

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

## Rates of Reaction of Benzoyl Chloride with Representative Aromatic Hydrocarbons in Ethylene Dichloride Solution under the Influence of Aluminum Chloride. Partial Rate Factors for the Benzoylation Reaction<sup>1</sup>

BY HERBERT C. BROWN AND GIANLORENZO MARINO<sup>2</sup>

RECEIVED OCTOBER 18, 1958

The second-order rate constant at 25.0° for the reaction of benzoyl chloride-aluminum chloride (0.3 *M*) with benzene in ethylene chloride solution is  $0.00928 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. This leads to a relative rate, toluene/benzene of 117, as compared to the value 110 observed in benzoyl chloride solution. The ratio of *ortho/para* isomers in the benzoylation of toluene in ethylene dichloride is identical with that realized in benzoyl chloride. Assuming that the *meta* is also the same, this leads to the partial rate factors for this reaction of *o*<sub>t</sub> 32.6, *m*<sub>t</sub> 4.9, *p*<sub>t</sub> 626. These data provide an excellent fit with the Selectivity Relationship. The rates of benzoylation of the three xylenes agree with the rates calculated from the partial rate factors to within a factor of two.

Partial rate factors for the aluminum chloride-catalyzed benzoylation of toluene in nitrobenzene<sup>3</sup> and in benzoyl chloride<sup>4</sup> solution have been determined previously. The first system suffers from the disadvantage of complex kinetics. The second system, although kinetically simple, requires experimental techniques of major difficulty. The observation that the reaction of benzoyl chloride-aluminum chloride with toluene in ethylene chloride solution<sup>5</sup> is relatively simple, both kinetically and experimentally, encouraged us to undertake a determination of the partial rate factors for this reaction and to test their utility in predicting the rates of benzoylation of the three xylenes.

### Results and Discussion

The rates of benzoylation were determined by following volumetrically the decrease in concentration of the benzoyl chloride in aliquots of the reaction mixture.<sup>5</sup> Benzene is much less reactive than toluene. Consequently, its rate constant,  $k_2$   $0.00928 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, was measured at relatively high concentration of the reactants, 0.300 *M* each, and compared with the rate constant for toluene,  $k_2$   $1.088 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, obtained under identical conditions, to obtain the relative rate value. The rate ratio for toluene/benzene, 117, obtained in this way, agrees closely with the corresponding ratio, 110, for the reaction in benzoyl chloride solution.<sup>4</sup>

In order to determine the isomer distribution, toluene was treated with benzoyl chloride-aluminum chloride under the conditions of the kinetic experiments. The product was analyzed by infrared absorption. Examination of the spectrum revealed the presence of *o*-methylbenzophenone and *p*-methylbenzophenone, with only minor amounts of the *meta* isomer. Accordingly, the presence of the latter was ignored and the spectra were compared with those of standard solutions of *o*- and *p*-methylbenzophenones in carbon disulfide solution, using the peak at 13.2  $\mu$  for the *ortho* isomer and that at 12.8  $\mu$  for the *para*. The analysis

indicated the presence of the two isomers in a molar ratio, *p*-/*o*- = 9.3. Within the limits of experimental uncertainty, this is identical with the corresponding ratio for these two isomers, 9.6, observed for the benzoylation reaction in benzoyl chloride solution.<sup>4,6</sup>

The accurate determination of the small amount of the *meta* isomer requires a long and tedious fractional crystallization of the mixed methylbenzophenones in order to separate a major fraction of the predominant isomer, *p*-methylbenzophenone, followed by infrared examination of the residual material.<sup>3,4</sup> In view of the similarities between the toluene/benzene rate ratios, the *o*-/*p*- isomer distributions and the activation entropies<sup>4</sup> observed in the corresponding reactions in benzoyl chloride and in ethylene chloride, we decided to assume that there would likewise be no significant difference in the distribution of the *meta* isomer in the two systems. Accordingly, we adopted the isomer distribution determined in benzoyl chloride: *ortho*, 9.3%; *meta*, 1.4%; *para*, 89.3%. Combined with the toluene/benzene rate ratio of 117, these lead to the partial rate factors: *o*<sub>t</sub>, 32.6; *m*<sub>t</sub>, 4.9; *p*<sub>t</sub>, 626. These partial rate factors agree closely with the Selectivity Relationship (Fig. 1).

These partial rate factors permit one to calculate the relative rates of reactions of the three xylenes. To test the reliability of these calculations, we

TABLE I  
RATE CONSTANTS FOR THE REACTION OF BENZOYL CHLORIDE-ALUMINUM CHLORIDE WITH BENZENE AND REPRESENTATIVE METHYLBENZENES IN ETHYLENE DICHLORIDE AT 25.0°

Compound	Complex concn., <i>M</i>	Rate constants, $k_2 \times 10^3$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>	
		Individual values	Average
Benzene	0.300	0.00930, 0.00926	0.00928
Toluene <sup>a</sup>	.300	1.075, 1.100, 1.089	1.088
Toluene <sup>a</sup>	.100	0.778, 0.741, 0.779, 0.775	0.763
<i>o</i> -Xylene	.100	9.091, 9.090	9.09
<i>m</i> -Xylene	.100	24.1, 26.9, 26.4	25.8
<i>p</i> -Xylene	.100	1.61, 1.57, 1.65, 1.56, 1.56	1.59

<sup>a</sup> Reference 5.

(1) Directive Effects in Aromatic Substitution. XXXII.

(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 H. L. Young, *J. Org. Chem.*, **22**, 719, 723 (1957).

(4) H. C. Brown and F. R. Jensen, *This Journal*, **80**, 2291, 2296 (1958).

(5) F. R. Jensen, G. Marino and H. C. Brown, *ibid.*, **81**, 3303 (1959).

(6) F. R. Jensen, *ibid.*, **79**, 1226 (1957), has also determined the percentage *ortho* isomer formed in this reaction. His results, calculated for 0.300 *M* solution, agree closely with our value. However, he has observed a small variation in the percentage *ortho* isomer with initial concentration of the benzoyl chloride-aluminum chloride complex.

measured the rate constants for the reaction of benzoyl chloride-aluminum chloride with the three xylenes. The results are summarized in Table I. The precision realized is indicated by the individual values, observed in individual determinations.

The calculated and observed relative rates are listed in Table II. It is evident that the agreement is only fair, considerably poorer than the excellent agreement previously observed for related studies of the mercuration<sup>7</sup> and the bromination<sup>8</sup> of the methylbenzenes.

TABLE II

CALCULATED AND OBSERVED RELATIVE RATES FOR THE BENZOYLATION OF BENZENE AND THE METHYLBENZENES IN ETHYLENE CHLORIDE AND BENZOYL CHLORIDE AT 25.0°

Compound	Relative rates		
	Calcd.	Obsd.	Obsd./calcd.
A. Ethylene chloride solvent			
Benzene	1.00	1.00	
Toluene	117	117	
<i>o</i> -Xylene	1076	1393	1.29
<i>m</i> -Xylene	698	396	0.57
<i>p</i> -Xylene	106	243	2.28
B. Benzoyl chloride solvent <sup>a</sup>			
Benzene	1.00	1.00	
Toluene	110	110	
<i>o</i> -Xylene	993	1120	1.13
<i>m</i> -Xylene	619	396	0.64
<i>p</i> -Xylene	99	140	1.41

<sup>a</sup> Reference 4.

The relative reactivities in ethylene chloride parallel the relative reactivities in benzoyl chloride reasonably well. Only in the case of *p*-xylene do the reactivities appear to differ by a factor significantly larger than the cumulative experimental uncertainty. We considered the possibility that the relatively high rate observed for this derivative might arise from a side reaction causing utilization of the benzoyl chloride for other purposes than the benzylation of *p*-xylene. However, infrared examination of a reaction mixture, for which analysis indicated 50% reaction, revealed the presence of 94% of the calculated quantity of 2,5-dimethylbenzophenone. After hydrolysis, there was recovered benzoic acid corresponding to 92% of the calculated quantity of residual benzoyl chloride. It was concluded that the high rate did not arise from side-reactions of any significance.

In making calculations of relative rates from partial rate factors, we are making the implicit assumption that each methyl substituent will make an additive contribution to the free energy of activation. There is growing evidence that this assumption holds with considerable precision. The rate of a substitution reaction will depend not only upon the stability of the transition state, presumably similar in nature to the  $\sigma$ -complex, but it must also depend upon the nature of the initial state. To the extent that the aromatic and reagent form  $\pi$ -complexes, the stability of the latter

(7) H. C. Brown and C. W. McGary, Jr., *THIS JOURNAL*, **77**, 2310 (1955).

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

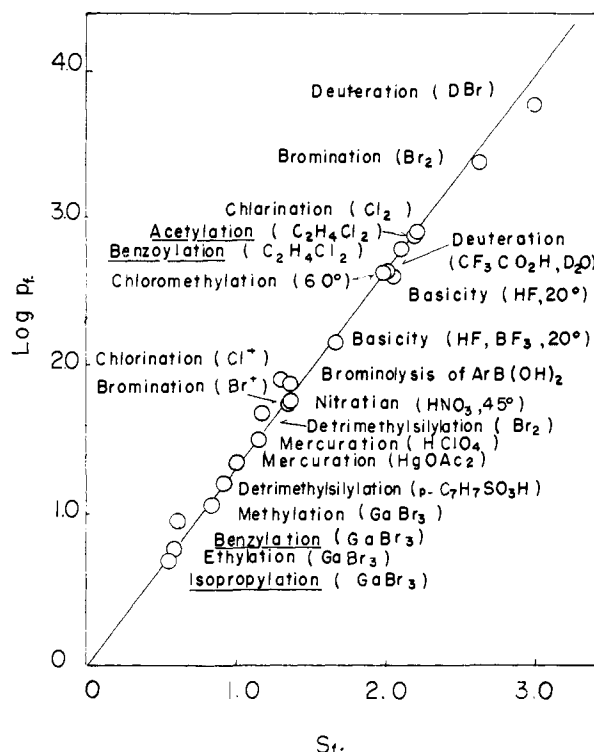


Fig. 1.—The selectivity relationship for substitution reactions of toluene (25° except where otherwise indicated). New reactions reported in this group of papers are underlined.

will also influence the reaction rate.<sup>9,10</sup> This treatment ignores the contribution of the  $\pi$ -complex to the rate. Fortunately, the stability of the  $\pi$ -complex appears to vary far less with structure than the  $\sigma$ -complex,<sup>11</sup> so that neglect of this factor does not introduce major errors. It is possible that the discrepancies between the calculated and observed relative rates noted in the present study are due to this factor.

This discussion of the discrepancies which are observed should not obscure the extent of agreement. The partial rate factors do predict relative rates as large as 1000 to within a factor of approximately 2 (Table II).

### Experimental Part

**Materials.**—Ethylene chloride, benzoyl chloride and alu-

TABLE III

REACTION OF BENZOYL CHLORIDE-ALUMINUM CHLORIDE WITH EXCESS TOLUENE IN ETHYLENE CHLORIDE AT 25.0°

Time, min.	NaOH, ml.	Reac-tion, % <sup>a</sup>	Time, min.	NaOH, ml.	Reac-tion, % <sup>a</sup>
0	8.73 <sup>b</sup>		83.0	3.25	62.8
2.00	8.50	2.63	128	2.02	76.9
34.0	5.60	35.8	2860	0.08	99.1
56.0	4.31	50.6	2860	0.09	99.0

<sup>a</sup> Initial concentrations:  $[C_6H_5COCl \cdot AlCl_3]$ , 0.100 M;  $[CH_2C_6H_5]$ , 0.300 M. <sup>b</sup> Calcd.

(9) K. L. Nelson and H. C. Brown, Chapt. 56, in "The Chemistry of Petroleum Hydrocarbons," ed. by B. T. Brooks, *et al.*, Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955.

(10) V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955).

(11) H. C. Brown and J. D. Brady, *THIS JOURNAL*, **74**, 3570 (1952)

TABLE IV  
TYPICAL RATE DATA FOR THE REACTION OF BENZOYL  
CHLORIDE-ALUMINUM CHLORIDE WITH BENZENE AND WITH  
*p*-XYLENE IN ETHYLENE CHLORIDE AT 25.0°

Time, min.	NaOH, ml.	Reaction, %	$\frac{x}{a-x}$	Rate constant <sup>c</sup> $k_s \times 10^3$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
A. Benzene <sup>a</sup>				
0	20.55 <sup>d</sup>			
14.0	20.50	5.0		
1660	16.10	21.65	0.2763	0.00925
2922	13.80	32.85	.4892	.00930
3998	12.32	40.05	.6680	.00930
7194	9.28	54.84	1.214	.00937
11171	6.76	69.10	2.039	.01014
B. <i>p</i> -Xylene <sup>b</sup>				
0	6.85 <sup>d</sup>			
60	4.27	37.66	0.604	1.67
127	3.18	53.57	1.154	1.51
167	2.64	61.45	1.594	1.59
248	2.10	69.34	2.262	1.52

<sup>a</sup> Initial concentrations: [C<sub>6</sub>H<sub>5</sub>COCl-AlCl<sub>3</sub>], 0.300 *M*; [C<sub>6</sub>H<sub>6</sub>], 0.300 *M*. <sup>b</sup> Initial concentrations: [C<sub>6</sub>H<sub>5</sub>COCl-AlCl<sub>3</sub>], 0.100 *M*; [1,4(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>], 0.100 *M*. <sup>c</sup> Graphical determination of the constant yields 0.00930 × 10<sup>-3</sup> for benzene, 1.56 × 10<sup>-3</sup> for *p*-xylene. <sup>d</sup> Calcd.

minum chloride were purified in the manner previously described.<sup>8</sup> The hydrocarbons were samples previously available<sup>4</sup> which had been demonstrated to possess purities of 99.5% or greater through cooling curve determinations.

**Techniques.**—The procedures followed were those described earlier.<sup>5</sup> In the case of benzene, the reaction was very slow and sealed ampules were used instead of the usual nitrogen-protected reaction flask.

To test our techniques for preparing and handling the solutions, a kinetic run was made with toluene (0.300 *M*) in large excess over the benzoyl chloride-aluminum chloride complex, and the reaction was followed to completion. As shown in Table III, the reaction proceeded to 99% utilization of benzoyl chloride, and this was considered to represent a confirmation of the adequacy of our methods.

Typical rate data are summarized in Table IV.

**Benzoylation of *p*-Xylene.**—*p*-Xylene (Phillips, 99%) was benzoylated on a 0.7-mole scale. The reaction product, 2,5-dimethylbenzophenone, m.p. of material recrystallized from methanol 36.0–36.5°, was obtained in a yield of 79%.<sup>12</sup>

A reaction mixture in ethylene chloride, 1.00 *M* in complex and *p*-xylene, was allowed to stand for 105 minutes. An aliquot of the reaction mixture was removed for the usual titration, indicating 50.4% reaction, and the remainder was poured into sodium hydroxide and crushed ice. There was isolated 2.33 g. of crude 2,5-dimethylbenzophenone, a yield of 94%. Infrared indicated a purity of at least 94%. From the alkaline phase, 1.30 g. of benzoic acid was isolated, 92% of the calculated quantity.

(12) K. Elbs and E. Larson, *Ber.*, **17**, 2847 (1884), report m.p. 36°. LAFAYETTE, IND.

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

## The Relative Rate and Isomer Distribution in the Acetylation of Benzene and Toluene in Ethylene Dichloride under the Influence of Aluminum Chloride<sup>1,2</sup>

By HERBERT C. BROWN, GIANLORENZO MARINO<sup>3</sup> AND LEON M. STOCK<sup>4,5</sup>

RECEIVED OCTOBER 18, 1958

The aluminum chloride-catalyzed acetylation of benzene and toluene has been examined in ethylene dichloride solution. The rate constants (× 10<sup>3</sup>) in the acetylation of benzene have been determined at 0 and 25° as 0.339 ± 0.015 and 2.65 ± 0.13 l. mole<sup>-1</sup> sec.<sup>-1</sup>, respectively. The relative rate of acetylation of toluene to benzene is 128/1.00. The isomer distribution under these conditions is established as *o*- 1.17 ± 0.23, *m*- 1.25 ± 0.25 and *p*-methylacetophenone 97.6 ± 0.3 mole per cent. These data provide the partial rate factors for the acetylation reaction, *o*<sub>r</sub> 4.5, *m*<sub>r</sub> 4.8 and *p*<sub>r</sub> 749. The relative rates are very similar to those established for the corresponding benzoylation reaction and adhere to the Selectivity Relationship governing electrophilic substitution in toluene. The steric requirements of the acetylation reagent appear to be larger than those of the benzoylation reagent as evidenced from the reduced rate in the *ortho* position in the former reaction. This fact is attributed to the non-coplanar conformation of the methyl group in the acetylating species.

The Friedel-Crafts acetylation reaction has been reported to provide only a small difference in reactivity between toluene and benzene. Ogata and Oda<sup>6</sup> observed a relative rate of 8.35, and McDuffie and Dougherty<sup>7</sup> reported this rate ratio to be 13.3 in a competitive reaction employing acetyl chloride, aluminum chloride and the hydrocarbons as solvent at 10°. On the basis of these observations and the Selectivity Relationship,<sup>8–10</sup>

it would be predicted that significant concentrations of the *meta* isomeride would be produced in the acetylation. However, this isomer has not been detected in the products of the reaction,<sup>11</sup> although it has been reported that the reaction with *t*-butylbenzene yields 1.8% *m-t*-butylacetophenone.<sup>12</sup> These conflicting observations promoted a thorough examination of the acylation process utilizing the experimentally advantageous benzoylation reaction in nitrobenzene,<sup>11</sup> benzoyl chloride<sup>13,14</sup> and ethylene dichloride.<sup>15,16</sup> In each solvent the benzoylation reaction is highly selective, the relative rate, toluene to benzene, is large (110 to 151), and the amount of the *meta* isomer produced is small (1.1 to 1.45%).

(1) Directive Effects in Aromatic Substitution. XXXIII.

(2) Based in part upon a thesis submitted by Leon M. Stock in partial fulfillment of the requirements for the Ph.D. degree.

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

(4) Monsanto Chemical Co. Fellow at Purdue University, 1957–1958.

(5) This research supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(6) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, **21**, 728 (1942).

(7) H. F. McDuffie and G. Dougherty, *THIS JOURNAL*, **64**, 297 (1942).

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

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

(10) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

(11) For a discussion of this point and other pertinent references see H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 723 (1957).

(12) J. C. Butler, L. L. Ferstandig and R. D. Clark, *THIS JOURNAL*, **76**, 1906 (1954).

(13) H. C. Brown and F. R. Jensen, *ibid.*, **80**, 2291, 2296 (1958).

(14) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 3039 (1958).

(15) F. R. Jensen, G. Marino and H. C. Brown, *ibid.*, **81**, 3303 (1959).

(16) H. C. Brown and G. Marino, *ibid.*, **81**, 3308 (1959).