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 $\sigma$- and $\pi$-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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[17] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3622 (1955); *ibid.*, 2743 (1956).

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

[19] H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421 (1957).

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

# Electrophilic Hydrogen Isotope Substitutions. III. The Polyalkylbenzenes

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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.

[2] W. M. Lauer, G. W. Matson and G. Stedman, THIS JOURNAL, **80**, 6437 (1958).

[3] H. C. Brown and J. W. McGary, *ibid.*, **77**, 2300 (1955); H. C. Brown and L. M. Stock, *ibid.*, **79**, 1421 (1957).

[4] F. E. Condon, *ibid.*, **70**, 1963 (1948).

methanol. Some compounds were kindly supplied by Professor L. I. Smith. Other materials were used as described in previous papers.[2]

**Kinetic Measurements.**—The same procedure used for the monoalkylbenzenes was used for the polyalkylbenzenes. The more reactive compounds were deuterated at lower temperatures in order to obtain a measurable rate, and in these cases stoppered reaction vessels were used in place of sealed ampoules. Deuterium analyses were carried out as previously described.[2]

**Calculations.**—Relative rates were calculated both by the integrated form of rate equation (see paper I) and from the ratio of the times needed to reach a given % reaction. In the cases of 1,2,4-trimethylbenzene, *o*-diethylbenzene, *p*-diethylbenzene and *p*-*t*-butyltoluene, difficulties were encountered due to the presence of a small amount of a much more reactive compound, in the latter three cases probably the *m*-isomer. In these cases the reactivity was calculated from the residual rate after the reactive impurity had come to isotopic equilibrium with the solvent.

**Results and Discussion.**—The experimental results, expressed as reactivities relative to benzene = 6 are given in Table I. The relative reactivities were calculated as the ratio of the rate constants and also as the reciprocal of the ratio of the times needed to reach a given % reaction (usually $D' = 0.05, 0.10, 0.15$). The two methods gave similar results, although the relative reactivities calculated by the latter method are consistently 10–15% lower than those calculated by the former method. The wide range of reactivities made it necessary to measure some of the more reactive hydrocarbons at temperatures lower than 70°. In order to relate these values to those measured at 70°, the rate of deuteration of *m*-xylene was measured at several temperatures, 70°, 40.1° and 29.65°. These rates gave an Arrhenius activation energy of 17.6 kcal. This value was used to relate the rates measured at 40.1 and 0° to those obtained at 70°. Because of the existence of a solvent effect due to the high concentration of aromatic compound used,[2] the results in Table I have been corrected to allow for this factor. The same correction used for the monoalkylbenzenes was used for the present results.[2]

TABLE I

RELATIVE RATES OF DEUTERATION OF POLYMETHYLBENZENES

| Compound | $T$, °C. | Observed[a] | Observed[b] | Calculated |
|---|---|---|---|---|
| Benzene | 70 | 6 | 6 | 6 |
| Toluene | 70 | 934 | 934 | 934 |
| *p*-Xylene | 70 | $5.10 \times 10^3$ | $4.76 \times 10^3$ | $3.84 \times 10^3$ |
| *o*-Xylene | 70 | $6.18 \times 10^3$ | | $5.12 \times 10^3$ |
| *m*-Xylene | 70 | $1.84 \times 10^5$ | $1.66 \times 10^5$ | $2.77 \times 10^5$ |
| Pseudocumene | 40.1 | $5.05 \times 10^{5c}$ | $4.54 \times 10^5$ | $6.51 \times 10^5$ |
| Hemimellitene | 40.1 | $6.58 \times 10^{6c}$ | $5.80 \times 10^5$ | $8.14 \times 10^6$ |
| Durene | 30 | $1.67 \times 10^{6d}$ | $1.35 \times 10^{6e}$ | $1.85 \times 10^6$ |
| Mesitylene | 0 | $5.70 \times 10^{7f}$ | $5.02 \times 10^7$ | $8.08 \times 10^7$ |
| Isodurene | 0 | $1.50 \times 10^{8f}$ | $1.38 \times 10^8$ | $2.04 \times 10^8$ |
| Pentamethylbenzene | 0 | $1.59 \times 10^{8g}$ | ........ | $3.88 \times 10^8$ |

[a] Relative rates obtained from rate constants. [b] Relative rates obtained from time needed to reach a given deuterium content. [c] Compared with *m*-xylene at 40.1°. [d] Competitive experiment with *m*-xylene. [e] Run in benzene solution at 40.1°. [f] Compared with *m*-xylene at 0° calculated from measured activation energy. [g] Competitive experiment with mesitylene; $[ArH]_0 = 24.6$, $[D_2O] = 12.5$, $[CF_3COOH] = 62.9$; all concentrations in moles %.

These relative reactivities are in the same sequence as those observed in basicity,[5] halogenation[3] and mercuration.[3] From the spread in reactivities between benzene and pentamethylbenzene, it is clear that deuteration in trifluoroacetic acid is a reaction of similar selectivity to basicity in hydrofluoric acid. From *p*-xylene to pentamethylbenzene there appears to be a good linear relationship between basicity in hydrofluoric acid and deuteration in trifluoroacetic acid; the log–log plot has a slope close to unity. Deviations are observed for toluene and to a much greater extent for benzene; these results are shown graphically in Fig. 1.

The work of Condon[6] and Brown[3] has shown that the reactivities in electrophilic aromatic substitution of the polymethylbenzenes can be successfully predicted from the partial rate factors for toluene. We have found that for deuteration of toluene under our conditions $o_f = 250$ and $p_f = 420$. We also have obtained an approximate value for $m_f$ of 3.8. The relative reactivities calculated from these figures are given in the last column of Table I and may be compared with the observed relative reactivities (corrected for solvent effects). It can be seen that the agreement is good; over a reactivity range of between $10^7$ and $10^8$ the average deviation is about 25%. This good agreement confirms that the partial rate factors for toluene quoted above are, at worst, not much in error.

These results suggest that steric effects do not play an important role in deuteration of the polymethylbenzenes in trifluoroacetic acid. Brown, in a study of mercuration[3] and bromination,[3] has found that mesitylene, isodurene and pentamethylbenzene, and in the former case durene also, show considerably lower reactivities than predicted by the above method. This has been ascribed to increased importance of steric effects in positions doubly flanked by methyl groups compared to positions singly flanked. In the present case the agreement between observed and calculated rates is satisfactory for durene, mesitylene and isodurene, while in the case of pentamethylbenzene the observed reactivity is a little less than half of the predicted value. The calculated rate for mesitylene does not depend on the value of $m_f$; for isodurene the calculated rate depends on it to the first power, and for durene and pentamethylbenzene the calculated rate depends on $m_f$ to the second power. We conclude from these results that steric effects do not play a very important role in deuteration in trifluoroacetic acid. Because of the uncertainty in the value for $m_f$ this is not a sufficiently sensitive test to detect small steric effects. Even if a very accurate value for $m_f$ were available, the existence of solvent effects, the fact that measurements were made at different temperatures and the fact that it is not known how accurately the additivity relation should hold in the absence of steric effects render discussion of the cause of small deviations of doubtful significance.

**Isomer Distribution.**—The distribution of deuterium in deuterated *o*-xylene and *m*-xylene has been determined by methods similar to those used

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(5) M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953); D. A. Macaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(6) F. E. Condon, *ibid.*, **70**, 1963 (1948).

for the monoalkylbenzenes. For *o*-xylene the relative deuterium contents of the 3- and 4-positions were found to be 0.68:1. Condon's theory predicts that they should be in the ratio $o_f$:$p_f$ for toluene, *i.e.*, 0.60:1. The results are subject to a considerable error as the deuterium contents were determined as the differences between deuterated *o*-xylene and its purified nitro derivatives. These deuterium contents differ by only about 25% on average, thus considerably magnifying the possible error.

For *m*-xylene the relative deuterium content of the 2- and 4-positions were found to be 0.59:1. Theory again predicts they should be in the ratio $o_f$:$p_f$ for toluene, *i.e.*, 0.60:1. The good agreement is probably fortuitous in view of the possible experimental error. By arguments similar to those outlined above it is concluded that as the relative reactivity of positions singly and doubly flanked by methyl groups is close to that predicted from the partial rate factors for toluene, there are no large steric effects involved.

**The Polyalkylbenzenes. Steric Effects.**—The relative reactivity of 1,3,5-triethylbenzene and mesitylene was determined at 30° by a competitive experiment. It was thought that this would provide a particularly favorable case for observing the occurrence of non-additive steric effects. The relative reactivities can be predicted from the *ortho* and *para* partial rate factors for toluene and ethylbenzene alone, and these quantities are known with some accuracy. It was found that the observed relative rates of mesitylene:1,3,5-triethylbenzene were 1.34:1. The predicted ratio is 0.909:1. It is difficult to decide how much significance is to be placed on this difference because it is not clear how well the additivity rule holds. It is believed that the difference is outside the experimental error and that it is significant and indicates the presence of a small steric effect in 1,3,5-triethylbenzene.

***meta* Partial Rate Factors.**—If it is assumed that the additivity relationship found for the polymethylbenzenes also holds for the polyalkylbenzenes, excluding special steric effects in doubly flanked positions, then from the known values of $o_f$ and $p_f$ for the monoalkylbenzenes and the reactivities of suitable polyalkylbenzenes one can calculate approximate values for $m_f$ for the other alkyl groups. Measurements were made on *p*-diethylbenzene, *o*-diethylbenzene and *p*-*t*-butyltoluene. The calculation of results was complicated by the presence of small amounts of a much more reactive impurity, probably the *meta* isomer. The reactivities were determined therefore by comparing the residual rates after this impurity had come to isotopic equilibrium with the solvent, as shown by a sharp change in slope of the reaction–time curve. After correction for solvent effects, it was found that $m_f$ for the ethyl group was 4.3 from *p*-diethylbenzene and 4.4 from *o*-diethylbenzene; for the *t*-butyl group, $m_f$ was 7. These results can only be regarded as approximate values, indicating that the *meta* partial rate factors of the monoalkylbenzenes are quite similar.

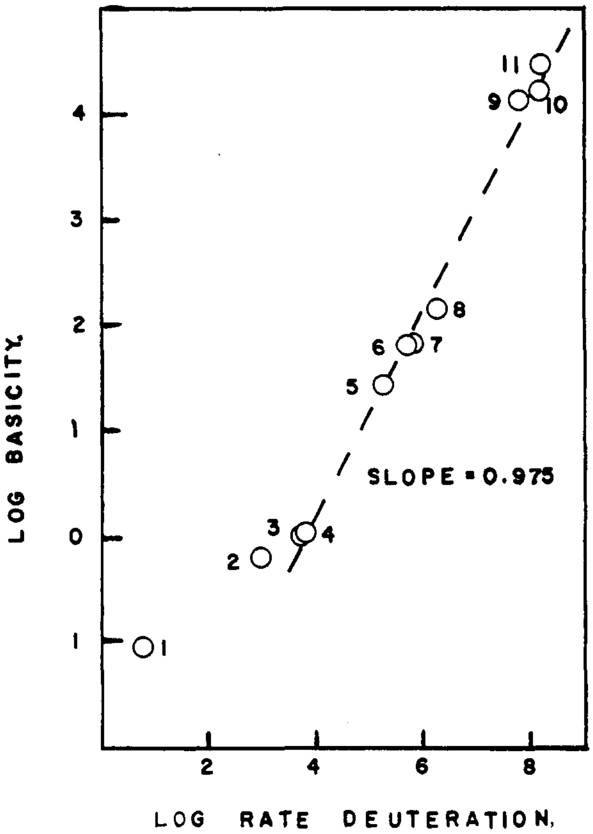

Fig. 1.—Relation between basicity[5] and rate of deuteration: 1, benzene; 2, toluene; 3, *p*-xylene; 4, *o*-xylene; 5, *m*-xylene; 6, pseudocumene; 7, hemimellitene; 8, durene; 9, mesitylene; 10, isodurene; 11, pentamethylbenzene.

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