16; some of it is given in Table III.

The relative reactivities of the *o*- and *p*-positions depend quite specifically on the attacking reagent and even in the absence of steric effects, for a given value of p_f, the value of o_f may vary considerably from reaction to reaction. This could account for the higher *ortho–para* ratios observed for hydrogen exchange in sulfuric acid and bromination by the Br^+ or $BrOH_2^+$ ions in aqueous dioxane.

TABLE III

PARTIAL RATE FACTORS FOR SUBSTITUTION IN TOLUENE AND *t*-BUTYLBENZENE

Reaction	o_f	m_f	p_f	o_f/p_f	
Nitration by NO_2^+	42	2.5	58	0.72	Toluene[13]
	5.5	4.0	75	0.073	*t*-Butylbenzene[15]
Bromination by	76	2.5	59	1.29	Toluene[11]
Br^+ or $BrOH_2^+$	13.6	2.6	38.5	0.35	*t*-Butylbenzene[11]
Bromination by	450	..	1990	.23	Toluene[12]
Br_2	30	..	600	.05	*t*-Butylbenzene[12]
Isopropylation	2.4	1.8	4.3	.56	Toluene[9,14]
	0	2.0	4.0	.0	*t*-Butylbenzene[15,16]

The above data contain examples of reagents of widely varying selectivity and examples in which the substituting agent invokes mainly the induc-

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tive effect, as in nitration, and the hyperconjugative effect, as in both examples of bromination. Table III includes examples where the attacking reagent is an ionic species and where it is a covalent species. In all cases the o_f/p_f ratio decreases sharply from toluene to *t*-butylbenzene, by at least a factor of 3.5. This is in marked contrast to the present results for deuteration in trifluoroacetic acid where the o_f/p_f ratio decreases from 0.60 in toluene to 0.41 in *t*-butylbenzene, a change involving a factor of *ca.* 1.5.

Lauer, Leister and Matson have found that for the deuteration of toluene and isopropylbenzene under heterogeneous conditions with 50 mole % H_2SO_4 at 50° the o_f/p_f ratios were 0.95 and 0.85, respectively. Gold and Satchell[17] have presented evidence suggesting that hydrogen exchange of benzene and toluene under similar conditions involves σ- and π-complexes between the entering and leaving hydrogen ions and the aromatic ring, a mechanism that would be expected to involve relatively small steric effects. The change in the o_f/p_f ratio that we observe for deuteration of toluene and isopropylbenzene in trifluoroacetic acid, 0.62 to 0.52, is quite similar to that observed for hydrogen exchange in sulfuric acid and is much less than the changes of 0.79 to 0.24 observed for nitration,[13] and 0.56 to 0.073 for isopropylation.[16] This again argues for a very small steric effect in the present case. In nitration and isopropylation the o_f/p_f ratios decrease steadily from toluene to ethylbenzene, isopropylbenzene and *t*-butylbenzene.[16] For deuteration in trifluoroacetic acid, the o_f/p_f ratios for toluene and ethylbenzene are almost identical and the decrease begins with the isopropyl and *t*-butylbenzenes. This suggests that steric effects are almost constant in toluene and ethylbenzene and presumably small.

Some further evidence on the magnitude of steric effects can be obtained from a study of the polyalkylbenzenes. We have examined the distribution of deuterium in a sample of *m*-xylene deuterated under similar conditions to those used in the present work. We find that the relative reactivities of the 2-position, flanked on each side by a methyl group, and the 4- and 6-positions, flanked by only one methyl group, are 0.58:1.0. Condon[18] has shown that the reactivities of the polymethylbenzenes in chlorination can be predicted with remarkable accuracy by assuming that the activating effects of the methyl groups are additive. On this basis we predict the relative reactivities of the 2- and 4-positions in *m*-xylene to be equal to the ratio of the *ortho* and *para* partial rate factors of toluene; *i.e.*, 0.60. Brown[8] has shown that in mercuration, a reaction with large steric requirements, the reactivity of a position doubly flanked by methyl groups is considerably lower than that predicted from the partial rate factors for toluene. He has also found indications of the same effect for bromination in acetic acid.[19] The agreement between the 2:4 ratio in *m*-xylene and the o_f/p_f ratio in toluene therefore argues that in deuteration no large steric effect is involved.

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MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Electrophilic Hydrogen Isotope Substitutions. III. The Polyalkylbenzenes

BY WALTER M. LAUER AND GEOFFREY STEDMAN[1]

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The rates of deuteration of a number of polyalkylbenzenes in mixtures of deuterium oxide and trifluoroacetic acid have been measured. The rate of exchange closely parallels the basicity of the hydrocarbon and can be predicted from the partial rate factors for the deuteration of the monoalkylbenzenes. The results provide further evidence that steric effects are small for deuteration in trifluoroacetic acid and give approximate values for the *meta* partial rate factor for several alkyl groups.

In previous papers[2] we have described the results of a study on the relative rates of deuteration of benzene, toluene and various monoalkylbenzenes in mixtures of trifluoroacetic acid and deuterium oxide. A useful extension of this work was a study of the deuteration of the polyalkylbenzenes under similar conditions. Our previous work had left some uncertainty about the *meta* partial rate factor for toluene and had provided only tentative values for the *meta* partial rate factors of the other monoalkylbenzenes studied. As the relative reactivities of the polymethylbenzenes can be predicted with some accuracy from the partial rate factors of the monoalkylbenzenes,[3,4] such a study promised to provide at least approximate values for these missing numbers. It was also hoped to obtain information about the magnitude of steric effects by comparison of positions singly and doubly flanked by methyl groups. A few of the results obtained in the present study have been described earlier.[2]

Experimental Part

Materials.—Aromatic hydrocarbons were purified by fractional distillation and recrystallization from aqueous

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(1) du Pont Postdoctoral Fellow 1955–1956, Atomic Energy Commission Postdoctoral Fellow 1956–1957, Contract AT(11-1)478.

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