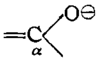
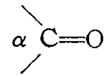
In going to the excited state, the energy change relative to an unstrained example would be decreased at γ and increased at α (*i.e.*  $=\underset{\alpha}{C}{<}^{O^{\ominus}}$ less easily distorted than α  $>C=O$).[25] It can only be guessed whether there would be a net increase or decrease in strain on excitation, compared to cyclohexenone. It would appear difficult, however, to account for the *large* decrease in λ_{max} for cyclopentenone as compared to cyclohexenone mainly on the basis of a net increase in strain for the former. Cyclopentenones in general absorb at a lower wave length than cyclohexenones.[10]

This discussion has assumed that one can estimate which ionic forms are more important in the spectrally excited hybrid state. With dienes, the treatment would be more obscure than with α,β-unsaturated carbonyl compounds. It may be that with dienes or similar chromophores in which polarization may occur with about equal probability in either direction in the excited state, the introduction of strain into one part of the chromophores would produce a splitting of the unstrained absorption band into two bands. One of these bands (at shorter wave length) would correspond to polarization toward the site of strain, and the other (at longer wave length) to polarization away from the site of strain. Splitting of diene absorption bands has been attributed to superimposed vibrational levels.[26a,b]

The possibility that strain in the 1,4-cyclohexadiene ring of 1-acetylcyclohexadiene-1,4 might contribute to the increase in λ(λ_{max} = 245, ϵ 4,000) over that of 1-acetylcyclohexene,[27a,b,c] compound 2, was considered. However, there appears to be little, if any, strain in this ring system.

SEATTLE, WASHINGTON

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[25] No doubt the strain problem is even more complicated than this; fixing attention only on the change in strain at α and γ is probably an oversimplification.

[26] (a) E. P. Carr, L. W. Pickett and H. Stucklen, *Rev. Mod. Phys.*, **14**, 260 (1942); (b) L. Dorfman, *Chem. Revs.*, **53**, (1953).

[27] (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1946); (c) E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates and Isomer Distribution in the Mercuration of Benzene and Toluene. A Proposed Extension of the Quantitative Relationship Governing Isomer Distribution in Aromatic Substitution[1]

BY HERBERT C. BROWN AND CHARLES W. McGARY, JR.[2]

RECEIVED JUNE 18, 1954

A detailed study has been made of the perchloric acid catalyzed mercuration of benzene and toluene in glacial acetic acid at 25, 50 and 75°. Under the experimental conditions the isomer distribution in toluene changes with time and approaches a statistical distribution of the three tolylmercuric acetates. By extrapolating the data to zero time it has been established that the three isomers are formed at 25° with the distribution: *ortho*, 21.0 ± 0.5; *meta*, 9.5 ± 0.5; *para*, 69.5 ± 1.0%. At 50° the distribution is: *ortho*, 20.0; *meta*, 11.5; *para*, 68.5%. At 75° the observed distribution is: *ortho*, 18.3; *meta*, 12.6; *para*, 69.1%. At 25° both competition experiments and absolute rate measurements lead to a toluene/benzene reactivity of 7.9 ± 0.2. At 50 and 75° this ratio changes to 7.0 and 5.9, respectively. These data are consistent with the linear relationship previously proposed to account for isomer distribution in toluene substitutions and thereby remove a discrepancy provided by the mercuration data previously available. It now has been established that the linear relationship satisfactorily accounts for isomer distribution in toluene substitution for isopropylation, sulfonylation, mercuration, nitration, chloromethylation and chlorination. An extension of the theory is proposed to permit the quantitative correlation of isomer distribution in the substitution of all benzene derivatives.

The high proportion of meta isomer formed in the alkylation of toluene under non-isomerizing conditions has been considered to be an anomalous characteristic of the Friedel–Crafts reaction.[3,4] In an earlier paper it was proposed that no anomaly was involved in this reaction, that the high percentage of *meta* isomer is to be attributed to the high activity and consequent low selectivity of the substituting species.[5] The relative rate of substitution of toluene to benzene was adopted as a measure of the activity or selectivity of the substituting agent. A simple quantitative relationship was then demonstrated for a number of reactions between this activity of a given substituting agent and the relative amounts of substitution in the *para* and *meta* positions of toluene.

However, in the case of mercuration the available data[5,6] neither agreed with each other, nor with the proposed generalization.[7] Klapproth and Westheimer[6] reported that in glacial acetic acid with perchloric acid as catalyst, toluene is mercurated by mercuric acetate to give 6% of the *meta* isomer at 25°. Data from this Laboratory subsequently indicated 12% *meta* under similar conditions.[5] In the former case a radiochemical technique was employed in establishing orientation, whereas infrared analysis was utilized in the latter. Furthermore, the toluene/benzene reactivity of 30, reported in

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[1] Directive Effects in Aromatic Substitution. IV. Previous publications in this series: THIS JOURNAL, **73**, 5605 (1951); **75**, 6292 (1953); **76**, 605 (1954).

[2] American Cyanamid Fellow, 1953–1954.

[3] C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapt. I.

[4] A. W. Francis, *Chem. Revs.*, **43**, 257 (1948).

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

[6] W. J. Klapproth and F. H. Westheimer, *ibid.*, **72**, 4461 (1950).

[7] The mercuration of toluene has been carried out under a variety of conditions and the percentage of *meta* isomer formed in these reactions varies from 6 to 21. For a summary of the available data, see ref. 5.

the latter case, did not agree with the linear relationship of partial rate factors established by similar data from other reactions.

Therefore, in view of the importance of both the theoretical and practical implications of the orientation-rate correlation, a detailed study of the mercuration reaction appeared desirable. As a result of this study, the discrepancy now has been resolved. A redetermination of the isomer distribution and relative rate indicates excellent agreement with the linear relationship of orientation and relative rate. Moreover, higher proportions of the meta isomer form at higher temperatures. This change is accompanied by a change in the relative rates in agreement with the quantitative relationship. These results lend further support to the importance of the activity and the selectivity of the attacking agent on the isomer distribution in aromatic substitution.

Results and Discussion

Mercuration of Toluene.—The mercuration of toluene was carried out in glacial acetic acid with perchloric acid catalyst. Aliquots were quenched at various time intervals, the products then being converted to tolylmercuric bromides, which then were converted to tolyl bromides by reaction with bromine in carbon disulfide suspension. The resulting solutions of the tolyl bromides were analyzed directly by infrared absorption.

The observed isomer distribution is essentially constant over the first hour of reaction. This is shown by the results for reaction times of 3, 6, 15 and 60 min., respectively: *ortho*, 20.3, 21.4, 20.7, 20.9%; *meta*, 9.2, 9.5, 9.5, 9.9%; *para*, 70.5, 69.1, 69.8, 69.2%. The mercuration reaction is largely over at this time. However, with longer reaction times, the isomer distribution shows a marked shift (Fig. 1).

It is apparent from these data that the mercuration product, tolylmercuric acetate, must undergo isomerization under the reaction conditions and approach an equilibrium distribution with time. The data suggest an approach to a statistical distribution of the three components, 40% *ortho*, 40% *meta* and 20% *para*. However, further work will be required to establish this point with certainty.

In view of these results it is evident that an accurate determination of the isomer distribution must involve either a correction for isomerization or the utilization of experimental conditions under which isomerization may be considered negligible. The possibility for isomerization under these mild reaction conditions has not been recognized previously. The larger amount of *meta* isomer, 12%, previously reported[5] may have resulted from isomerization accompanying the mercuration reaction.

To determine under what conditions dimercuration[6] is significant, the ratio of toluene to mercuric acetate was varied and the reaction carried to approximately 30% completion. The data (Table I) indicate that a ratio as low as 5 to 1 can be tolerated if the extent of reaction does not exceed 30%. With a ratio of toluene to mercuric acetate of 2 to 1, there was observed a definite decrease in the amount of the *ortho* isomer in the product. This decrease in the *ortho* isomer is attributed to a selective reaction of this isomer with the mercuric acetate. This interpretation is rendered reasonable by the observation that mercuric acetate possesses a marked preference for the *para* position in toluene, while the *o*-tolylmercuric acetate retains a free and unhindered position *para* to the methyl group.[8]

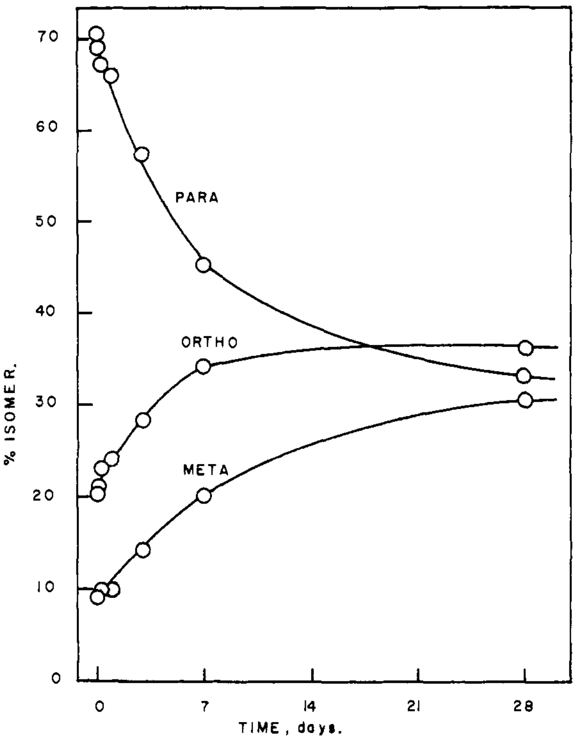

Fig. 1.—Variation in the isomer distribution with time of the tolylmercuric acetates.

TABLE I

VARIATION IN THE ISOMER DISTRIBUTION WITH THE RATIO OF TOLUENE TO MERCURIC ACETATE

Initial molar ratio toluene/ mercuric acetate	Extent of reacn., %	Isomer distribution *Ortho*	*Meta*	*Para*
20	31	21.3	10.0	68.7
10	20	21.4	10.0	68.7
5	27	21.8	9.6	68.6
2	23	18.3	10.5	71.2

From the data given, along with additional check determinations, the isomer distribution in the mercuration of toluene at 25° is considered to be 21.0 ± 0.5% *ortho*, 9.5 ± 0.5% *meta* and 69.5 ± 1.0% *para*. These data are based upon a large number of individual determinations. There remains a relatively minor disagreement with the values reported by Klapproth and Westheimer[6] (6% *meta*) for which we are unable to account.

Rates of Mercuration of Benzene and Toluene.—The competitive mercuration of benzene and toluene was carried out under conditions identical to those in which the orientation was studied. The product was converted by bromine into a mix-

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[8] This argument would be vitiated were the acetoxymercuri group to possess a strong orientation effect. However, the available evidence is that the directive effects of this group are relatively weak [F. Challenger and E. Rothstein, *J. Chem. Soc.*, 1258 (1934)].

ture of phenyl and tolyl bromides and analyzed by infrared absorption. The results showed an apparent variation of the toluene/benzene ratio with time. Pertinent data are summarized in Table II.

TABLE II

VARIATION WITH TIME OF THE RELATIVE RATE OF MERCURATION OF BENZENE AND TOLUENE AT 25°

Time	Isomer distribution *Ortho*	*Meta*	*Para*	Relative rate toluene/benzene
3 min.	20.9	10.2	68.9	8.5
6 min.	21.8	10.5	67.7	8.5
15 min.	24.9	10.0	65.1	9.5
60 min.	21.8	10.3	67.9	7.5
6 hr.	22.1	10.7	67.2	7.6
1 day	25.1	11.1	62.8	7.4
4 days	34.4	14.6	51.0	5.9

The apparent decrease with time in the relative rate of substitution of toluene and benzene is accompanied by a decrease in the amount of the *para* isomer and by a corresponding increase in the *ortho* and *meta* isomers. These results suggest that the reaction must be reversible, with the *para* isomer being most susceptible to protolytic attack. The selective loss of the *para* isomer in this demercuration reaction would account both for the apparent isomerization previously discussed and the apparent change in the toluene/benzene ratio under discussion here.[9] Reversibility of the mercuration reaction in nitric acid has been demonstrated previously.[10]

The observed increase with time of the *ortho* isomer at the expense of the *para* suggests that the steric requirements of the acetoxymercuri group must be rather small. In the sulfonation of toluene under isomerization conditions there is observed the opposite effect, an increase in the *para* isomer at the expense of the *ortho* derivative.[11] The difference in the results in the two reversible reactions presumably arises from the marked differences in the steric requirements of the two substituents.

In treating the arylmercuric bromides with bromine to form the aryl bromides for the analysis, there was observed a significant difference in the ease with which the different arylmercuric bromides reacted with bromine. Phenylmercuric bromide appeared to react more sluggishly than the tolyl isomers and special care was required to obtain a quantitative conversion. Failure to recognize this difficulty may have been the cause for the high value of the toluene/benzene reactivity ratio previously reported.[5]

In view of these difficulties inherent in the competitive procedure for determining the toluene/benzene reactivity ratio, it appeared desirable to examine the feasibility of obtaining this ratio by a direct measurement of the rate of mercuration of the two hydrocarbons. The mercuration of benzene has been studied previously and shown to follow second-order kinetics, first order in benzene and first order in mercuric acetate.[10]

The reactions were followed in different determinations both by precipitating and weighing the arylmercuric bromide and by following the decrease in the mercuric ion concentration by titration with thiocyanate. The reactions followed simple second-order kinetics in the initial stages with deviations in the latter stages, depending upon the aromatic/mercuric acetate ratio. At a mole ratio of 5, the reaction could be followed without deviation out to 80% reaction.

The experimental data are summarized in Table III. All of the data, both from competitive studies and from rate measurements, result in a toluene/benzene reactivity ratio at 25° of 7.9 ± 0.2.

TABLE III

RATES OF MERCURATION OF BENZENE AND TOLUENE AT 25°

Hydrocarbon	Concentration of reactants Perchloric acid	Mercuric acetate	Hydrocarbon	Rate constant[a] k_2 (l. mole^{-1} min.$^{-1}$)
Benzene	0.294	0.196	1.960	0.0060[b]
	.099	.096	0.228	.00429[c]
	.095	.092	.585	.00400
Toluene	.285	.190	1.900	.048[b]
	.099	.096	0.096	.0335[c]
	.098	.095	.193	.0335
	.098	.095	.212	.0322
	.096	.093	.388	.0314
	.095	.091	.478	.0307
	.088	.086	.958	.0310

[a] The rate constant is a function of the perchloric acid concentration. [b] Toluene/benzene = 8.0. Rate data for these runs shown in Fig. 4. [c] Toluene/benzene = 7.8.

The competitive mercuration was also studied at 50 and 75°. Isomer distribution and relative rates were determined by infrared analysis and are summarized in Table IV.

TABLE IV

VARIATION OF ISOMER DISTRIBUTION AND RELATIVE RATES WITH TEMPERATURE

Temp., °C.	Isomer distribution *Ortho*	*Meta*	*Para*	Relative rate Toluene/benzene
25	21.0	9.5	69.5	7.9
50	20.0	11.5	68.5	7.0
75	18.3	12.6	69.1	5.9

Theoretical Implications.—The relative reactivity of toluene and benzene toward substitution and the amount of *meta* isomer obtained in that reaction have been related to the "activity" of the substituting species.[5] Thus a highly active species gives a low toluene/benzene relative rate and relatively large amounts of the *meta* isomer in the substitution of toluene. In other words an active species is neither selective between toluene and benzene, nor selective between the *para* and *meta* positions of toluene, resulting in an approach toward purely statistical distribution. Such a situation is encountered in isopropylation where 28% *meta* is obtained under non-isomerizing conditions with a reactivity ratio of 2.1.[12]

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(9) Professor Robert A. Benkeser and O. H. Thomas of this Department have demonstrated recently that in the analogous reaction, detrimethylsilylation, $ArSi(CH_3)_3 + H_3O^+ \rightarrow ArH + (CH_3)_3SiOH + H^+$, the relative rates are: *p*-tolyl > *m*-tolyl > phenyl.

(10) R. M. Schramm, W. Klapproth and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951); F. H. Westheimer, E. Segel and R. Schramm, THIS JOURNAL, **69**, 773 (1947).

(11) A. F. Holleman and P. Caland, *Ber.*, **44**, 2519 (1911).

(12) F. E. Condon, THIS JOURNAL, **70**, 2265 (1948); **71**, 3544 (1949).

TABLE V

PARTIAL RATE AND BASICITY FACTORS

Reaction	Conditions	Isomer distribution			C/B[a]	Partial rate factors			Reference
		Ortho	*Meta*	*Para*		o_f	m_f	p_f	
Chlorination	Cl_2 in HOAc at 24°					611	5.3	887	[b]
Chloromethylation	CH_2O in HOAc at 60° with HCl and $ZnCl_2$	34.7	1.3	64.0	112	117	4.37	430	5
Basicity	A, HF at 20°					145	3.6	414	[c]
	B, HF–BF_3					103	3.1	145	[d]
Nitration	HNO_3 in 90% HOAc at 45°	56.5	3.5	40.0	24.5	42	2.5	58	[e]
Mercuration	A, $Hg(OAc)_2$ in HOAc with $HClO_4$ at 25°	21.0	9.5	69.5	7.9	4.98	2.25	32.9	[f]
	B, same, at 50°	20.0	11.5	68.5	7.0	4.20	2.41	28.8	[f]
	C, same, at 75°	18.3	12.6	69.1	5.9	3.24	2.23	24.5	[f]
Detrimethylsilylation	$ArSi(CH_3)_3$ with *p*-toluenesulfonic acid in HOAc at 25°					17.5	2.0	16.5	[g]
Sulfonation	A, $MeSO_2Cl$ with $AlCl_3$ in excess toluene at 100°	49	15	36		5.44	1.67	7.99	[h]
	B, *p*-$BrC_6H_4SO_2Cl$ with $AlCl_3$ in aromatic soln. at 30°				3.7				[i]
Isopropylation	C_3H_4 with $AlCl_3$ in CH_3NO_2 at 40°	37.6	28.5	33.9	2.1	2.37	1.80	4.27	12
Nitration	*t*-Butylbenzene with HNO_3 in 90% HOAc at 45°	12.0	8.5	79.5	15.7	5.5	4.0	75	[e]
	Benzyl chloride with HNO_3 in Ac_2O at 25°	32.0	15.5	52.5	0.302	0.290	0.140	0.951	[j]
	Ethyl phenylacetate with HNO_3 in Ac_2O at 25°	42.0	10.6	47.4	3.66	4.62	1.16	10.41	[j]
	Ethyl benzoate with HNO_3 in Ac_2O at 18°	24.1	72.0	4.0	0.00367	0.0026	0.0079	0.0009	[k]
	Chlorobenzene with $AcONO_2$ in CH_3NO_2 at 25°	29.6	0.9	69.5	.0312	.0277	.00084	.1302	[l,m]
	Bromobenzene with HNO_3 in CH_3NO_2 at 25°	36.5	1.2	62.4					[l]
	Bromobenzene with $AcONO_2$ in CH_3NO_2 at 25°				.0276	.0303	.0010	.1033	[m]
	Iodobenzene with $AcONO_2$ in CH_3NO_2 at 25°	38.3	1.8	59.7	.22	.253	.0119	.789	[l]
	Benzal chloride with HNO_3 in Ac_2O at 20–30°	23.3	33.8	42.9					[n]
	Benzotrichloride with HNO_3 in Ac_2O at 20–30°	6.8	64.5	28.7					[n]
	Nitrobenzene with HNO_3 at 0°	6.4	93.3	<0.3					[o]
Phenylation	Diphenyl with benzoyl peroxide at 80°	48.5	23.0	28.5	4.0	2.9	1.4	3.4	[p]

[a] Reactivity ratio: compound/benzene. Compound is toluene except where otherwise indicated under "Conditions." [b] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948). [c] Partial equilibrium factors calculated from the data of M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953). [d] Partial equilibrium factors calculated by F. E. Condon, *ibid.*, **74**, 2528 (1952), from data of D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951). [e] H. Cohn, E. D. Hughes, M. H. Jones and M. A. Peeling, *Nature*, **169**, 291 (1952). These data give a better fit than those previously available (ref. 5). [f] Present study. [g] Calculated from data on acid cleavage of phenyl, tolyl and xylyl trimethylsilanes. Data kindly provided by Professor R. A. Benkeser and represents unpublished work with Dr. H. R. Krysiak and Mr. O. H. Thomas. [h] W. E. Truce and C. W. Vriesen, THIS JOURNAL, **75**, 5032 (1953). [i] S. C. J. Olivier, *Rec. trav. chim.*, **33**, 163 (1914.) [j] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 575 (1949). [k] C. K. Ingold and M. S. Smith, *ibid.*, 905 (1938). [l] J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, THIS JOURNAL, **76**, 4525 (1954). [m] M. J. Bird and C. K. Ingold, *J. Chem. Soc.*, 918 (1938). [n] A. F. Holleman, J. Vermeulen and W. J. deMooy, *Rec. trav. chim.*, **33**, 1 (1914). [o] A. F. Holleman and B. R. de Bruyn, *ibid.*, **19**, 79 (1900). [p] J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 794 (1954).

In order to avoid minor complications arising from the effect of steric factors in modifying substitution into the *ortho* position, the partial rate factor p_f is utilized in place of the toluene/benzene relative rate. Pertinent data are summarized in Table V. A plot of log p_f *vs.* log p_f/m_f results in a simple linear relationship for all reactions for which good data are available (Fig. 2).[13]

According to theory, a plot of this kind should pass through the origin. That is, a substituting agent of infinitely high activity should show no selectivity between benzene and toluene or between the *para* and *meta* positions in toluene. Under these circumstances substitution would be entirely statistical and both p_f and p_f/m_f would be unity.

At the time the relationship was originally proposed[5] there were available satisfactory data for only three reactions, chlorination, nitration and isopropylation. These defined a straight line which intersected the ordinate slightly above the origin. This line therefore was utilized as an empirical relationship which served to correlate data for these three reactions as well as data for other, less well investigated, reactions. It is gratifying that the additional data which are now available on mercuration clearly show the line to follow the theoretical path to the origin (Fig. 2).

It was previously postulated that an electrophilic catalyst which increased the electrophilic properties of the attacking species would result in a less selective reagent and a higher degree of attack at the *meta* positions.[5] It is of considerable importance that the data on the partial basicity factors both agree quantitatively with the rate correlation and support the above postulate.

The available data on the acid–base interactions of aromatic hydrocarbons with hydrogen fluoride and with hydrogen fluoride–boron trifluoride are presented in Table V and Fig. 2. It is apparent that hydrogen fluoride, as the weaker acid, is more selective of the position to which a proton is transferred in toluene. It follows that to obtain the largest difference in basicity in the methylbenzenes, one should use the weakest acid capable of transferring a proton to the aromatic ring.

An Extended Treatment.—It was suggested in the previous paper that a similar treatment should apply to all monosubstituted aromatics. It was there suggested that the lines representing the data

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(13) It should be recalled that p_f and m_f give the rate of substitution of the *para* position and of one of the two *meta* positions in toluene relative to the rate of substitution of one of the six equivalent positions in benzene.

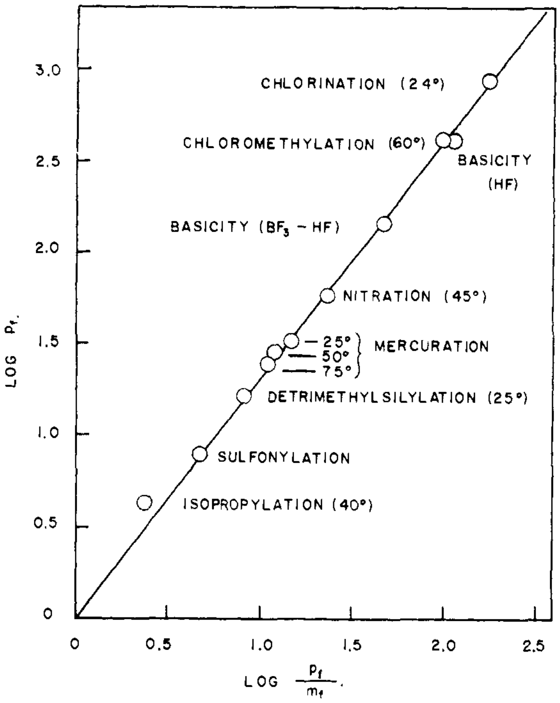


Fig. 2.—Relationship between the "activity" of the reagent and the degree of *meta* substitution, in terms of the partial rate factors.

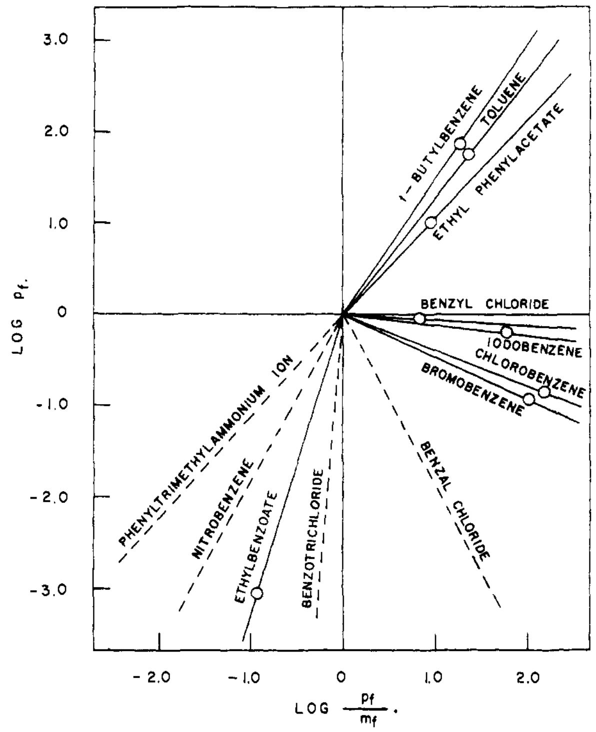


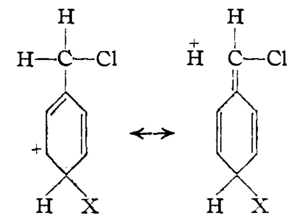
Fig. 3.—Diagram illustrating the proposed extension for monosubstituted benzene derivatives.

should run more or less parallel to toluene. In view of the present results we wish to revise these views. On the assumption that for attacking species of infinitely high activity the substitution would necessarily be statistical, all lines should pass through the origin. This clearly fixes one point. Considering the very limited data now available for monosubstituted benzene derivatives other than toluene, it is our belief that the experimental data on substitution will be represented by individual lines, radiating from the origin into the various quadrants.

Thus nitrobenzene will define a line in the lower left-hand quadrant (p_f for nitrobenzene <1; p_f/m_f for nitrobenzene <1). Similarly, the data for chlorobenzene define a line in the lower right-hand quadrant (p_f for chlorobenzene <1; p_f/m_f for chlorobenzene >1). The proposed relationship may be rendered clearer by an examination of Fig. 3. In this figure the available data on the partial rate factors in the nitration of various monosubstituted aromatics (Table V) have been used to fix each line for a given monosubstituted benzene. The broken lines are estimates involving compounds for which partial rate data are not available.

The series of compounds toluene, benzyl chloride, benzal chloride and benzotrichloride provide a particularly interesting sequence of compounds for discussion. The behavior of toluene has been examined previously. In the case of benzyl chloride the value of p_f is only slightly less than unity, so that the compound defines a line that just falls within the lower-right quadrant. In spite of the fact that the rate of substitution in the *para* position of benzyl chloride is almost identical with that of benzene, the diagram shows that the ratio of p_f/m_f in benzyl chloride must vary over wide limits. In other words, the ratio of *para* to *meta* substitution will vary with the activity of the substituting species, in spite of the fact that the benzyl chloride/benzene ratio will be relatively insensitive to this factor.

This apparent peculiarity may be clarified by considering the relative energies of the three different intermediates involved in the substitution reaction. (Hyperconjugation structures involving the chlorine substituent are considered to be of much less importance than those involving hydrogen interaction.)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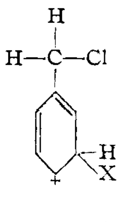
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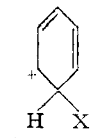
(3 forms)

III

From the value of the partial rate factor for substitution in the *para* position of benzyl chloride, it is concluded that the energy of formation of I and III must be quite similar. Consequently, the attacking group will not distinguish between them. However, the partial rate factor for II reveals that it is considerably less stable than III, as well as less stable than I. Presumably the decreased stability of II relative to III arises from the powerful inductive effect of the chlorine substituent, which cannot be compensated for in II, as in I, by hyperconjugation. Since I and II differ so greatly in energy, the relative amount of *para* and *meta* substitution will depend upon the activity of the attacking species.

This interpretation also may be extended to benzal chloride and to benzotrichloride. In the latter compound, with no α-hydrogen atoms available, the energies of intermediates corresponding to I and II become similar and the *para/meta* substitution becomes almost statistical in distribution.

Substitution in the *ortho* position has not been considered in this discussion because of the probable important role of steric effects in controlling substitution in the *ortho* position.[14] Since the *ortho/para* ratio is 0.151 for *t*-butylbenzene and 0.237 for benzotrichloride, it is apparent that the decreased amount of substitution in the latter compound could well result from the operation of steric effects.[15] At the present time we are unable to estimate with any accuracy the importance of such steric effects in controlling substitution in the *ortho* position. However, the continued development of a quantitative theory for *meta* and *para* substitution should provide a basis for a systematic attack on the problem of *ortho* substitution. It is hoped that an investigation of this kind may soon be possible.

The present discussion has been restricted to electrophilic substitutions. The question necessarily arises whether the same approach may be utilized for free radical and nucleophilic attack. In this connection, as a first effort in this direction, we have tested recent data on the partial rate factors in the reactions of benzene and biphenyl with phenyl free radicals (Table V). There is some reason for believing that the activating effect of a phenyl group on the benzene ring is similar to that of a methyl group. In any event phenyl free radical appears to be an attacking species of high activity and low selectivity, and the data define a point near the origin which falls exactly on the line in Fig. 2.

The agreement may be purely fortuitous, or it may result from the relatively low polar characteristics of the two substituents involved. Certainly in the case of nitrobenzene it appears that the data would necessarily be represented by a different line (in the upper right quadrant) than that which should represent electrophilic substitution data for this compound (lower left quadrant). It is hoped that a rigorous test of the utility of the proposed relationship in free radical reactions may soon be possible in view of the excellent data which are now becoming available for such reactions.[16]

Experimental Part

Mercuration of Toluene.—To a 1-l., 3-necked round-bottomed flask equipped with stirrer, thermometer and condenser were added 106.4 ml. (1.00 mole) of toluene (J. T. Baker, C.P., rectified in a 50-plate column, n^{20}_{D} 1.4962) and 300 ml. of glacial acetic acid (Baker and Adamson, reagent). To this mixture there was added rapidly at 25°, with vigorous stirring, a solution consisting of 12.5 ml. of 70% perchloric acid (J. T. Baker, reagent), 31.9 g. (0.100 mole) of mercuric acetate (J. T. Baker, reagent) and 100 ml. of glacial acetic acid. Aliquots were removed with a 50-ml. pipet and quenched in an equal volume of water. The mixture was aspirated until the excess toluene was removed. The resultant solution was treated with sufficient aqueous sodium bromide to maintain a molar ratio of bromide ion to mercury of 2. The precipitate was filtered, washed and thoroughly dried in a vacuum desiccator. The mixture of tolylmercuric bromides was added to sufficient carbon disulfide to make the final solution approximately 0.3 M in aromatic. The resulting solution was treated slowly with bromine (J. T. Baker, reagent) until a permanent red color developed. After standing for several hours, the mixture was washed with sodium bisulfite solution and water, and then dried over calcium hydride.

Quantitative analysis of these solutions was carried out by the comparison of infrared spectra of known mixtures with those of the unknown. Interpolations were made by means of a calibration curve of the Beer's law type. Typical data are reported in Fig. 1 and Table I.

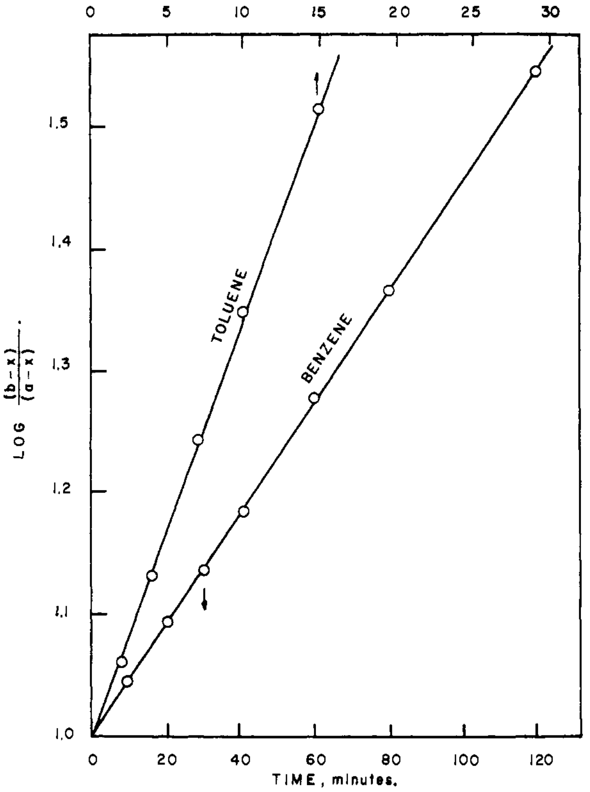

Fig. 4.—Rate data for the mercuration of benzene and toluene at 25°.

Competitive Mercuration of Benzene and Toluene.—The competitive mercuration was carried out identically with the previous experiment except that 53.2 ml. (0.50 mole) of toluene and 111 ml. (1.25 moles) of benzene (thiophene-free, rectified in a 50-plate column, n^{20}_{D} 1.5008) were utilized as the aromatic component of the reaction mixture. Treatment of the mixture of the arylmercuric bromides in carbon disulfide with bromine had to be carried out with particular care to ensure the conversion of all of the phenyl derivative. The four component system which resulted from this treatment also was analyzed by infrared. The results were somewhat less precise than in the case of the simpler three-component reaction product.

Experiments at 50 and 75° were carried out competitively in a manner similar to that at 25°. Reaction times of 1 min. and 30 sec. were used, resulting in reactions of 40 to 60% completion, in order to minimize the possibility of disturbance of the isomer ratio through secondary changes. Actually, reactions carried out at slightly longer reaction times showed no orientation differences greater than the

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[14] H. C. Brown and W. H. Bonner, THIS JOURNAL, **76**, 605 (1954).

[15] For a discussion of this question see M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949), and P. B. D. de la Mare, *ibid.*, 2871 (1949).

[16] D. H. Hey, A. Nechvatal and T. S. Robinson, *ibid.*, 2892 (1951); D. R. Augood, D. H. Hey and A. H. Williams, *ibid.*, 2094 (1952), 44 (1953), 3412 (1953); J. I. G. Cadogan, D. H. Hey and G. H. Williams, *ibid.*, 794 (1954); R. L. Dannley and E. C. Gregg, Jr., THIS JOURNAL, **76**, 2997 (1954); R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps and C. B. Coleman, *ibid.*, **76**, 445 (1954).

experimental error in the analysis. At 75° a 20 to 1 molar ratio of toluene to mercuric acetate was used to avoid possible errors arising from dimercuration.

Rate of Mercuration.—The reaction mixtures were prepared precisely as described above for determining the isomer distribution in the mercuration of toluene at 25°. At intervals of time, aliquots were removed and treated with sodium bromide solution to precipitate the arylmercuric bromide. These precipitates were collected in sintered glass funnels, dried, and weighed. Excellent second-order rate data were obtained over 80% reaction. Typical rate data are shown in Fig. 4 for two runs involving benzene and toluene. The data are for the first kinetic study for each hydrocarbon listed in Table III.

The reaction also was followed by the change in ionic mercury concentrations. The agreement in the ratio of the rates of toluene and benzene, obtained by the two procedures, was excellent.

The rate constants for the mercuration of benzene and toluene are summarized in Table III.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Effect of Perchloric Acid on the Reactivity Ratio and Isomer Distribution in the Mercuration of Benzene and Toluene. Modification of the Activity and Selectivity of an Electrophilic Substituting Agent[1,2]

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

RECEIVED NOVEMBER 12, 1954

A study has been made of the reaction of benzene and toluene with mercuric acetate in glacial acetic acid and in the presence and absence of perchloric acid and sodium perchlorate. As previously reported by Westheimer and co-workers, the presence of perchloric acid results in an enormous enhancement of the rate of reaction (the rate of mercuration of toluene at 25° proceeds 2000-fold faster in the presence of 0.095 M perchloric acid). On the other hand, sodium perchlorate results in a relatively minor increase (the rate of mercuration at 25° proceeds 5-fold faster in the presence of 0.092 M sodium perchlorate). From the rates of reaction of benzene and toluene with mercuric acetate at several temperatures, the toluene/benzene reactivity ratios are determined to be 5.0, 4.3 and 3.6 at 50°, 70° and 90°, respectively. The results indicate that the attacking species in the uncatalyzed reaction is a less selective agent than that involved in the perchloric acid-catalyzed reaction. The uncatalyzed reaction of toluene with mercuric acetate at 50° produces the monosubstituted isomers with the distribution: *ortho*, 30.7; *meta*, 13.2; and *para*, 56.1%. At 70° the distribution is: *ortho*, 32.0; *meta*, 14.5; and *para*, 53.5%. At 90°, the distribution is: *ortho*, 32.5; *meta*, 15.7; and *para*, 51.8%. These distributions are in accord with the linear relationship previously proposed to account for isomer distribution in toluene substitutions.

In an earlier paper a linear relationship was proposed to correlate the "selectivity" of electrophilic substituting agents and the observed isomer distribution in toluene[4] and other monosubstituted aromatics.[5] It was suggested that the "activity" or "selectivity" of electrophilic substituting agents might be modified by the presence or absence of catalytic agents.[4] The present investigation was undertaken to examine the validity of this prediction.

It was shown previously by Westheimer and his co-workers that the reaction of benzene with mercuric acetate in 97% acetic acid is strongly catalyzed by perchloric acid. For example, the presence of 0.05 M perchloric acid results in a 1000-fold increase in the second order rate constant.[6] We have demonstrated recently that this perchloric acid-catalyzed mercuration of benzene and toluene obeys the proposed linear relationship between relative reactivity and isomer distribution.[5] It therefore appeared that a study of the effect of the uncatalyzed mercuration reaction on the toluene/benzene reactivity ratio and the isomer distribution in toluene should provide a suitable test for the proposal that catalysts might affect these quantities. Accordingly, a study was made of the uncatalyzed reaction of benzene and toluene at several temperatures.

Results

Rates of Mercuration of Benzene and Toluene.—The reactions were followed by determining the decrease in the mercuric ion concentration with time by titrating the residual mercuric ion with thiocyanate. However, deviations were observed in the second-order kinetics. Investigation of these irregularities revealed that mercuric acetate was undergoing a reaction with the solvent resulting in a loss of mercuric ion at a rate comparable to that involved in the mercuration of benzene. This loss of mercuric ion with time was not altered by a careful purification of the solvent which included distillation from sodium dichromate followed by distillation from mercuric acetate. Even with this purified solvent there was observed, after three hours of reflux, a decrease of 50% in the original titer for mercuric ion.

From the observation that the rate of loss of mercuric ion is not altered by the careful purification of the solvent, it appears certain that the reaction is not due to the presence of an impurity. Although we did not investigate the exact nature of the side reaction, it appears from these observations as well as related observations reported in the literature, that the loss of mercuric ion must result from a reaction of mercuric ion with either acetate ion or with acetic acid.[7-9] A number of experiments invariably led to a maximum loss of 50% of the original titer. It therefore appears that the

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(1) Directive Effects in Aromatic Substitution. V.

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

(5) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955).

(6) R. M. Schramm, W. Klapproth and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

(7) R. E. Vollrath, *ibid.*, **62**, 1310 (1940).

(8) N. V. Subba Rao and T. R. Seshadi, *Proc. Indian Acad. Sci.*, **11A**, 23 (1940); *C. A.*, **34**, 3677 (1940).

(9) F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Company, Inc. (Reinhold Publ. Corp.), New York, N. Y., 1921, p. 141.