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Relative Rates of the Aluminum Chloride-Catalyzed Benzoylation of the Methylbenzenes in Nitrobenzene Solution^{1,2}

HERBERT C. BROWN, BRIAN A. BOLTO,³ AND FREDERICK R. JENSEN⁴

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The rates of the aluminum chloride-catalyzed benzoylation of benzene and the polymethylbenzenes have been measured in nitrobenzene solution at 25° and compared with the relative rates calculated from the partial rate factors for the benzoylation reaction. Relatively large discrepancies are observed between the calculated and experimental rates, particularly in the case of the more reactive derivatives. Possible reasons for the discrepancies are examined. Intense colors are developed by nitrobenzene solutions containing aluminum chloride and certain of the polymethylbenzenes. It is suggested that the discrepancies in part arise from the presence of ternary nitrobenzene-aluminum chloride-polymethylbenzene complexes.

It was originally suggested by Condon that the reactivities of the polymethylbenzenes could be calculated from the partial rate factors obtained from rate data for benzene and toluene and the observed isomer distribution in toluene.⁵ Excellent agreement has been realized in applying this procedure to the mercuriation⁶ and bromination of the methylbenzenes.⁷

We recently determined the partial rate factors for the aluminum chloride-catalyzed reaction of benzoyl chloride with toluene in nitrobenzene solution⁸ and developed a convenient procedure for following the reaction rate.⁹ Accordingly, it appeared desirable to apply this procedure to the determination of the rates of benzoylation of the polymethylbenzenes and a comparison of the observed and calculated reaction rates.

Results. The rates of reaction of benzoyl chloride with the methylbenzenes were measured in nitrobenzene solvent at 25° using equimolar concentrations of benzoyl chloride, aluminum chloride, and the aromatic hydrocarbon. The reactions were followed by determining the amount of residual benzoyl chloride using the technique described in the preceding paper.⁹

The benzoylation reaction appears to be first order in aromatic, and first order in benzoyl chloride, but of complex order with respect to aluminum

chloride. At any given aluminum chloride concentration, the kinetics of the reaction with benzene follow a third order expression, but the third order constant decreases with increasing concentration of aluminum chloride. The corresponding reaction with toluene appears to agree more closely with a seven-halves order rate law.⁸

The kinetics of the present compounds proved to be similar to toluene—they followed a seven-halves order rate expression quite closely.

In order to minimize the effects of the difficulties, the rate constants were measured with all components at equal concentrations: 0.200*M* for the less reactive derivatives and 0.100*M* for the more reactive compounds. Toluene and *m*-xylene were

TABLE I

RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED REACTION OF BENZOYL CHLORIDE WITH THE METHYLBENZENES IN NITROBENZENE SOLUTION AT 25°

Aromatic	Rate Constants, k _{3,5} (l. ^{2.5} mole ^{-2.5} min. ⁻¹)		
	0.400 <i>M</i> ^a	0.200 <i>M</i> ^a	0.100 <i>M</i> ^a
Benzene	0.00632 ^b 0.00607 ^b		
Toluene	0.964 ^b 0.950 ^b	2.23 ^b 2.18 ^b	4.95 4.90
<i>o</i> -Xylene		19.8 19.4	
<i>m</i> -Xylene		54.4 56.8	134 119
<i>p</i> -Xylene		2.07 2.00	
Hemimellitene			413 438
Pseudocumene			238 248
Mesitylene			3,940 4,050
Prehnitene			1,150 1,120
Isodurene			6,820 6,530
Durene			349 352
Pentamethylbenzene			4,370 4,510

^a [ArH] = [C₆H₅COCl] = [AlCl₃] at molar concentrations indicated. ^b From Ref. (9).

(1) Directive Effects in Aromatic Substitution. XX.

(2) Based in part upon a thesis submitted by F. R. Jensen in partial fulfillment of the requirements for the Ph.D. degree.

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(4) Research assistant on a project supported by the Atomic Energy Commission, 1953-54; National Science Foundation Predoctoral Fellow, 1954-55.

(5) F. E. Condon, *J. Am. Chem. Soc.*, **70**, 1963 (1948).(6) H. C. Brown and C. W. McGary, *J. Am. Chem. Soc.*, **77**, 2311 (1955).(7) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957).(8) H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 724 (1957).(9) H. C. Brown, B. A. Bolto, and F. R. Jensen, *J. Org. Chem.*, **23**, 414 (1958).

examined at both concentrations to permit reduction of the data to a single scale of relative reactivities.

The observed rate constants are summarized in Table I.

Whereas in the case of benzene and toluene the reaction solutions were pale yellow, very similar in color to solutions of aluminum chloride in nitrobenzene itself, the more highly alkylated aromatics produced much more intensely colored solutions, varying from orange-yellow for hemimellitene, to red-orange for isodurene, to dark red for pentamethylbenzene.

This phenomenon was examined further by preparing solutions in nitrobenzene of the aromatic hydrocarbon and aluminum chloride, 0.2M in each component. The observations are summarized in Table II.

TABLE II

COLORS EXHIBITED BY SOLUTIONS OF ALUMINUM CHLORIDE AND METHYLBENZENES IN NITROBENZENE^a

Aromatic	Color of Solution	Calcd. Relative Rate Obsd. Relative Rate
Benzene	Pale yellow	1.0
Toluene	Yellow	1.0
<i>p</i> -Xylene	Darker yellow	0.7
<i>o</i> -Xylene	Orange-yellow	1.0
<i>m</i> -Xylene		2.3
Pseudocumene		3.0
Durene		0.7
Mesitylene		3.4
Hemimellitene	Yellow-orange	3.5
Prehnitene	Light red-orange	5.9
Isodurene	Red-orange	6.7
Pentamethylbenzene	Dark red	25

^a [ArH] = [AlCl₃] = 0.2M.

Discussion. The observed relative rates for the benzoylation reaction, $k_{\text{toluene}}/k_{\text{benzene}} = 151$, and the observed isomer distribution in toluene, 7.2% *ortho*, 1.1% *meta*, and 91.7% *para*, yield the partial rate factors: o_f 32.6, m_f 5.0, p_f 831. Utilizing these rate factors, the relative rates of benzoylation of the methylbenzenes have been calculated. These calculated values are summarized in Table III along with the observed values of the relative rates.

In the case of the mercuration and bromination reactions, excellent agreement was realized between the observed reaction rates and those calculated from the partial rate factors. However, in the present case serious discrepancies exist between the observed and calculated rates (Fig. 1).¹⁰

We have carefully reviewed the experimental technique for following the benzoylation rates. Although some of these reactions are exceedingly fast,

(10) To obtain a graphical estimate of the marked difference in the agreement realized in these three reactions, compare Fig. 1 with the corresponding diagrams for the mercuration and bromination reactions. H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

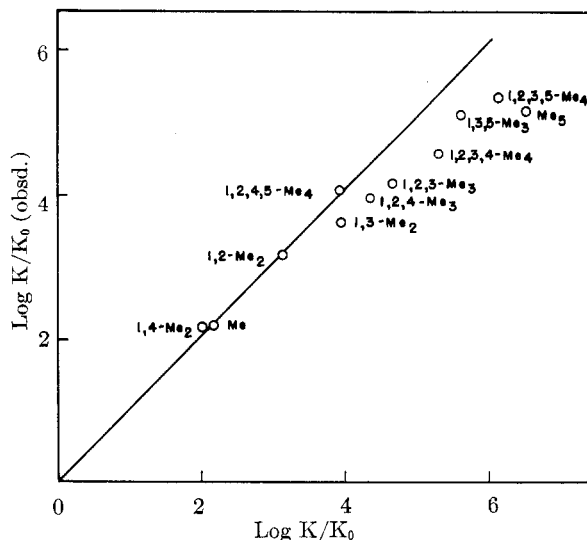


Fig. 1. Comparison of observed and calculated relative rates of the aluminum chloride-catalyzed reaction of benzoyl chloride with the methylbenzene

TABLE III

OBSERVED AND CALCULATED RELATIVE RATES FOR THE ALUMINUM CHLORIDE-CATALYZED BENZOYLATION OF THE METHYLBENZENES IN NITROBENZENE AT 25°

Aromatic	Relative Rate	
	Observed	Calculated ^a
Benzene	1.00	1.00
Toluene	154	151
<i>o</i> -Xylene	1,360	1,440
<i>m</i> -Xylene	3,910	9,210
<i>p</i> -Xylene	142	108
Hemimellitene	13,300	48,600
Pseudocumene	7,600	23,700
Mesitylene	125,000	442,000
Prehnitene	35,500	225,000
Isodurene	212,000	1,470,000
Durene	11,000	8,850
Pentamethylbenzene	139,000	3,690,000

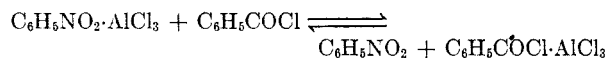
^a Calculated from the factors: o_f 32.6; m_f 5.0; p_f 831 (ref. 8).

introducing the possibility of an appreciable error in the measurement of the rate constants, we do not believe that the large discrepancies between the observed and calculated values can be attributed to this cause. We have been able to check our measurements of the rate constants with a reproducibility of $\pm 5\%$ and, even in the case of the very fast reactions, we doubt that the uncertainty can be very much larger than this.

In the case of the mercuration reaction, we observed certain minor discrepancies which pointed to an enhanced steric effect when the position undergoing substitution is flanked by two methyl groups, particularly when these are buttressed by additional methyl substituents. However, the present data show good agreement between the observed and calculated rates for durene (with buttressed double-*ortho* substituents) and a very large discrepancy for the related structure, pentamethyl-

benzene. Consequently, this factor cannot be responsible for the large discrepancies observed.

We also considered the possibility that the rate of transfer of aluminum chloride from nitrobenzene to benzoyl chloride might become a factor in the very fast reactions and thereby account for the observed drop below the calculated values. In these solutions the aluminum chloride is presumably associated with the nitrobenzene as a 1:1 addition compound, with a minor amount of the aluminum chloride associated with the benzoyl chloride.



The available evidence indicates that such transfers are very fast. If so, the rate of transfer would not be involved in the measured rate of reaction. However, in the case of the very fast benzoylations there exists the possibility that the rates of these reactions may be comparable to the rate of transfer and result in a decrease in the observed rate from that calculated from the partial rate factor.

On the basis of the available evidence, we cannot completely eliminate this possibility as a factor. However, we believe that it cannot be the entire answer and can, at most, only account for a portion of the effect. Were this a factor in the fast reactions, it should also be present in durene. Yet the agreement between the calculated and observed rates for durene is good. On the other hand, relatively large discrepancies exist for *m*-xylene and pseudocumene, which react at rates comparable to that for durene.

Previously, in studying the aluminum chloride-catalyzed reaction of 3,4-dichlorobenzyl chloride with aromatics in nitrobenzene solution, we encountered certain peculiarities which we attributed to the formation of ternary complexes of aluminum chloride, nitrobenzene, and the aromatic hydrocarbons.¹¹ In the present case we also encountered the intensely colored solutions characteristic of such complexes.

Solutions of aluminum chloride and the aromatic hydrocarbon in nitrobenzene were prepared at 0.2*M* and the colors which developed were compared (Table II). Benzene and toluene yield solutions whose colors differed but little from those of binary aluminum chloride-nitrobenzene solutions. However, the colors deepened with the more highly methylated aromatics and a rough correlation was observed between both the shift in the color and its

intensity and the magnitude of the discrepancy between the observed and calculated rates (Table II).

It is not possible on the basis of such qualitative evidence to conclude that the discrepancy is due to this factor. However, it is apparent that the formation of complexes within the reacting solution involving a portion of both aluminum chloride-nitrobenzene and the aromatic hydrocarbon might well result in a decrease in the equilibrium concentration of the benzoyl chloride-aluminum chloride complex which is believed to be responsible for the benzoylation reaction, with a resulting decrease in the experimentally observed rate.

We are attempting to test this possibility by examining in more detail the interactions of aluminum chloride in nitrobenzene solution with benzoyl chloride and with aromatic hydrocarbons individually. However, it appears that the aluminum chloride-nitrobenzene system possesses a number of complicating characteristics which render it undesirable for studies directed to the quantitative determination of rates of aromatic substitution. Consequently, we are examining other solvents which may permit the determination of benzoylation rates free of the difficulties encountered with nitrobenzene as the medium.

EXPERIMENTAL

Materials. The nitrobenzene, benzoyl chloride and aluminum chloride were purified as previously described.⁸

The aromatic hydrocarbons were obtained from stocks available in the laboratory.^{6,7} All compounds had been carefully purified and had been shown to possess minimum purities of at least 99.5% purity by cooling curve measurements.

Analytical procedure. The analytical procedure was the same as reported previously for the benzoylation of the alkylbenzenes in nitrobenzene⁹ except with the more reactive compounds, where it was feared that contacting the solution with the immiscible water layer might not be sufficiently effective to stop the reaction instantly. Therefore, for mesitylene, pentamethylbenzene, and 1,2,3,5-tetramethylbenzene, a more rapid procedure for halting the reaction was devised. Standard solutions of the hydrocarbon in nitrobenzene and of benzoyl chloride and aluminum chloride in nitrobenzene were prepared. Aliquot portions of these solutions were brought together, using fast delivery pipets. The reactions were stopped by pouring 10 ml. of a 0.5*M* benzophenone solution in chlorobenzene into the reaction vessel. The ready miscibility of the benzophenone solution with that of the reaction mixture permitted the instant coordination of the aluminum chloride by the benzophenone and the practically instantaneous halting of the reaction. The samples were then worked up in the manner previously described.

LAFAYETTE, IND.

(11) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953).