of *o*-vanillin, m.p. 141–142°. 3-Methoxy-6-nitrosalicylaldehyde[13] was synthesized by nitration of the benzenesulfonate of *o*-vanillin and then basic hydrolysis of the ester, m.p. 103–104°. 4-Nitrosalicylaldehyde, m.p. 133–134°, and 3-bromo-5-nitrosalicylaldehyde, m.p. 149–150°, were prepared at Boston University under the direction of Professors J. P. Mason and W. J. Gensler.

1,3,3-Trimethylindolinobenzopyrylospirans. General Directions.[14]—A mixture of equimolar amounts of the salicylaldehyde and commercially available 2-methylene-1,3,3-trimethylindoline in absolute ethanol (25 ml./0.01 mole of aldehyde) was refluxed on a steam-bath for two to five hours. The resultant highly colored mixture was cooled in an ice-water-bath, filtered, washed with cold ethanol, and recrystallized from ethanol or an ethanol–water mixture. The yields, melting points and elemental analyses for the compounds prepared are given in Table II.

Rate Measurements. Procedure.—The photochromic spiropyran was dissolved in absolute ethanol (U.S.I. Reagent Grade) and placed in a quartz, glass-stoppered spectrophotometer cell. The cell was placed in a cell holder equipped with a thermostat and allowed to come to thermal equilibrium. After 30 minutes, the temperature was measured by placing a thermocouple junction in the cell. The cell was then exposed to ultraviolet light from a four watt "Blak-Ray" (Ultra-violet Products Inc., San Gabriel, Calif.) or a 100 watt source (George W. Gates and Co., Long Island, N. Y.) for one to five minutes and immediately placed in either a Beckman DK-1 recording spectrophotometer or a Beckman DU spectrophotometer. The disappearance of the colored form of the photochromic spiran was followed automatically or manually by recording the absorbance at the maximum visible peak. The reaction was followed to 95–100% of completion. Absorbance at infinite time (A_∞) was zero or was taken as the absorbance after several days. Figure 3 gives results typical of those obtained.

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DAYTON 9, OHIO

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[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rate Data and Isomer Distributions in the Reaction of *t*-Butylbenzene with Mercuric Acetate in Acetic Acid Solution. Partial Rate Factors for the Mercuration Reaction[1–3]

BY HERBERT C. BROWN AND M. DUBECK[4]

RECEIVED MARCH 21, 1959

The rate constants for the mercuration of *t*-butylbenzene with mercuric acetate in glacial acetic acid are (l. mole^{-1} sec.$^{-1}$) 8.40×10^{-5} at 90.0°, 1.52×10^{-5} at 70.0° and 0.245×10^{-5} at 50.0°. Substitution occurs predominantly in the *meta* and *para* positions, with substitution in the *ortho* position amounting to less than 1% of the total. The isomer distribution observed is 34.9% *m*-, 65.1% *p*- at 90.0°; 32.9% *m*-, 67.1% *p*- at 70.0°; 31.0% *m*-, 69.0% *p*- at 50.0°. Utilizing previously available data on the mercuration of benzene under these conditions, the following partial rate factors at 25.0° are calculated m_f 3.41, p_f 17.2. Consequently, in this reaction substitution *meta* to a *t*-butyl group occurs more readily than *meta* to a methyl group (m_f 2.23), whereas substitution *para* to a *t*-butyl group occurs less readily than *para* to a methyl group (p_f 23.0).

Different electrophilic substitution reactions result in major changes in the relative rates of reaction of the *meta* and *para* positions of toluene. The Selectivity Relationship (1) was proposed as a quantitative correlation of these data.[5]

$$\log p_f^{\mathrm{Me}} = b \log (p_f^{\mathrm{Me}}/m_f^{\mathrm{Me}}) \qquad (1)$$

Data for some forty-seven electrophilic substitution reactions are now available. These data are correlated by the Selectivity Relationship with quite satisfactory precision.[6]

It was suggested that the Selectivity Relationship might be applicable to benzene derivatives other than toluene.[7] Unfortunately, with the exception of the detailed nitration data of Ingold and his co-workers,[8] the available data were far too sparse to permit a satisfactory test of this possibility.[9]

Accordingly, it appeared desirable to undertake a determination of the relative rates and isomer distributions in the substitution of several typical aromatic derivatives. As representative substitution reactions, we selected uncatalyzed mercuration,[10] acylation[11] and halogenation,[12] and applied them to *t*-butylbenzene and other selected aromatic compounds.

The results of the mercuration study with *t*-butylbenzene are presented in the present publication. The acylation[13] and halogenation[14] studies are reported in the following papers. In the final paper of this group,[15] the utility of the Selectivity Relationship in correlating all of the available substitution data for *t*-butylbenzene is examined.

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[1] Directive Effects in Aromatic Substitution. XXXVIII.

[2] This research supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

[3] Based upon a thesis submitted by M. Dubeck in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] Monsanto Chemical Co. Fellow, 1956–1957.

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Results

The rates of mercuration of *t*-butylbenzene by mercuric acetate in glacial acetic acid were determined by following the decrease in mercuric acetate concentration titrimetrically with standard thiocyanate solution. A large excess of the aromatic was used to avoid significant incursion of polymercuration.

At 25° the rate of the reaction is too slow to be followed conveniently. Accordingly, the rates were measured at 90.0, 70.0 and 50.0° and these data, together with the isomer distribution results, used to calculate the rate constant at 25.0°.

These rate data are summarized in Table I.

TABLE I

RATES OF REACTION OF BENZENE AND *t*-BUTYLBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., °C.	Rate constant, k_2 (l. mole^{-1} sec.$^{-1}$) × 10^5 *t*-Butylbenzene	Benzene[a]	Relative rate
90.0	8.40	3.42	2.46
70.0	1.52	0.565	2.69
50.0	0.245	0.0750	3.27
25.0	0.0165[b]	0.00413[b]	4.00

[a] Ref. 9. [b] Calculated from data at other temperatures.

The isomer distribution studies on the mercuration of *t*-butylbenzene were carried out on reaction mixtures that were similar in all respects to those employed in the kinetic measurements. The reaction mixtures were quenched at appropriate time intervals in equal volumes of water, the isomeric *t*-butylphenylmercuric acetates were precipitated quantitatively as the insoluble bromides and these were converted into the corresponding isomeric bromo-*t*-butylbenzenes by treatment with bromine. The proportions of the isomeric bromo-*t*-butylbenzenes present in the reaction products were established by means of infrared analysis.[7]

It had been established previously that isomerization, which is important in the perchloric acid-catalyzed mercuration of toluene, is not important in the uncatalyzed mercuration.[10] Similarly, no evidence for such isomerization was observed in the present study of *t*-butylbenzene.

Only trace amounts of the *ortho* isomer were observed, definitely less than 1%. Since an accurate estimate of the small quantities of the *ortho* isomer was not of prime importance for our present objectives, we decided to ignore this minor component and to determine only the *meta* and *para* derivatives.

The results of these isomer distribution studies are summarized in Table II.

TABLE II

ISOMER DISTRIBUTIONS IN THE MERCURATION OF *t*-BUTYLBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., °C.	Isomer distribution, % *Meta*	*Para*
90.0	34.9	65.1
70.0	32.9	67.1
50.0	31.0	69.0
25.0	28.4[a]	71.6[a]

[a] Calculated from rate constants and isomer distributions at higher temperatures.

Discussion

The substitution of a molecule such as toluene or *t*-butylbenzene to form isomeric products is a complex reaction, made up of three individual reactions leading to the three isomeric reaction products. Each of these three reactions will have its own energy of activation. Consequently, the usual practice of using the observed gross rate constant at several temperatures to calculate the rate constant at another temperature must be considered to be incorrect, suitable only in rough approximations, except in those cases where substitution occurs predominantly in one position.

Accordingly, the observed rate data and isomer distributions at 90.0, 70.0 and 50.0° were utilized to calculate partial rate constants at each of these temperatures. These partial rate constants were then utilized to calculate the energies, heats and entropies of activation, as well as the partial rate constants and isomer distributions at 25.0°. These data are summarized in Table III.

Partial rate factors for the mercuration of *t*-butylbenzene and toluene are summarized in Table IV.

It was pointed out previously that the relative magnitudes of the *ortho* and *para* partial rate factors for toluene indicate the mercuration reaction to be one of relatively large steric requirements.[10] The insignificant quantity of *ortho* substitution observed in the mercuration of *t*-butylbenzene is in accord with this conclusion.

From the relative magnitudes of the partial rate factors, p_f^{Me} and $p_f^{t\text{-Bu}}$, it is apparent that substitution *para* to a methyl group occurs more readily than *para* to a *t*-butyl group. With the sole exception of one reaction, nitration,[16] for which full experimental details are not yet available, the phenomenon appears to be general. Such higher reactivity *para* to a methyl group than to a *t*-butyl group has been attributed to the greater hyperconjugative contributions of α-hydrogen–carbon bonds in toluene as contrasted with those of α-carbon–carbon bonds in *t*-butylbenzene.[17,18] However, alternative interpretations have been proposed.[19,20]

Substitution *meta* to the *t*-butyl group is considerably faster than *meta* to the methyl group. From the dipole moments of *t*-butylbenzene (0.70D.) and toluene (0.37D),[21] it appears that the inductive effect of the *t*-butyl group is considerably greater than that of the methyl group. It therefore appears that the relative inductive effects of these two alkyl groups exert a dominant control on the relative rates of substitution in the *meta* position.[22]

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TABLE III

PARTIAL RATE CONSTANTS AND DERIVED KINETIC DATA FOR THE MERCURATION OF *t*-BUTYLBENZENE AND BENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Compound	Partial rate constant k_2(l. mole^{-1} sec.$^{-1}$) × 10^6 25.0°	50.0°	70.0°	90.0°	ΔE_{act}, kcal./mole	log *A*	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./deg.
Benzene[a]	0.00688	0.125	0.942	5.70	22.2	8.12	21.6	−23.6
t-Butylbenzene								
-*meta*[a]	.0234	0.380	2.50	14.7	21.3	7.98	20.6	−24.3
-*para*	.118	1.69	10.2	54.7	20.3	7.93	19.6	−24.5
Benzene[b]	.0413	0.750	5.65	34.2	22.2	8.91	21.6	−19.6
t-Butylbenzene[c]	.165	2.45	15.2	84.0	20.6	8.31	19.9	−22.8

[a] One position. [b] For all six positions. [c] Total rate constant.

TABLE IV

PARTIAL RATE FACTORS FOR THE MERCURATION OF TOLUENE AND *t*-BUTYLBENZENE WITH MERCURIC ACETATE IN GLACIAL ACETIC ACID

Temp., C.	Toluene[a] o_f^{Me}	m_f^{Me}	p_f^{Me}	*t*-Butylbenzene $o_f^{t\text{-Bu}}$	$m_f^{t\text{-Bu}}$	$p_f^{t\text{-Bu}}$
90.0	3.51	1.70	11.2	<0.1	2.58	9.61
70.0	4.03	1.83	13.5	< .1	2.66	10.8
50.0	4.60	1.98	16.8	< .1	3.04	15.6
25.0	5.71	2.23	23.0	< .1	3.41	17.2

[a] Ref. 10.

It is of interest to note the constancy in the entropies of activation for substitution *meta* (−24.3 e.u.) and *para* (−24.5 e.u.) to the *t*-butyl group. These values are in good agreement with the corresponding values for mercuration *ortho* (−25.4 e.u.), *meta* (−24.9 e.u.) and *para* (−25.0 e.u.) to the methyl group in toluene.[10] The essential constancy in the entropy of activation for substitution at the three isomeric ring positions in the nitration of ethyl benzoate also has been established in a recent detailed study by le Noble and Wheland.[23] Consequently, the usual assumption of essential constancy of the entropy of activation in aromatic substitution[24] is supported by these results.

Discussion of the applicability of the Selectivity Relationship to the correlation of these data will be deferred to the final paper of this group.[15]

Experimental Part

Materials.—*t*-Butylbenzene (Phillips Petroleum Co., pure grade) was treated in a solution of acetic acid with mercuric acetate at 70° for 12 hours to remove minor amounts of any active impurities which might result in kinetic difficulties. The reaction mixture was diluted with water, the hydrocarbon layer was separated, and the residual traces of mercury containing compounds removed from the *t*-butylbenzene by a rapid vacuum distillation. The distillate then was fractionated through a 50-plate column and the center cut, n^{20}D 1.4924, was retained for kinetic and isomer distribution measurements.

The mercuric acetate (Mallinckrodt analytical reagent) was used as the mercurating agent without further purification. The glacial acetic acid (Baker and Adamson reagent grade) was approximately 0.1 *M* in water, as determined by Karl Fischer analysis. Experiments revealed that minor changes in the water content did not result in any significant variation in the rate data.

The three isomeric bromo-*t*-butylbenzenes were prepared for use as infrared standards. The *ortho* and *meta* isomers were prepared from a large, carefully purified sample of *p*-nitro-*t*-butylbenzene, b.p. 135° at 10 mm., n^{20}D 1.5337, obtained by nitration of *t*-butylbenzene.[25]

o-Bromo-*t*-butylbenzene was prepared by the following procedure. *p*-Nitro-*t*-butylbenzene was brominated to form 2-bromo-4-nitro-*t*-butylbenzene.[26] The nitro group was reduced catalytically and the amine was deaminated with hypophosphorus acid.[18] The product fractionated in a column under vacuum, b.p. 118° at 27 mm., n^{20}D 1.5441, was obtained in an over-all yield of 40% based on the *p*-nitro derivative.

m-Bromo-*t*-butylbenzene was obtained from the *p*-nitro derivative by transformation to the amine, acetylation, bromination, deacetylation and deamination.[18] The fractionated product, b.p. 118° at 27 mm., n^{20}D 1.5351, was obtained in an over-all yield of 40%.

p-Bromo-*t*-butylbenzene was prepared by a direct bromination of *t*-butylbenzene.[14] One mole of *t*-butylbenzene was dissolved in 800 ml. of 92% aqueous acetic acid. One mole of bromine was added and the mixture was allowed to stand in the dark for 9 days. The mixture then was poured into 1 l. of water and the crude heavy oil and the aqueous solution extracted with carbon disulfide. Bromine was removed from the extracts by washing with sodium bisulfite, and then by water. After drying, the carbon disulfide was removed by distillation, and the product was fractionated, b.p. 118° at 27 mm., n^{20}D 1.5333. Traces of the *o*- and *m*-isomers were removed by cooling the product and decanting the mother liquor from the crystals. Infrared spectra indicated the absence of the *o*- and *m*-isomers. The yield of pure *p*-bromo-*t*-butylbenzene was 45%.

Rate Measurements.—Stock solutions of mercuric acetate, 0.150 *M*, and *t*-butylbenzene, 3.00 *M*, were prepared and utilized for the kinetic measurements. In preparing a reaction mixture for rate measurements 50.00 ml. of mercuric acetate and 25.00 ml. of *t*-butylbenzene solution were pipetted into a reaction flask and thoroughly mixed. This gave a resultant solution that was 0.100 *M* in mercuric acetate and 1.00 *M* in the aromatic at 25.0°. Ten-ml. aliquots were introduced into thin walled glass bulbs which were sealed subsequently. These bulbs were placed in a constant temperature bath maintained at the appropriate temperature. Five minutes was allowed for the reaction solution in the bulbs to attain thermal equilibrium. A bulb then was removed, quickly crushed in ice-water, and the mercuric ion content was determined titrimetrically by means of standard potassium thiocyanate solution. This analysis was taken as the initial mercuric acetate concentration. The rate of reaction then was followed by removing the bulbs at appropriate time intervals and measuring the decrease in concentration of mercuric ion.

First-order rate constants were calculated on the basis of the disappearance of the mercuric acetate. Appropriate corrections were made for the minor losses of mercuric acetate through reaction with acetic acid.[27,28] The second-

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than methyl; Y. Okamoto, T. Inukai and H. C. Brown, THIS JOURNAL, **80**, 4972 (1958). Such inversion has not been observed in aromatic substitution—substitution *meta* to *t*-butyl is invariably faster than substitution *meta* to methyl (ref. 15).

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order rate constant was obtained by dividing the corrected first-order rate by the average aromatic concentration followed by multiplication with a thermal factor consisting of the ratio of the density of acetic acid at 25° to that of the reaction temperature.

Isomer Distribution Measurements.—The reaction mixtures utilized for the isomer distributions were identical in all respects to those employed in the kinetic measurements. To minimize possible complications arising from polymercuration, the aromatic was used in a 10-fold excess over the mercuric acetate present and the reaction was quenched after it had proceeded to approximately 30% completion.

In a typical experiment, 100 ml. of 3.00 *M* *t*-butylbenzene in glacial acetic acid and 200 ml. of 0.150 *M* mercuric acetate in the same solvent were allowed to come to thermal equilibrium with the bath at the desired temperature and then were quickly mixed. When the reaction had reached approximately 30% completion, calculated from the rate constants, the reaction mixture was quickly cooled and quenched in an equal volume of water. Excess unreacted *t*-butylbenzene was removed by aspiration under vacuum at room temperature and the soluble *t*-butylphenylmercuric acetates were converted into the insoluble bromide derivatives by addition of a 2- to 3-fold excess of bromide ion relative to the total mercuric concentration. The bromide derivatives were filtered, dried thoroughly under vacuum, and weighed. The yields of these derivatives were nearly quantitative.

The isomeric *t*-butylbenzenemercuric bromides were suspended in carbon disulfide and converted to the isomeric bromo-*t*-butylbenzenes by careful treatment with bromine. A slight excess of bromine was added, as evidenced by a slight red color in the carbon disulfide solution, and the mixture was then allowed to stand for several hours to ensure complete conversion of the mercuric derivatives. Excess bromine was removed by washing with sodium bisulfite solution followed by water. The carbon disulfide solution was thoroughly dried over calcium hydride and the proportions of the isomeric bromo-*t*-butylbenzenes were determined by infrared analysis. The conversions to the isomeric bromo-*t*-butylbenzenes, as based on the infrared analysis, were essentially quantitative.

Infrared analyses for the isomeric derivatives were generally carried out on solutions that were about 0.3 *M*. The wave lengths utilized for the *m*- and *p*-bromo-*t*-butylbenzenes were 12.8 and 12.2μ, respectively. *o*-Bromo-*t*-butylbenzene possesses a characteristic absorption band at 13.3 μ. Absorbancies at each of the above wave lengths were determined by means of the base line technique.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rate Data and Isomer Distributions in the Acetylation and Benzoylation of Ethyl-, Isopropyl- and *t*-Butylbenzene. Partial Rate Factors for the Acylation Reaction[1]

BY HERBERT C. BROWN AND GIANLORENZO MARINO[2]

RECEIVED MARCH 21, 1959

Rate constants have been determined for the reaction at 25° of benzoyl chloride–aluminum chloride in ethylene chloride solution with ethylbenzene, isopropylbenzene and *t*-butylbenzene, yielding the relative rates: benzene, 1.00; toluene, 117; ethylbenzene, 101; isopropylbenzene, 93; *t*-butylbenzene, 70. In these reactions the isomer distributions are: ethylbenzene, 3.6% *o*-, 3.4% *m*- and 93.0% *p*-; isopropylbenzene, 3.1% *o*-, 4.0% *m*- and 92.9% *p*-; *t*-butylbenzene, 0% *o*-, 5.4% *m*- and 94.6% *p*-. In the series of four alkylbenzenes, the values of o_f decrease from 29.5 for toluene, to 10.9 for ethyl-, to 8.6 for isopropyl-, to 0 for *t*-butylbenzene. Similarly, p_f exhibits a decrease with increasing branching of the alkyl group: 633, 563, 519 and 398, respectively. On the other hand, m_f exhibits a marked increase from toluene to ethylbenzene, and then increases moderately: 4.9, 10.3, 11.1, 11.4. Under the same conditions, the relative rates of acetylation were determined competitively: benzene, 1.00; toluene, 128; ethylbenzene, 129; isopropylbenzene, 128; *t*-butylbenzene, 114. The isomer distributions were determined to be: ethylbenzene, 0.3% *o*-, 2.7% *m*- and 97.0% *p*-; isopropylbenzene, 0% *o*-, 3.0% *m*-, 97.0% *p*-; *t*-butylbenzene, 0% *o*-, 3.8% *m*- and 96.2% *p*-. The lack of significant substitution in the *ortho* position indicates a higher steric factor for the acetylation reaction than for the corresponding benzoylation reaction. The changes in m_f in the four alkylbenzenes, 4.8, 10.4, 11.5 and 13.0, respectively, paralleled these quantities in the benzoylation reaction. However, the values of p_f, 749, 753, 745, 658, are surprisingly constant, in contrast to the consistent decrease in p_f with branching of the alkyl group observed in the benzoylation and other substitution reactions. It appears that hyperconjugative contributions of the alkyl substituent must be less important in the acetylation reaction than in the related benzoylation reaction.

The Selectivity Relationship[3] correlates with excellent precision the available data on the substitution reactions of toluene.[4] In order to test the applicability of this treatment to other aromatic derivatives, quantitative data on the rates and isomer distributions are required for a number of representative electrophilic substitution reactions.

We have adopted mercuration (k_T/k_B 6.4),[5] nitration (k_T/k_B 25),[6] acylation (k_T/k_B 120)[7] and halogenation (k_T/k_B 344 for chlorination, 605 for bromination)[8] as reactions of low, moderate and high selectivity to obtain the required data for this test. In the present study we undertook to obtain the relative rates of reaction of benzoyl chloride and acetyl chloride in ethylene chloride solution, under the influence of aluminum chloride, with ethyl-, isopropyl- and *t*-butylbenzene. The isomer distributions realized in the acylation reactions were also determined to permit calculation of the partial rate factors.

Results

Rates of Benzoylation.—A kinetic procedure had been developed previously to determine the second-order rate constants for the benzoylation of benzene and toluene.[7] This procedure was utilized without change to determine the rate con-

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[1] Directive Effects in Aromatic Substitution. XXXIX.

[2] Post-doctorate research associate, 1957–1959, on project no. At(11-1)-170 supported by the Atomic Energy Commission.

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

[4] L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

[5] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2306, 2310 (1955).

[6] Fortunately, a considerable quantity of satisfactory nitration data is available through the efforts of C. K. Ingold and his co-workers. For a summary of the data and pertinent references, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VI.

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