Rates of Mercuration.—Mercuric acetate was dissolved in sufficient glacial acetic acid to make a 0.1 *M* solution. This solution and the aromatic were measured and mixed at 25°, the reaction being very slow at this temperature. Then, 10-ml. aliquots were removed and sealed off in thin glass bulbs and were placed in the appropriate constant temperature bath. After a period of five minutes, a bulb was quenched as the initial point. The reaction was followed by determining the decrease in the mercuric ion concentration by titration with standard thiocyanate using ferric alum indicator. The rate constants were reproducible to a precision of less than 3% and are summarized in Table I.

The reactions involving perchloric acid and sodium perchlorate were followed similarly. The results in which the perchloric acid was less than 0.09 *M*, were somewhat less precise since the second-order rate constants dropped off in the latter stages of the reaction. Data are summarized in Table II.

Mercuration of Toluene.—At 50°, 77 ml. (0.72 mole) of toluene was added to a 500-ml. round bottomed flask containing 300 ml. of a 0.24 *M* (0.072 mole) mercuric acetate solution in glacial acetic acid. Aliquots were removed with a 50-ml. pipet and quenched in an equal volume of water. The product was then converted to a mixture of bromotoluenes and analyzed by infrared as described previously.[5]

The mercuration in glacial acetic acid at 70 and 90° was carried out similarly except that 154 ml. of toluene was added, thus raising the toluene-to-mercuric acetate ratio to twenty. The data together with those at 50° are reported in Table III.

Bromination of Toluene.—A homogeneous solution of 4.0 ml. (0.037 mole) of toluene and 3.3 g. (0.0062 mole) of aluminum bromide (prepared from bromine and aluminum and distilled) was prepared in a small flask. To this solution at 30°, 1.0 g. (0.0062 mole) of bromine was added. The reaction was quenched immediately in ice-water and was analyzed by infrared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Rates of Mercuration of the Monoalkyl- and the Polymethylbenzenes. Calculation of Relative Reactivities for the Mercuration Reaction[1,2]

BY HERBERT C. BROWN AND CHARLES W. McGARY, JR.[3]

RECEIVED NOVEMBER 17, 1954

The rates of mercuration of the polymethylbenzenes and a series of monoalkylbenzenes have been measured using mercuric acetate in glacial acetic acid at 50°. The relative reactivities of the polymethylbenzenes may be calculated with the assumption of additivity of the partial rate factors with a mean deviation of 12%. By taking into account steric factors involving substitution in the *ortho* position, the rate constants can be calculated with a mean deviation of 6%. The rate of mercuration decreases from toluene to ethyl-, isopropyl- and *t*-butylbenzene with the latter compound undergoing mercuration at a rate 36% less than that of toluene. The decrease in rate appears to be only slightly greater than can be accounted for by a decrease in substitution in the *ortho* position. It is concluded that mercuration is a reaction of low selectivity which shows only low discrimination between hydrogen and methyl as substituents in benzene, as well as between methyl and *t*-butyl.

It was shown previously by Condon that the relative reactivities of the polymethylbenzenes in halogenation could be calculated by the use of partial rate factors calculated from data for toluene.[4] The relative rates calculated in this way agreed with the available experimental data within a factor of 2.

In the preceding paper the partial rate factors for the mercuration of toluene were determined.[5] The mercuration reaction exhibits simple second-order kinetics. The rates of mercuration can be measured readily with a precision of 2–3%. This reaction therefore offered a promising method for determining the relative reactivities of the polymethylbenzenes to provide a test of the generality of the treatment utilized by Condon.[4] Accordingly, a study was made of the rates of reaction of mercuric acetate in acetic acid with the three xylenes and all of the higher methylbenzenes.

In the bromination reaction, toluene has been reported to react five times as fast as *t*-butylbenzene.[6] The decreased reactivity of *t*-butylbenzene was attributed to the decreased importance of hyperconjugation as the α-hydrogen atoms are replaced by methyl groups. However, in the case of nitration[7] and isopropylation,[8] the decreased reactivity is small and appears to be due entirely to the decreased substitution in the *ortho* position. These two seemingly contradictory sets of data have been considered to be anomalous.[9] It therefore appeared of interest to examine the behavior of toluene, ethyl-, isopropyl- and *t*-butylbenzene in the mercuration reaction.

Results and Discussion

Mercuration of Alkylbenzenes.—The rates of mercuration of a series of alkylbenzene derivatives were determined, using the uncatalyzed reaction with mercuric acetate in glacial acetic acid at 50°. The reaction was followed by quenching aliquots at various time intervals and titrating with standard thiocyanate. The reactions followed second-order kinetics, first in both aromatic and mercuric acetate, and were carried out to 30–70% completion. The rate constants were reproducible to better than 3%. The results are summarized in Table I.

The Methylbenzene Series.—In Table II, columns one and two, the experimental reactivity

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(1) Directive Effects in Aromatic Substitution. VI.

(2) Based upon a thesis submitted by C. W. McGary, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Purdue Research Foundation Fellow, 1952–1953; American Cyanamid Corp. Fellow, 1953–1954. Research assistant on a grant from the National Science Foundation, 1954.

(4) F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

(5) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2306 (1955).

(6) E. Berliner and F. Berliner *ibid.*, 1195 (1949).

(7) H. Cohn, E. D. Hughes, M. H. Jones and M. A. Peeling, *Nature*, **169**, 291 (1952). The authors report that the rates of substitution in the *meta* and *para* positions of *t*-butylbenzene are slightly greater than in toluene.

(8) F. E. Condon, THIS JOURNAL, **70**, 2265 (1948)

(9) P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

TABLE I

RATE CONSTANTS FOR THE REACTION OF ALKYL SUBSTITUTED BENZENES WITH MERCURIC ACETATE AT 50°

Compound	Reactants: Mercuric acetate (mole/l.)	Reactants: Hydrocarbon (mole/l.)	Rate constant $k_2 \times 10^4$, l. mole^{-1} min.$^{-1}$
Benzene	0.089	0.94	0.450
Toluene	.088	.93	2.26
	.099	.57	2.33
	.109	.94	2.37
Ethylbenzene	.098	.61	1.95
Isopropylbenzene	.097	.57	1.82
t-Butylbenzene	.096	.57	1.49
o-Xylene	.091	.50	7.54
m-Xylene	.095	.50	16.2
p-Xylene	.090	.51	3.84
Hemimellitene	.091	.45	32.2
Pseudocumene	.092	.38	23.6
Mesitylene	.093	.42	99
Prehnitene	.096	.41	60
Isodurene	.099	.39	122
Durene	.099	.45	14.2
Pentamethylbenzene	.099	.53	105

ratios of the polymethylbenzenes are compared with the values calculated from the experimental partial rate factors.[5] The agreement, in general, is quite satisfactory with a mean deviation of 12.5% for the 12 compounds.

TABLE II

COMPARISON OF RELATIVE RATES OF MERCURATION WITH CALCULATED VALUES

Compound	Experimental	Calcd.[a]	Calcd.[b]	Calcd.[c]
Benzene	1.00	1.00	1.00	1.00
Toluene	5.0	5.0	5.3	5.28
o-Xylene	16.0	14.1	16.0	14.7
m-Xylene	34.5	30.0	34.5	35.0
p-Xylene	8.2	6.1	8.2	7.2
Hemimellitene	68	62	78	71.5
Pseudocumene	49	35.5	48.2	41.4
Mesitylene	209	178	235	194
Prehnitene	126	101	147	121
Isodurene	257	235	353	255
Durene	30.0	27.8	50.6	30.4
Pentamethylbenzene	224	233	388	255

[a] Calculated from factors: p_f 16.8; m_f 1.98; o_f 4.61. [b] Calculated from factors: p_f 15.8; m_f 2.26; o_f 5.45. [c] Calculated from factors: p_f 16.8; m_f 1.98; o_f 5.45 (single *ortho*); o_f 4.8 (double *ortho*).

The data indicate a peculiarity: except for pentamethylbenzene the calculated values are consistently low. This suggests that better agreement with the experimental values might be obtained with a set of partial rate factors which were somewhat higher than the experimental values utilized.

It is possible to arrive at a set of partial rate factors by solving simultaneously the three equations for the xylenes.

$$2o_fm_f + 2m_fp_f = 6 \times 16.0$$
$$4o_fm_f = 6 \times 8.2$$
$$o_f^2 + 2o_fp_f + m_f^2 = 6 \times 34.5$$

This procedure leads to the values: $o_f = 5.45$; $m_f = 2.26$; $p_f = 15.8$. Rates of mercuration calculated with the aid of these factors are reported in the third column of Table II.

It is evident that rate constants calculated with the aid of these factors are only partially satisfactory for the trimethylbenzenes, and are far too high for the tetra- and pentamethylbenzenes. The results are therefore less satisfactory than the relative rates calculated with the aid of the experimental partial rate factors.

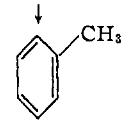
In our opinion these partial rate factors can be discarded for another reason. The *para*-to-*meta* ratio of isomers was determined with great care in the study of the mercuration of toluene and the *para*/*meta* ratio calculated with these partial rate factors (15.8/2.26) is in poor agreement with the experimentally determined value.

Unfortunately, we cannot have the same confidence in the precise amount of the *ortho* isomer formed in the mercuration reaction. The *o*-tolylmercuric acetate has an unhindered position *para* to the methyl group available for substitution.[10] Although we utilized the utmost precaution to minimize polymercuration, some polymercuration could not be entirely avoided. There is the possibility that the *ortho* isomer was selectively dimercurated and the apparent amount of *ortho* substitution thereby reduced.

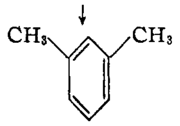
We, therefore, adopted the experimental values for the *meta* and *para* partial rate factors and determined the value for the *ortho* partial rate factor which would give the best agreement with the experimental rate data.

It soon became apparent that no single value for the *ortho* partial rate factor would give satisfactory agreement. A value which gave reasonable agreement for compounds with a single *ortho* substituent, gave high values for compounds with double *ortho* substitution, such as mesitylene and durene.

The mercuration reaction is one with large steric requirements. Thus in the mercuration of toluene at 50° only 30.7% of the *ortho* isomer is formed in comparison to 56.1% of the *para*. In view of the widely recognized generalization that steric effects increase very rapidly with increasing steric requirements, it is quite reasonable that the steric effect of the structure II should not be simply twice that of structure I.



I
(single *ortho*)



II
(double *ortho*)

We, therefore, adopted the partial rate factor 5.45 for single *ortho* (I) and then calculated partial rate factors for double *ortho* (o_f^2). The following values of o_f^2 were obtained: 20.0 (*m*-xylene); 24.9 (mesitylene); 22.2 (isodurene); 22.8 (durene); 20.2 (pentamethylbenzene) Adopting from this the value 4.8 for the partial rate factor for double *ortho*, the fourth column of relative reactivities in Table II was calculated. These values show a mean deviation of only 6% with the experimental data.

A more complete treatment of the *ortho* effect would probably require taking into account the but-

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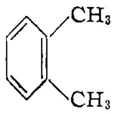
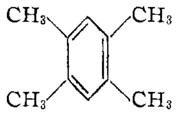
(10) H. C. Brown and C. W. McGary, Jr., THIS JOURNAL, **77**, 2300 (1955).

tressing effect. Thus a case can be made for different factors for single *ortho* (I), double *ortho* (II), buttressed single *ortho* (III) and buttressed double *ortho* IV.



III
(buttressed single *ortho*)



IV
(buttressed double *ortho*)

For example, the data for mesitylene and pentamethylbenzene clearly point to an important buttressing effect in the latter compound.

Mesitylene: $3o_f{}^2p_f = 6 \times 209$

Pentamethylbenzene: $o_f{}^2m_f{}^2p_f = 6 \times 224$

By letting m_f equal 1.98, the ratio of the respective *ortho* factors may be calculated to be 1.11. In other words, the *ortho* partial factor for pentamethylbenzene (buttressed double *ortho*) should be 11% smaller than the corresponding factor for mesitylene (double *ortho*). In view of the limited data available a further examination of this treatment does not appear warranted at this time.

In summary, the experimental partial rate factors permit the calculation of the relative reactivities with a mean deviation of 12%. Utilization of derived single and double *ortho* partial rate factors permit reproduction of the experimental relative reactivities with a mean deviation of 6%. Such close agreement between the experimental and calculated rate data in the mercuration reaction lends support to the conclusion that the treatment utilized by Condon may represent a general procedure for handling data for the substitution reactions of polysubstituted aromatic derivatives.

The Monoalkylbenzene Series.—The relative rates of mercuration for *t*-butylbenzene and toluene at 50° are 3.2 and 5.0, respectively (Table III).

TABLE III

RELATIVE RATES OF MERCURATION OF THE MONOALKYLBENZENES AT 50°

Compound	Relative rate (RC_6H_5/C_6H_6)
Benzene	1.00
Toluene	5.0
Ethylbenzene	4.2
Isopropylbenzene	3.9
t-Butylbenzene	3.2

The *t*-butyl group possesses large steric requirements which markedly reduce substitution in the *ortho* position. For example, nitration produces 56.5% of the *ortho* isomer in toluene, but only 15.8% in *t*-butylbenzene.[7,11]

It has been pointed out that the mercuration reaction is evidently one of large steric requirements, yielding but 31% of the *ortho* isomer in toluene. On the assumption that the mercuration of *t*-butylbenzene proceeds with little or no *ortho* substitution, a maximum decrease in rate of the order of 31% can be attributed to this factor. Since the observed decrease is 36%, there must be a relatively small decrease in the rate of substitution in the *meta* or *para* positions.

It, appears therefore, that mercuration resembles nitration[7] and isopropylation[8] in that the replacement of the methyl group in toluene by a *t*-butyl group produces relatively minor changes in the reaction rate in positions other than those *ortho* to the alkyl group. These reactions contrast strongly with bromination where the same change results in a several fold decrease in rate of substitution.

It was pointed out previously that the high selectivity of the bromination reaction means that the carbon–bromine bond in the transition state must require a large electronic contribution from the aromatic ring.[12]

On the other hand, the less selective reactions such as nitration, mercuration and isopropylation apparently involve attack by a species with a large amount of ionic character. In these cases the new bonds being formed in the transition state do not require very large contributions from the aromatic ring. Under these circumstances hyperconjugative contributions from the alkyl groups are of much smaller importance and the effects of methyl and *t*-butyl substituents are relatively small and do not differ significantly among themselves.

Experimental Part

Rates of Mercuration.—The procedure for following the rates of mercuration in glacial acetic acid at 50° has been described previously. The rate constants were reproducible under identical conditions to within 1%. However, over the large concentration range of aromatics utilized (to minimize polymercuration), Table I, deviations sometimes amounted to a maximum of 3%.

In the case of the higher methylbenzenes, the end-points faded in the titration with thiocyanate and ferric alum in the latter stages of reaction. In these cases the reaction was followed to only 30–50% and the latter points were obtained by adding excess thiocyanate and back titrating with silver thiocyanate.

The rate data were corrected for the side reaction of mercuric acetate with acetic acid as indicated previously.[5] The corrections amounted to less than 5% depending upon the speed of the reaction.

Materials.—Glacial acetic acid (Baker and Adamson, reagent) and mercuric acetate (Merck reagent) were used directly. With two exceptions the benzene derivatives were highly purified samples with purities of better than 99.5%. Pentamethylbenzene (m.p. 52.2–53.1°) was a sample supplied by Professor L. I. Smith of the University of Minnesota, and prehnitene (b.p. 204° (742 mm.), m.p. −68°, $n^{20}D$ 1.5203) was prepared by the Jacobsen rearrangement.

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[11] K. L. Nelson and H. C. Brown, THIS JOURNAL, **73**, 5605 (1951).

[12] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).