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

Electrophilic Hydrogen Isotope Substitutions. I. Benzene and Toluene

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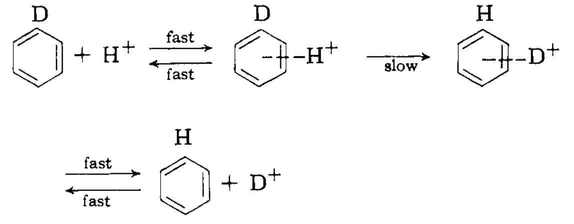
The initial rates of deuteration of benzene and toluene in deuterium oxide and trifluoroacetic acid mixtures have been measured, and the isomer distribution of the deuterium substituted in the toluene determined. The partial rate factors found were $o_f = 250$, $m_f = 4$, $p_f = 420$. Methods for checking these partial rate factors are described. The results are compared with those for other electrophilic aromatic substitution reactions.

Introduction

The exchange of hydrogen atoms between aromatic compounds and aqueous acid solvents was shown by Ingold and his co-workers[3] to be an electrophilic aromatic substitution reaction. As such, it is of particular interest for several reasons: (1) the incoming and outgoing groups should possess perhaps smaller intrinsic steric requirements than in other reactions of the same type; (2) the reaction is reversible and can be studied from either side of the equilibrium position; and (3) there are data available on the basicity of aromatic compounds.

Several recent investigations have provided valuable information on this problem. Gold and Satchell[4] have studied the exchange between deuterated aromatic compounds and concentrated sulfuric acid under homogeneous conditions. They propose a mechanism in which the slow stage is the conversion of a π-type complex with the proton and the aromatic compound in facile equilibrium with the solvent, to a π-type complex with the proton in the aromatic ring and the deuteron loosely bound to it.



Investigations by Melander and Olsson[5] of the exchange between the isomeric *o*-, *m*- and *p*-, tritio- and deuteriotoluenes and 80.8% sulfuric acid under heterogeneous conditions at 25° gave results similar to those of Gold and Satchell. Tiers[6] has studied the exchange of the monodeuteriotoluenes with 70.8% perchloric acid, and with anhydrous heptafluorobutyric acid.

The present paper is the first of a series of papers on hydrogen exchange between aromatic compounds and acid solvents, and describes the deuteration under homogeneous conditions of benzene and toluene in mixtures of trifluoroacetic acid and deuterium oxide. This solvent is acid enough to cause exchange to occur at a reasonable rate, and yet is an excellent solvent for aromatic compounds. The distribution of the deuterium substituted in the molecule was found by nitration, followed by a determination of the deuterium content of the various purified nitro- compounds, and of the original deuterated hydrocarbon. It has been shown that there is no hydrogen isotope effect in aromatic nitration.[7]

Experimental

Materials.—Eastman Kodak Co. white label trifluoroacetic acid was used without further purification. Eastman Kodak Co. white label thiophene-free benzene and toluene were purified by fractional distillation and had the following physical constants: benzene, b.p. (uncorrected) 78.5°, $n^{25}\text{D}$ 1.4970; toluene, b.p. (uncorrected) 108.5°, $n^{25}\text{D}$ 1.4938. Deuterium oxide (99.7%) was supplied by the Stuart Oxygen Co.

Procedure for Kinetic Runs.—The reaction mixture was made up by weighing out the hydrocarbon, and adding the desired quantity of deuterating reagent from a calibrated glass syringe; this avoided losses due to the volatility of the trifluoroacetic acid. It was shown that this method was accurate and reproducible. Studies at 70° were carried out in sealed ampoules. Exchange was slow enough for the time required for thermal equilibrium to be negligible. Reaction was stopped by sudden cooling to room temperature, and then adding to an excess of cold alkali. The non-aqueous layer was separated, washed with concentrated alkali and then with water, dried over sodium sulfate or magnesium sulfate, and purified by distillation.

Analysis of Deuterium Content.—A modification of the method of Lauer and Noland[7] was used. A sample of the hydrocarbon was burned completely in a stream of dry oxygen which passed through a hot tube packed with copper oxide. The water formed was reduced to hydrogen and deuterium by passing over granulated zinc, 20 mesh, at approximately 420°, and the gas was analyzed mass-spectroscopically. When nitro compounds were being analyzed, care was needed to ensure a smooth combustion, and it was found that the oxides of nitrogen produced tended to deactivate the zinc rather readily. Analyses usually were reproducible to better than 1%. There were no signs of any significant isotope fractionation in the present work.

The combustion and reduction train showed a small memory effect, which could be eliminated by analyzing the samples in order of increasing deuterium content, and by discarding the first sample of a series of analyses on a given specimen of hydrocarbon. Tests showed that the memory effect was almost equally distributed between the combustion and reduction halves of the apparatus, and corresponded to a contamination of about 5% for an average sized sample.

Analyses of a heavily deuterated hydrocarbon, and of a sample diluted a known amount by isotopically normal hydrocarbon confirmed the self-consistency of the analytical method. The ratio of the isotope abundances in the acid solvent, and in the hydrocarbon at isotopic equilibrium were close to those observed by other workers in this field.

The Deuterating Reagent.—The reagent used in this work was prepared by weighing out 5.000 g. of deuterium oxide and diluting to 100 ml. with trifluoroacetic acid.

Preparation of Nitro Compounds.—Nitrations were carried out using mixtures of sulfuric and nitric acids as the nitrating reagent. Liquid nitro compounds were purified

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[3] C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1637 (1936).

[4] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955); 2743 (1956).

[5] L. Melander and S. Olsson, *Acta Chem. Scand.*, **10**, 879 (1956).

[6] G. V. D. Tiers, THIS JOURNAL, **78**, 4165 (1956)

[7] (a) L. Melander, *Arkiv. Kemi*, **2**, 213 (1950–1951); (b) W. M. Lauer and W. E. Noland, THIS JOURNAL, **75**, 3689 (1953); (c) T. G. Bonner, F. Bowyer and G. Williams, *J. Chem. Soc.*, 2650 (1953).

by fractional distillation under reduced pressure using a Piros–Glover spinning band column. Solid nitro compounds were purified by recrystallization.

Relative Rates.—In the present work the chemical composition of the medium did not change appreciably during reaction. Apart from any medium effect due to the transfer of deuterium from the solvent to the aromatic hydrocarbon, the only variables were the deuterium content of the acid solvent and the amount of deuterium substitution in the aromatic compound. To avoid complications due to the reversibility of the exchange reaction, deuteration was only followed during the initial stages.

The relative reactivities of benzene and toluene were determined by studying the initial rates of deuteration under similar conditions.

Infrared spectra were measured on a Perkin–Elmer spectrometer, model 21. Sodium chloride cells were used.

Results and Discussion

Relative Rates.[8]—It was established that all of the deuteration occurred in the aromatic ring, and none in the side chain, by comparing the deuterium contents of a sample of deuterated toluene and of the benzoic acid produced from it by alkaline permanganate oxidation. The infrared spectrum of the deuterated toluene showed no sign of the band at 2170 cm.$^{-1}$, characteristic of mono-α-deuteriotoluene.

The relative rates of deuteration of benzene and toluene at 70° were determined at two different medium compositions. Toluene was found to deuterate 127 times as fast as benzene using a medium of the following molar composition: 24.6% aromatic hydrocarbon, 12.5% deuterium oxide and 62.9% trifluoroacetic acid, whereas a value of 115 was obtained when a medium composed of 39.4% aromatic hydrocarbon, 10.1% deuterium oxide and 50.5% trifluoroacetic acid was used.

The relative rates are subject to a solvent effect due to the high concentration of aromatic compound used, and an estimate of the magnitude of this solvent effect can be obtained from the rates of deuteration of other monoalkylbenzenes. When these homologs were deuterated at 70° under conditions similar to those used for toluene, *i.e.*, 24.6 mole % aromatic, 62.9 mole % trifluoroacetic acid and 12.5 mole % deuterium oxide, the relative rates of toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene, *sec*-butylbenzene and *n*-butylbenzene were 1:0.82:0.67:0.72:0.55:0.59. When these compounds were deuterated "competitively" with toluene, by comparing the initial rates of deuteration in a solution containing the same concentration of total aromatic, but made up of an equimolar mixture of toluene and the other hydrocarbon being studied, the relative rates were found to be 1:1.04:0.98:1.09:0.95:1.12. These relative rates are independent of the ratios of the two aromatic components over a 22-fold change in relative amounts provided the total aromatic concentration is not changed, and are only slightly dependent on the total aromatic concentration.

When these monoalkylbenzenes were deuterated in solutions containing a much lower concentration of aromatic hydrocarbon, 1.8 mole % aromatic hydrocarbon, 81.9 mole % trifluoroacetic acid and 16.3 mole % deuterium oxide, the relative rates in the cases of toluene, ethylbenzene, isopropylbenzene, *n*-butylbenzene and *sec*-butylbenzene were found to be 1:1.13:1.19:1.19:1.08. No exact parallelism can be expected between relative rates measured in media made up largely of trifluoroacetic acid and deuterium oxide and in media containing in addition a large amount of non-polar aromatic compound, but these "low concentration" measurements clearly follow the pattern of the "competitive" experiments rather than that obtained with the higher concentrations of aromatic compounds.

From these results it is concluded that for deuteration with high concentrations of the aromatic hydrocarbons there is a marked solvent effect. If it is assumed that this solvent effect decreases the rates relative to toluene by a factor of $(1.22)^n$ for each additional carbon atom in the side chain, then the relatives rates of deuteration of toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene, *n*-butylbenzene and *sec*-butylbenzene become 1:1.00:1.00:1.07:1.07:1.00, very similar to the results observed from the competition experiments. If this factor can be applied to the results for toluene and benzene, then the relative rate of deuteration of toluene to benzene is 127 × 1.22; *i.e.*, 155.

A confirmation of this value can be obtained from measurements made on toluene and benzene at low concentrations of hydrocarbon. These are given in Table I.

TABLE I

DEUTERATION OF TOLUENE AND BENZENE AT 70°[a]

Compound	ArH_0	CF_3COOH	D_2O	t, hr.	$ArD/ArH_0 \times \frac{1}{t}$
Benzene	1.79	81.9	16.3	265.8	0.0000895
Benzene	1.76	81.9	16.3	576.7	.0000841
Toluene	1.76	81.9	16.3	6	.0134
Toluene	1.76	81.9	16.3	6	.0141
Toluene	3.27	80.7	16.1	6	.0131

[a] All concentrations in mole %, time in hours.

Under these conditions the concentration of undeuterated aromatic hydrocarbon and the deuterium content of the acid medium do not vary appreciably, so that the value of $ArD/ArH_0 \times (1/t)$ is proportional to the rate. Under these conditions

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[8] It was assumed that during the initial stages of deuteration the reaction can be viewed as a process which is first order in hydrocarbon and that dedeuteration of the product can be neglected without introducing serious error. The rate of deuteration is dependent upon the composition of the trifluoroacetic acid–heavy water mixture used, but in determining relative rates the aromatic hydrocarbons which were compared were always treated with deuterating mixtures of identical composition. Accordingly, since the composition of the deuterating mixture does not change appreciably during the initial stages of deuteration

$$\frac{\mathrm{d\,ArD}}{\mathrm{d}t} = k\ \mathrm{ArH} \text{ and } k = \frac{1}{t} \ln \frac{\mathrm{ArH_0}}{\mathrm{ArH_0 - ArD_t}}$$

The fraction of undeuterated hydrocarbon at the beginning of the reaction, ArH_0, is 1 and the mole fraction of ArD_t is obtained from the HD/H_2 ratio, R.

$$\frac{R}{R+2} = \frac{\mathrm{D}}{\mathrm{D+H}}$$

In the case of monodeuteriotoluene, $D/(D + H) = 0.125$. The mole fraction of ArD_t is, therefore

$$\frac{R}{0.125(R+2)}$$

$ArH_0/(ArH_0 - ArD_t) = 1/(1 - ArD_t)$, and $-\ln(1 - ArD_t)$, on expansion and elimination of higher powers of ArD_t, becomes equal to ArD_t. Consequently, $ArD_t = kt$ and plots of the mole fraction of ArD_t against time give straight lines passing through the origin. The relative rates of deuteration of aromatic hydrocarbons are obtained by a comparison of these slopes.

the concentration of aromatic is sufficiently low to have almost no effect on solvent properties, and the relative reactivity of toluene to benzene is approximately 155.

Isomer Distribution.—A sample of toluene deuterated under the conditions: 24.56 mole % toluene, 12.55 mole % deuterium oxide and 62.9 mole % trifluoroacetic acid at 70° for 144 hours was diluted with isotopically normal toluene, and nitrated. The pure *o-nitro*, *p-nitro* and 2,4,6-*trinitro* derivatives were prepared. The deuterium contents of these compounds and of the parent deuterated toluene were determined. The results are shown in Table II.

TABLE II

DEUTERIUM CONTENT OF NITRATED DEUTERIOTOLUENE

Toluene	0.1218	g. atom/mole, excess
o-Nitrotoluene	.0874	g. atom/mole, excess
p-Nitrotoluene	.0646	g. atom/mole, excess
2,4,6-Trinitrotoluene	.00197	g. atom/mole, excess

As there is no hydrogen isotope effect in aromatic nitration[7] the deuterium content of the *o*- and *p*-positions can be determined readily from these values. The method is subject to some error, as the deuterium contents are obtained as the difference between two numbers which differ by a factor of less than two. However, the deuterium contents so determined account for the directly determined deuterium content of the toluene to within the accuracy of the mass-spectrometric measurements. It is shown below that the deuterium content of the *m*-positions is very small. When a small correction is made to allow for the reactivity of the *m*-position, the above values can be combined with the relative rates of deuteration of benzene and toluene to give $o_f = 250$ and $p_f = 420$. A check on these values was obtained from measurements on the dedeuteration of *o*- and *p*-deuteriotoluenes with isotopically normal trifluoroacetic acid–water mixtures. The deuteriotoluenes were prepared by treating the corresponding bromotoluenes in ether with lithium wire. The lithium derivatives were then hydrolyzed with deuterium oxide for 30 minutes. The addition of water, followed by ether extraction and drying ($MgSO_4$) of the ether extract and distillation yielded the *o*- and *p*-deuteriotoluenes. The resulting samples were diluted with ordinary toluene for the dedeuteration studies. These studies were carried out at 70.1° using trifluoroacetic acid (62.0%), water (13.8%) and aromatic hydrocarbon (24.2%); values for k $\left(k = \frac{1}{t} \ln \frac{\mathrm{ArD_0}}{\mathrm{ArD_t}}\right)$ found: *o*-deuteriotoluene 3.62×10^{-5} min.$^{-1}$ and *p*-deuteriotoluene 6.0×10^{-5} min.$^{-1}$. The o_f/p_f ratio (0.6) is in agreement with that obtained from the deuteration studies.

The infrared spectrum of a sample of *p*-deuteriotoluene which had been subjected to exchange for 312 hr. at 70° showed peaks at 617 and 767 cm.$^{-1}$ characteristic of *o*-deuteriotoluene. These peaks were absent in the spectrum of the starting *p*-deuteriotoluene. Apparently re-introduction of deuterium into the ring becomes important under these conditions and for this reason only the initial rates of loss of deuterium were compared.

The case for the *meta* partial rate factor is more complex. Measurements of the infrared spectra of our sample of 2,4,6-trinitrotoluene showed the presence of a small amount of 2,4,5-trinitrotoluene; no other impurities could be detected. Because the 2,4,5-trinitrotoluene contains an unsubstituted *o*-position and the deuterium content of an *o*-position is very much greater than that of a *m*-position, it is necessary to correct the apparent deuterium content of our sample of 2,4,6-trinitrotoluene for the deuterium content of this impurity. This corrected value, assuming the presence of 2.9% of 2,4,5-trinitrotoluene, is 0.0010 g. atom of deuterium/mole. Because of the limitations of the infrared method of analysis, the estimate of the amount of 2,4,5-trinitrotoluene is subject to a considerable error, and we cannot exclude the possibility that other isomeric trinitrotoluenes may be present in our recrystallized product in amounts of less than 1%. Gibson[9] has found that the trinitration of toluene yields 95.5% of the 2,4,6-, 2.9% of the 2,4,5-, 1.3% of the 2,3,4- and 0.3% of the 2,3,6-trinitrotoluene. For these reasons the corrected value of the deuterium content of the 2,4,6-trinitrotoluene can be regarded only as an estimate.

The corrected trinitrotoluene result gave a value of 0.82% *m*-deuteration and a value for the *meta* partial rate factor of 3.8. Two pieces of evidence indicate that this estimate is not greatly in error. The values for the *para* and *meta* partial rate factors give a point falling quite close to the line correlating data for other electrophilic aromatic substitutions. A second check on this value can be obtained from the rates of deuteration of some of the polymethylbenzenes. The relative rates of deuteration of benzene, *p*-xylene and *o*-xylene in trifluoroacetic acid at 70° are 1:850:1030 (corrected for solvent effects). From these values and the partial rate factors for the *o*- and *p*-positions for toluene, one can calculate values for the *meta* partial rate factor by the method of Condon.[10] From the value of *p*-xylene one finds $m_f = 5.1$, and from *o*-xylene, $m_f = 4.6$.

Similarly, the relative rates of deuteration of isodurene and mesitylene at 0° are 2.6:1 (corrected for solvent effects). This leads to a value of $m_f = 3.9$. Condon's procedure correlates the rates of substitution of the polymethylbenzenes over a wide range of reactivities very well, but partial rate factors deduced from a few compounds are subject to some uncertainty. Nevertheless, these results do show that the value for m_f is probably not in error by more than ±25%.

Consequently, it is concluded that for deuteration of toluene in trifluoroacetic acid at 70°, $o_f = 250$, $m_f = 4$, $p_f = 420$. These values are in good agreement with those recently published by Mackor, Smit and van der Waals.[11] These investigators using an acid reagent more reactive than ours found these partial rate factors for toluene

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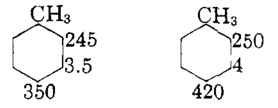
[9] W. H. Gibson, R. Duckham and R. Fairboirn, *J. Chem. Soc.*, 270 (1922).

[10] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[11] E. L. Mackor, P. J. Smit and J. H. van der Waals, *Trans. Faraday Soc.*, **53**, 1309 (1957).



Ref. 11, 25° Present work, 70°

Other Aromatic Substitution Reactions.—It is of interest to compare these results with the theory put forward by Brown and Nelson[12] to correlate the *meta* and *para* partial rate factors for electrophilic aromatic substitution in toluene. These authors have put forward the relation $\log_{10} p_f = C \log_{10} p_f/m_f$; this can be rewritten as $\log_{10} p_f = (c/(c - 1)) \log_{10} m_f$. A plot of some of the data collected by Brown and Nelson is given in Fig. 1, together with the results of de la Mare and Harvey[13] and Gold and Satchell[4] on bromination by hypobromous acid and on hydrogen exchange, respectively.

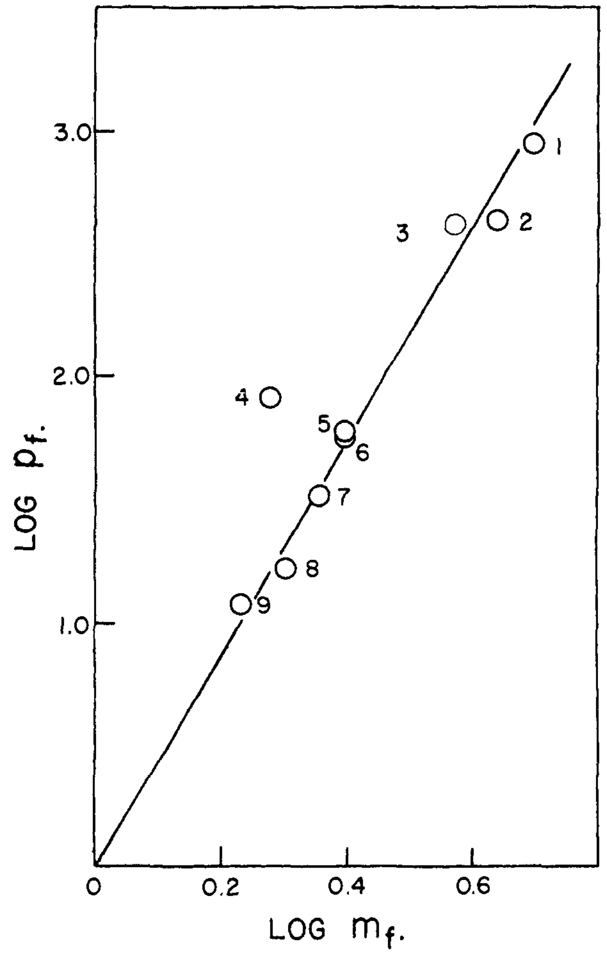


Fig. 1.—Relation between log p_f and log m_f: 1, chlorination; 2, chloromethylation; 3, present results; 4, hydrogen exchange in H_2SO_4; 5, bromination; 6, nitration; 7, mercuration; 8, detrimethylsilylation; 9, methylation.

It can be seen that the present data give a point falling on the line correlating most of the other data.

Halogenation in acetic acid is a very selective reaction and probably involves molecular halogen among the active species,[14] while nitration involves an attacking species with ionic character. Bromination by hypobromous acid in excess perchloric acid in aqueous dioxane involves the Br^+ or $BrOH_2^+$ ion. Both of these latter reactions are much less selective. The relatively high selectivity of deuteration in trifluoroacetic acid suggests that the active species in this case is less electrophilic and therefore is more selective.

The present results can be compared with those obtained by other workers. The o_f/p_f ratios for the deuteration of toluene and for the exchange of deuteriotoluenes with an isotopically normal acid solvent are the same, 0.6; Melander and Olsson[5] have shown that the $o_f:m_f:p_f$ ratios are 51:1:46 and 47:1:41 for the exchange of the isomeric deuterio- and tritiotoluenes with isotopically normal 80.8% sulfuric acid at 25°. Lauer and Leister[15] have obtained a very similar o_f/p_f ratio, 0.95, for deuteration in 50 mole per cent. sulfuric acid; this has been confirmed by infrared measurements. This indicates that we may validly compare $o_f:m_f:p_f$ ratios both for exchange in and out of the toluene nucleus with different isotopes.

Gold and Satchell[4] found $o_f = 83$, $m_f = 1.9$ and $p_f = 83$ exchange of the deuteriotoluenes in 68% aqueous sulfuric acid at 25°. It seems clear that trifluoroacetic acid is a less active reagent than 68% sulfuric acid in hydrogen exchange.

A more relevant comparison can be made with the investigation of Tiers[6] of the exchange between the deuteriotoluenes and heptafluorobutyric acid at 119°. Tiers observed an $o_f:m_f:p_f$ ratio of 8.5:1:21.1. The p_f/m_f ratio, 21.1, is lower than that observed for exchange in concentrated sulfuric acid, 40–45, which in turn is lower than that observed for exchange in trifluoroacetic acid, *ca.* 100. It is somewhat surprising that heptafluorobutyric acid should be a less discriminating reagent than 78% sulfuric acid while trifluoroacetic acid is a more discriminating reagent. The o_f/p_f ratio for exchange in 70.8% perchloric acid reported by Tiers is in good agreement with the value 1.00 reported by Gold and Satchell for 68% sulfuric acid, 1.11 and 1.15 found by Melander and Olsson for 80.8% sulfuric acid and 0.95 found by Lauer and Leister for 50% sulfuric acid. For exchange in heptafluorobutyric acid, Tiers found a value of 0.405. Thus the o_f/p_f ratio changes from *ca.* 1.1 in strong sulfuric acid to 0.6 in trifluoroacetic acid and 0.41 in heptafluorobutyric acid.

There are several possible explanations for this effect. It could be due to a steric effect. In strong sulfuric acid it appears that hydrogen exchange involves a mechanism of the type described in the introduction involving π- and σ-type complexes between the entering and leaving hydrogen ions and the aromatic ring; in this case steric effects are expected to be relatively small. In less acid and less polar media such as trifluoroacetic acid the mechanism may be different, possibly involving a cyclic transition state or intermediate of the type suggested by Ingold.[3] The bulkier heptafluorobutyric acid molecule should have greater steric requirements than the trifluoroacetic acid mole-

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(12) (a) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6992 (1953); (b) K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).

(13) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956).

(14) P. W. Robertson, *ibid.*, 1267 (1954).

(15) W. M. Lauer and D. Leister, unpublished work.

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.

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Hydrogen Isotope Exchange Reactions. II. Monoalkylbenzenes[1]

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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; $\mathrm{ArH_0}$ = 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.

[2] (a) General Electric Corporation Fellow 1955–1956, Ethyl Corporation Fellow 1954–1955; (b) du Pont Postdoctoral Fellow 1955–1956, Atomic Energy Commission Postdoctoral Fellow 1956–1957, Contract AT(11-1)478.

[3] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

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

[5] W. M. Lauer, G. W. Matson and G. Stedman, *ibid.*, **80**, 6433 (1958).