Kinetic Study of the Aluminum Chloride–Catalyzed Benzoylation of Benzene and Toluene in Nitrobenzene Solution.   Partial Rate Factors for the Benzoylation Reaction[1-3]

HERBERT C. BROWN AND HERBERT L. YOUNG[4]

The aluminum chloride–catalyzed reaction of benzoyl chloride with benzene in nitrobenzene solution exhibits complex kinetics. For any given concentration of the three reactants, the reaction appears to follow a third order rate expression: rate $= k_3[C_6H_6][C_6H_5COCl][AlCl_3]$. However, with increasing aluminum chloride concentrations, the rate constants decrease in magnitude. The data for the corresponding reaction with toluene appear to follow a seven-halves order rate expression. Comparison of the half-lives of the two reactions leads to a toluene/benzene rate ratio of 149. Comparison of the seven-halves order rate constants for benzene and toluene (with all reactants at equal concentrations) leads to the k_T/k_B value of 153. These values are in excellent agreement with the value of k_T/k_B of 149 predicted from the observed isomer distribution in the benzoylation of toluene (ortho, 7.2%; meta, 1.1%; para, 91.7%). Partial rate factors are calculated for the benzoylation reaction.

The isomer distribution in the aluminum chloride–catalyzed reaction of benzoyl chloride with toluene in nitrobenzene solution at 25° was established to be: ortho, 7.2; meta, 1.1; para, 91.7%.[5] These results indicate that benzoylation is a highly selective reaction.[6] In order to test whether this reaction obeys the quantitative treatment which has been proposed for aromatic substitution,[7,8] it was necessary to have the relative rate of benzoylation of toluene to benzene (k_T/k_B) under conditions identical with those used for establishing the isomer distribution.[9]

Attempts were made to establish the relative reactivities by competition experiments. However, it soon became apparent that the difference in reactivities of benzene and toluene was too great for such methods. Accordingly, we undertook a kinetic study of the benzoylation of benzene and toluene in the hope that the rate ratio might be accurately determined by a direct comparison of the two rate constants.

Kinetic studies have been made of the benzoylation reaction, using excess aromatic hydrocarbon as the reaction medium.[10-13] More recently, a kinetic

study has been made of the benzoylation of benzene and toluene in bromobenzene solution.[9] However, our isomer distribution study had utilized nitrobenzene as a reaction medium,[5] so that a kinetic study of the reaction was undertaken with this material as solvent.

RESULTS

The reaction components are highly sensitive to moisture and consistent results could be realized only after considerable experimentation and the development of special apparatus and techniques for handling the reagents and solutions under strictly anhydrous conditions.[14] Largely because of the special sensitivity of the reaction to trace quantities of water or other basic impurities, it proved desirable to operate at somewhat higher concentrations (0.2–0.4M) than are customary in kinetic work. Although we encountered difficulties with the kinetics, as far as we could ascertain these difficulties were not attributable to the high concentrations used or to the experimental procedure.

Standard solutions of aluminum chloride in nitrobenzene were prepared and stored in special flasks which permitted the measurement of aliquots without exposure to moisture. A known amount of benzoyl chloride was added to these aliquots, and they were diluted to the desired concentration with nitrobenzene. The reaction was initiated by addition of the aromatic. Aliquots were removed at suitable intervals and the reaction was followed by the change in concentration of benzoyl chloride. By this procedure the rate constants were reproducible to ±3–5%.

(1) Directive Effects in Aromatic Substitution. XVII.

(2) Supported in part by the Petroleum Research Fund of the AMERICAN CHEMICAL SOCIETY.

(3) Based upon a thesis submitted by Herbert L. Young in 1956 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Standard Oil Co. (Indiana) Fellow at Purdue University, 1953–1955.

(5) H. C. Brown and H. L. Young, J. Org. Chem., 22, 719 (1957).

(6) H. C. Brown and K. L. Nelson, J. Am. Chem. Soc., 75, 6292 (1953).

(7) H. C. Brown and C. W. McGary, J. Am. Chem. Soc., 77, 2300 (1955).

(8) H. C. Brown and C. R. Smoot, J. Am. Chem. Soc., 78, 6255 (1956).

(9) A value of k_T/k_B of 53 has recently been reported for benzoylation at 40° in bromobenzene solution. F. Smeets and J. Verhulst, Bull. soc. chim. Belg., 63, 439 (1954).

(10) B. D. Steele, J. Chem. Soc., 83, 1470 (1903).

(11) L. F. Martin, P. Pizzolato, and L. S. McWaters, J. Am. Chem. Soc., 57, 2584 (1935).

(12) S. C. J. Olivier, Rec. trav. chim., 37, 205 (1918).

(13) H. Ulich and G. Heyne, Z. Elektrochem., 41, 509 (1935); H. Ulich and P. V. Fragstein, Ber., 72, 620 (1939).

(14) We are indebted to Dr. Frederick R. Jensen who is largely responsible for developing these methods and procedures.

At any given concentration of aluminum chloride, the reaction with benzene appears to follow a simple third order rate expression (1) out to 70–80% reaction:

$$\text{rate} = k_3[\text{C}_6\text{H}_6][\text{C}_6\text{H}_5\text{COCl}][\text{AlCl}_3] \qquad (1)$$

While maintaining the benzoyl chloride and aluminum chloride concentrations essentially constant at $0.4M$, the benzene concentration was varied from $0.2M$ to $0.8M$ without variation in the value of k_3 (Table I). Similarly, with the benzene and aluminum chloride concentrations fixed at $0.4M$, a change in the benzoyl chloride concentration from 0.2 to $0.6M$ results in no important change in k_3. (The observed decrease from 3.8 to 3.4 may be significant, or it may be due to a minor solvent effect arising from the high concentrations of benzoyl chloride.)

With the acid chloride and benzene concentrations maintained constant, the aluminum chloride concentration was varied. An *increase* in the aluminum chloride concentration led to a *decrease* in the value of k_3 (Fig. 1). The effect is quite large. Thus,
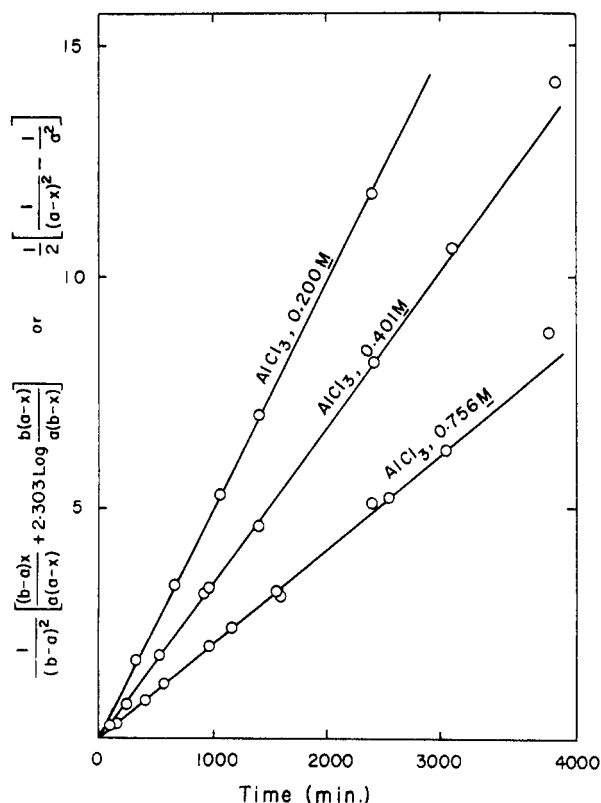

FIG. 1. THIRD ORDER RATE CONSTANTS FOR THE BENZOYLATION OF BENZENE (25°) WITH (C₆H₅COCl) = (C₆H₆) = 0.4 MOLE/LITER AND VARIABLE ALUMINUM CHLORIDE CONCENTRATION

with the acid chloride and benzene concentrations maintained at $0.4M$, k_3 varies with [AlCl₃] as indicated: $0.2M$, 5.0; $0.4M$, 3.4; $0.8M$, 2.1.

A reaction mixture was permitted to go essentially to completion and the product was isolated.

A 92% yield of spectroscopically pure benzophenone was isolated. Consequently, the reaction with benzene does not appear to involve any important side reaction.

The results are summarized in Table I.

TABLE I

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

Benzene	Reactants, M Benzoyl Chloride	AlCl₃	$10^3 k_3{}^a$ liter² Mole⁻² Min.⁻¹	Extent of Reaction, %[b]
0.199	0.398	0.397	3.26	
0.409	0.402	0.401	3.40^c	58
0.398	0.400	0.401	3.38^d	64
0.795	0.403	0.402	3.33	75
0.406	0.203	0.402	3.83	78
0.392	0.204	0.397	3.77	72
0.394	0.594	0.397	3.56	69
0.376	0.567	0.376	3.21	64
0.397	0.399	0.200	5.02	68
0.395	0.401	0.198	5.22	81
0.392	0.395	0.198	4.74	72
0.387	0.388	0.779	2.14	65
0.400	0.401	0.800	2.10	67
0.397	0.397	0.756	2.07	60
1.162	0.395	0.777	2.06	80
0.608	0.208	0.403	3.91	81
0.598	0.600	0.598	2.48^e	65

^{a} In cases where two or more concentrations are almost equal, mean concentrations were used in the calculations.
^{b} The extent of the reaction for which the third order plot was linear. See Fig. 1. The value in % is based upon the component present in limiting amount. ^{c} $k_{3.5}$ 6.25. ^{d} $k_{3.5}$ 6.05. ^{e} $k_{3.5}$ 3.90.

A new complication made its appearance in the corresponding kinetic study with toluene. Here the third order treatment, which had been satisfactory for benzene (Fig. 1), failed to give a linear relationship (Fig. 2). The curvature, although real, was not great and the data were approximately linear in the region between 30–40% to 70–80%. We therefore adopted this treatment to obtain an approximate value for the rate constant (k_3). The value of the rate constant obtained in this way was reasonably reproducible ($\pm 5\%$) and we utilized it to explore the effect of changes in the initial concentrations of the three components.

The results were similar to those described for benzene. The rate constant was essentially independent of the initial concentration of the aromatic, decreased moderately with an increase in concentration of benzoyl chloride, and decreased markedly with an increase in the concentration of aluminum chloride.

Typical results are summarized in Table II.

It was then noted that those experiments in which the three reactants were present in essentially equimolar concentrations ($0.2M$ or $0.4M$) gave good linear plots up to 70–80% reaction when the data were treated as a reaction of order seven-
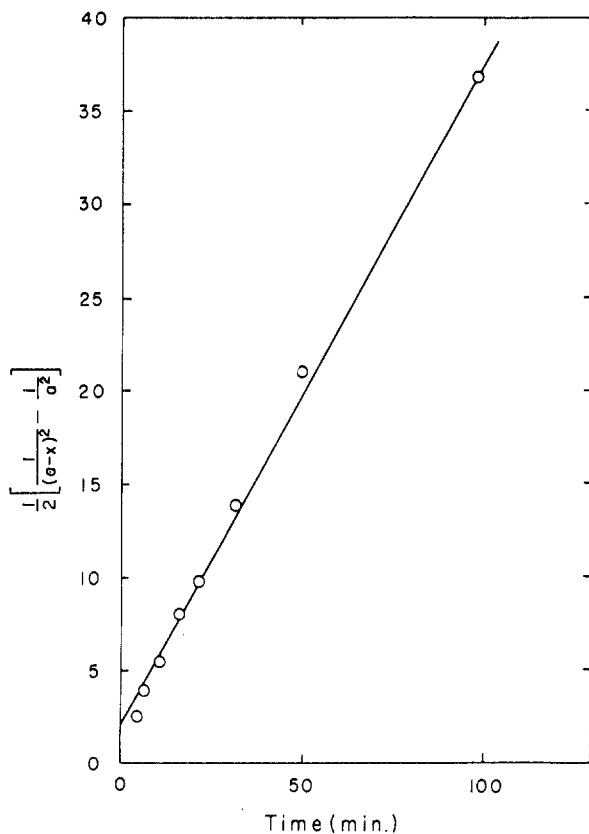
FIG. 2. THIRD ORDER RATE CONSTANTS FOR THE BENZO-YLATION OF TOLUENE (25°) WITH $(C_6H_5COCl) = (C_6H_5CH_3)$ = 0.4 MOLE/LITER
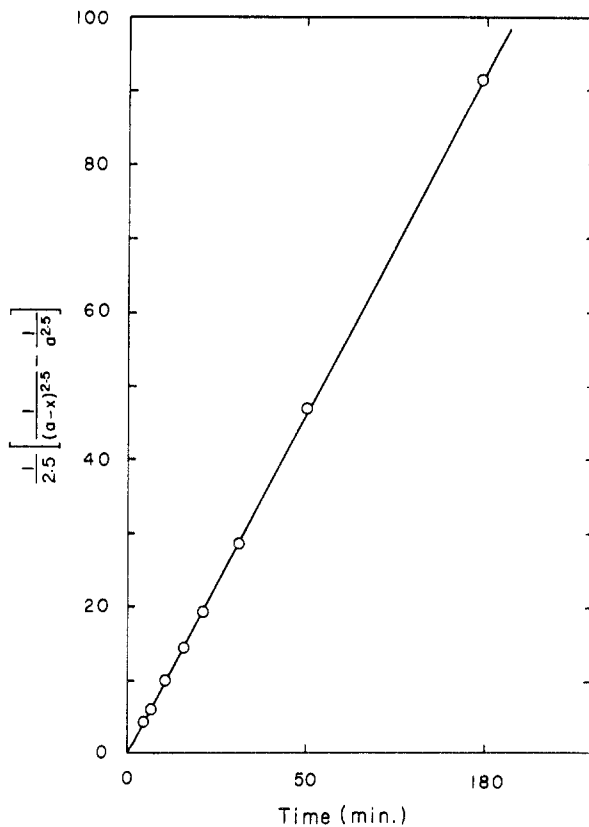

FIG. 3. SEVEN-HALVES ORDER RATE CONSTANT FOR THE BENZOYLATION OF TOLUENE (25°) WITH (C_6H_5COCl) = $(AlCl_3) = (C_6H_5CH_3) = 0.4$ MOLE/LITER

TABLE II
RATE CONSTANTS FOR THE ALUMINUM CHLORIDE–CATALYZED REACTION OF BENZOYL CHLORIDE WITH TOLUENE IN NITROBENZENE SOLUTION AT 25°

Reactants, M			$k_3{}^a$ Liter^2 Mole^{-2} Min.$^{-1}$	$k_{3.5}$ Liter$^{2.5}$ Mole$^{-2.5}$ Min.$^{-1}$
Toluene	Benzoyl Chloride	AlCl$_3$		
0.404	0.203	0.398	0.495	
0.404	0.199	0.398	0.488	
0.610	0.204	0.399	0.470	
0.603	0.206	0.401	0.474	
0.400	0.402	0.401	0.356	0.89
0.400	0.401	0.401	0.385	1.01
0.400	0.401	0.400	0.353	0.93
0.397	0.400	0.797	0.285	
0.398	0.400	0.801	0.298	
1.213	0.406	0.810	0.288	
1.221	0.412	0.807	0.339	
0.200	0.200	0.198	0.525	1.86
0.205	0.201	0.201	0.610	2.09

^{a} In cases where two or more concentrations are almost equal, mean concentrations were used.

halves. Thus, in Fig. 3, a significant upward deviation is evident only after the reaction is 85% complete.

This encouraged us to examine a seven-halves plot for benzene. Such a plot exhibited satisfactory linearity up to 40–50% reaction, but deviated upward beyond this point (Fig. 4). Thus in the case
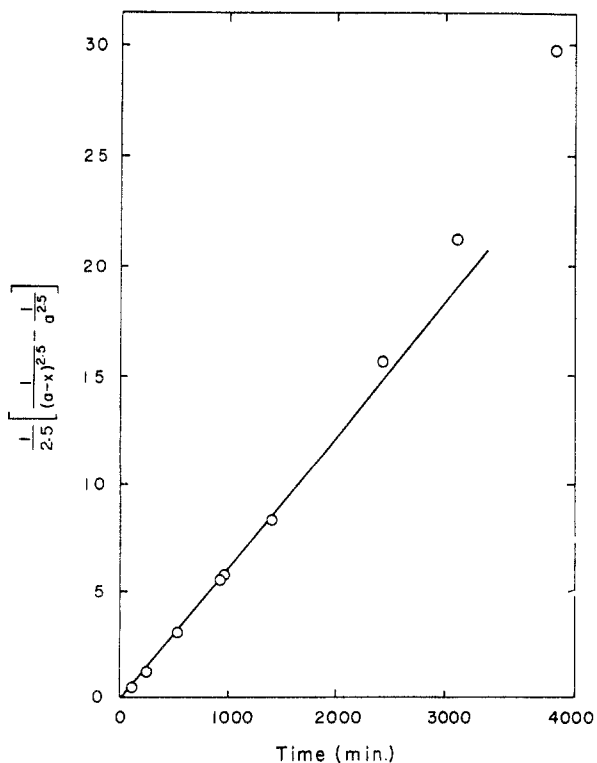

FIG. 4. SEVEN-HALVES ORDER RATE CONSTANT FOR THE BENZOYLATION OF BENZENE (25°) WITH (C_6H_5COCl) = $(AlCl_3) = (C_6H_6) = 0.4$ MOLE/LITER

of benzene such a treatment is less satisfactory than the third order analysis previously utilized. The values of $k_{3.5}$ (Tables I and II) appear to vary inversely with the first power of the initial concentration of aluminum chloride. Unfortunately, the treatment of seven-halves order kinetics for cases other than equal concentration of reactants is too cumbersome to be practical. Consequently, we were able to explore the change in rate constant only for the runs in which all reactants had been maintained essentially constant.

Efforts were made to determine the possible existence of any simple rate law by calculating the order of the reaction using means other than application of the integrated forms of various rate expressions. Thus, if all reactants have equal concentrations, any simple rate expression reduces to the form

$$- \frac{dc}{dt} = kc^n$$

and

$$\log \left(- \frac{dc}{dt} \right) = \log k + n \log c$$

The rates of reaction $\left(- \dfrac{dc}{dt} \right)$ were determined by constructing tangents with the aid of a small mirror at several points on the curve obtained by plotting the concentration of benzoyl chloride vs. time. The logarithm of the rate $\left[\log \left(- \dfrac{dc}{dt} \right) \right]$ was plotted vs. the logarithm of the concentration (log c) and the slope (n) determined. With all reactants at a concentration of 0.4 mole/liter, the over-all order (n) was 2.9 for benzene and 3.4 for toluene. This agrees with previous results that individual benzene experiments follow third order kinetics, while those of toluene are closer to seven-halves order.

DISCUSSION

Kinetics. Although a general rate expression was not obtained, several conclusions concerning the kinetics can be drawn. Thus, individual benzene runs are third order, while those of toluene are closer to seven-halves order. The reaction appears to be cleanly first order with respect to the aromatic component, indicating that the latter is involved in a rate-determining stage. The order with respect to the benzoyl chloride is only approximately unity, since the rate constants exhibit minor changes with change in the initial concentration of this component.

The order with respect to aluminum chloride is ill-defined. Individual experiments with benzene appear to be first order, and those with toluene three-halves order in this component. Moreover, the rate constants decrease markedly with an increase in the initial concentration of the metal halide. The over-all data clearly establish that the rate

is not a simple function of some power, integral or not, of the aluminum chloride concentration.

The question necessarily arises as to whether the complicated kinetics are a consequence of the acylation reaction itself, or are to be attributed to some peculiarity of the aluminum chloride-nitrobenzene system.

Rothstein and Saville previously examined the behavior of aluminum chloride in nitrobenzene solution on the reaction of pivaloyl chloride with a number of aromatic components.[15] The kinetics were complex. However, the reaction itself is not simple since it involves both acylation and alkylation (with loss of carbon monoxide). Consequently, no definite conclusion can be drawn from the complexity of the kinetics.

Recently we examined the kinetics of the aluminum chloride–catalyzed reactions of arylsulfonyl chlorides with aromatics.[16] Similar complex kinetics were observed. In a recent study of the aluminum chloride–catalyzed reaction of cyclohexyl chloride with benzene, Lebedev noted that the order with respect to aluminum chloride varied from 0.35 for 85% nitrobenzene–12.5% benzene to 1.5 for 22.5% nitrobenzene–75% benzene.[17] He concludes that the order approximates 0.5 for pure nitrobenzene and is near 2 for pure benzene, with rapidly changing intermediate values for mixtures of the two solvents.

On the other hand, there is evidence that the acylation reaction itself can be kinetically simple. Thus, Smeets and Verhulst report clean second order kinetics for the reaction of the benzoyl chloride-aluminum chloride complex with aromatics in bromobenzene solution.[9] Likewise in benzoyl chloride as solvent we have found the acylation reaction to be cleanly first order in aluminum chloride and first order in aromatic.[16]

Therefore, it appears that the complex kinetics are not the result of any peculiarity of the acylation reaction, but must be attributed instead to the peculiarities of the aluminum chloride-nitrobenzene system.[18] It is probable that the unraveling of the kinetics must await a better understanding of the molecular and ionic species present in a solution of aluminum chloride in nitrobenzene.

We explored a number of possible explanations for the observed kinetics. Since we were unable to

(15) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1954, 1959, 1961 (1949).

(16) Frederick R. Jensen, Ph.D. thesis, Purdue University Library.

(17) N. N. Lebedev, *J. Gen. Chem.* (*U.S.S.R.*), **24**, 664 (1954).

(18) E. P. Kohler, *J. Am. Chem. Soc.*, **24**, 385 (1900). R. E. Van Dyke and H. E. Crawford, *J. Am. Chem. Soc.*, **73**, 2018 (1951). V. A. Plotnikov and R. G. Vaisberg, *Rep. Inst. Chem. Acad. Sci. Ukrain. S.S.R.*, **3**, 337 (1936); *Chem. Abstr.*, **31**, 5689 (1937). V. A. Plotnikov and E. Y. Gorenbein, *Rep. Inst. Chem. Acad. Sci. Ukrain. S.S.R.*, **3**, 471 (1936); *Chem. Abstr.*, **31**, 7764 (1937).

TABLE III
HALF-LIVES AND RELATIVE RATES

Benzene	Reactants Benzoyl Chloride	AlCl$_3$	$t_{0.5}$ (Min.)	Toluene	Reactants Benzoyl Chloride	AlCl$_3$	$t_{0.5}$ (Min.)	k_T/k_B
0.413	0.210	0.399	1600	0.409	0.208	0.400	10.5	
0.406	0.203	0.402	1650	0.404	0.203	0.398	10.5	
0.392	0.204	0.397	1750	0.404	0.199	0.398	10.4	
0.399	0.202	0.400	1580					
		Mean	1640 ± 55			Mean	10.5 ± 0.03	156
0.409	0.402	0.401	2700	0.400	0.401	0.402	21.0	
0.398	0.400	0.401	2700	0.401	0.400	0.401	19.1	
				0.400	0.401	0.400	20.4	
		Mean	2735 ± 35			Mean	20.2 ± 0.7	136
0.397	0.399	0.200	1170	0.399	0.400	0.200	7.9	
0.395	0.401	0.198	1140	0.397	0.398	0.199	8.1	
0.392	0.395	0.198	1180					
		Mean	1160 ± 17			Mean	8.0 ± 0.1	145
0.387	0.388	0.779	1710	0.397	0.400	0.787	11.0	
0.400	0.401	0.800	1910	0.398	0.400	0.801	11.0	
0.397	0.397	0.756	1910					
		Mean	1840 ± 90			Mean	11.0 ± 0.0	167
0.795	0.403	0.402	1130	0.791	0.397	0.397	8.1	140
							Mean	149 ± 10

arrive at a satisfactory interpretation, we shall not attempt to discuss these here.[19]

Relative rate. The question remains whether the data can be used to answer the primary objective of this investigation, the relative rate of benzoylation of toluene and benzene.

The halogenation of aromatics exhibits certain complexities in the kinetics. In these cases the relative reactivities have been established with considerable reproducibility and consistency by comparing the 10% and 20% reaction times.[20,21] We therefore examined this approach. Since the speed of the toluene reaction is so great, we compared the half-lives ($t_{0.5}$) instead of the $t_{0.1}$ and $t_{0.2}$ values used in the halogenation studies. In all cases the rates were compared under closely comparable concentrations of reactants.

The results are summarized in Table III.

The relative rate is 149 ± 10 and appears to be essentially independent of the concentrations of the reagents, within the relatively large experimental uncertainty.

As was pointed out, the reaction of toluene exhibits a good fit with the seven-halves order treatment, whereas the corresponding treatment of benzene exhibits satisfactory linearity over the first 50% of reaction. Accordingly, we compared the two values of the rate constants calculated in this way for all concentrations essentially 0.4M (Tables I and II). The relative rate k_T/k_B calculated from the

mean value of three toluene runs (0.943 ± 0.045 liter$^{2.5}$ mole$^{-2.5}$ min.$^{-1}$) and the mean value of two benzene runs (0.00615 ± 0.00010 liter$^{2.5}$ mole$^{-2.5}$ min.$^{-1}$) is 153.

The determination of relative rates by such a comparison of rate constants involves two assumptions: (a) the rate determining step consists, in the case under discussion, of the reaction of the aromatic component with the substituting species, and (b) the rate expressions for the reactions with benzene and toluene are the same. Since the kinetics of the benzoylation reaction in nitrobenzene solution are not understood, neither of these conditions can be explicitly assumed to apply in this case.

Arguments can be advanced to support the position that both assumptions are approximately fulfilled in this reaction. Thus, the essentially clean first order dependence on the concentration of both benzene and toluene and the large difference in observed rate points to the aromatic being involved in a rate-determining reaction of the hydrocarbon with the substituting species, whatever that may be.

Second, the ratio of k_T/k_B as measured by the half-lives exhibits a remarkable constancy over large changes in the concentrations of the components. This also argues that the actual substitution step is the major controlling factor in the rates.

Finally, the agreement realized between the k_T/k_B value from the half-lives (149) and the k_T/k_B value from the ratio of the seven-halves rate constants (153) also supports the same conclusions. It would appear that the complex kinetics arise from those reactions which produce the molecular or ionic intermediate which reacts with the aromatic and that this complication is effectively eliminated by comparing the half-lives or seven-halves order rate constants under essentially identical conditions.

(19) For a fuller discussion of the kinetic investigation together with additional kinetic data obtained in our efforts to understand the reaction, the original theses should be consulted (refs. 3 and 16).

(20) P. W. Robertson, P. B. D. de la Mare and W. T. G. Johnston, *J. Chem. Soc.*, 276 (1943); P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

(21) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421 (1957).

In the absence of contrary evidence, the average value, $k_T/k_B = 151$, may be adopted for the relative rate of benzoylation of the two hydrocarbons.

Partial rate factors. Utilizing the k_T/k_B rate ratio of 151 and the observed isomer distribution[5] of 7.2% *ortho*, 1.1% *meta*, and 91.7% *para*, the partial rate factors may be calculated. These are listed in Table IV.

TABLE IV

OBSERVED AND CALCULATED VALUES OF THE PARTIAL RATE FACTORS FOR THE BENZOYLATION REACTION IN NITROBENZENE AT 25°

	Partial Rate Factors			Relative Rate, k_T/k_B
	o_f	m_f	p_f	
Obsd.[a]	32.6	5.0	831	151
Calcd.[b]	32.0	4.9	817	149

[a] This study. [b] Ref. 5.

Recently a procedure was proposed for the calculation of the partial rate factors for toluene substitution and the relative rates of reaction solely from the observed isomer distribution.[8] The values calculated in this way[5] are also listed in Table IV. The agreement is excellent, well within the probable uncertainty in the experimental k_T/k_B value. The correlation of the benzoylation reaction with other substitution reactions of toluene is indicated by Fig. 5. The excellent agreement realized lends sup-
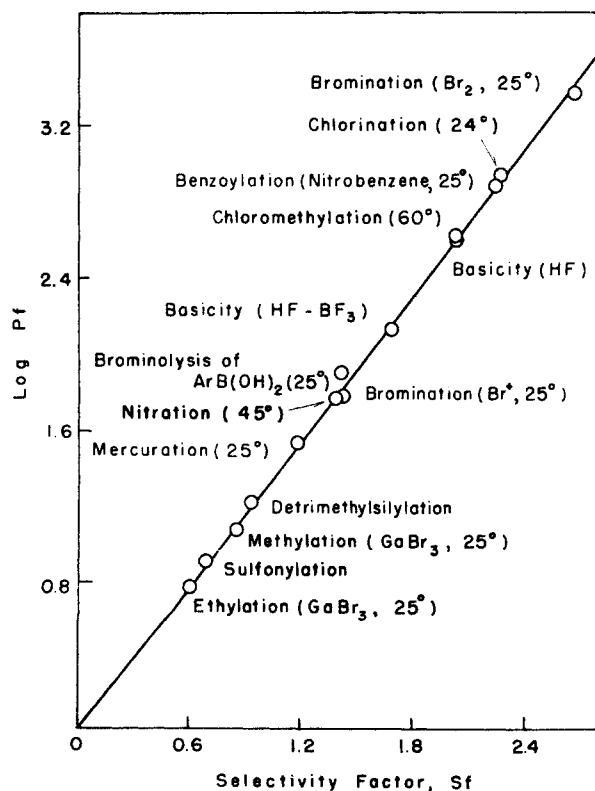
port to the conclusion that the reaction of the aromatic with the substituting species must be rate-controlling in the benzoylation reaction.

It is concluded that benzoylation, specifically, and presumably acylation, generally, obeys the Selectivity Relationship.

EXPERIMENTAL

Materials. The purification and properties of the various compounds used in this study are described in an earlier paper.[6]

The benzoyl chloride and nitrobenzene were distilled directly into special storage and dispensing flask equipped with a buret side arm. The solution of aluminum chloride in nitrobenzene was also prepared and stored in and dispensed from a special flask of this kind. All flasks were maintained under pressure of dry nitrogen ($\sim$1.3 atmos.).

Kinetic Procedure. The reaction flasks consisted of calibrated Pyrex graduated cylinders equipped with a side arm for dry nitrogen. The reagents were introduced into the reaction flask from the special dispensing flasks in a stream of dry nitrogen. With the reaction mixture (aluminum chloride and benzoyl chloride in nitrobenzene) at bath temperature (25.0 ± 0.03°), the reaction was initiated by the introduction of the aromatic by means of a syringe. Samples were removed at appropriate time intervals and the course of the reaction was followed by determining the concentration of unreacted benzoyl chloride.

Two analytical procedures were employed. In the first of these, 5-ml. aliquots of the reaction mixture were run into

FIG. 5. BENZOYLATION OF TOLUENE IN THE SELECTIVITY RELATIONSHIP

TABLE V

TYPICAL KINETIC DATA FOR THE BENZOYLATION OF BENZENE AHD TOLUENE IN NITROBENZENE SOLUTION AT 25°

Reagents, M					
Benzene	Toluene	Benzoyl chloride	$AlCl_3$	Time, Min.	x^a
0.397		0.399	0.200	320	0.043
				664	0.070
				1060	0.093
				1395	0.108
				2400	0.136
				2855	0.150
				3845	0.166
0.398		0.400	0.401	310	0.056
				750	0.103
				1175	0.134
				1525	0.151
				2350	0.187
				2830	0.205
				4165	0.225
				6065	0.254
				8220	0.277
0.400		0.401	0.800	275	0.058
				600	0.110
				960	0.143
				1265	0.161
				2320	0.222
				3751	0.269
	0.400	0.401	0.402	5.8	0.118
				12.1	0.167
				17.5	0.190
				27.4	0.218
				40.2	0.242
				70.2	0.272
				127.8	0.300

[a] Benzoyl chloride reacted, moles per liter.

20 ml. of 2M sodium hydroxide solution and the mixtures heated under reflux for 1–2 hr. The nitrobenzene phase was separated, washed with 10 ml. of water, which was joined with the aqueous phase. This was then acidified with 10 ml. of 6N hydrochloric acid and extracted with 25 ml. portions of ether. Each ether portion was washed with 10 ml. of water, which was added to the aqueous phase for the next extraction. The combined ether extracts were evaporated under reduced pressure at room temperature and the residue taken up in 50 ml. of 95% ethanol. This was then titrated with standard base. Blank determinations revealed that this procedure accounted for 98–99+% of the benzoyl chloride present in typical reaction mixtures.

A more convenient analytical procedure was developed subsequently.[16] This procedure involved the neutralization of the aluminum chloride and hydrogen chloride in the reaction mixture, followed by a direct titration of the benzoic acid and hydrochloric acid produced by the hydrolysis of the benzoyl chloride present. A detailed description of this procedure will be published shortly.[22]

Both procedures gave identical results.

Typical kinetic studies are reported in Table V.

LAFAYETTE, IND.

(22) H. C. Brown, F. R. Jensen, and B. A. Bolto, paper in preparation.


Formation of Naphthalenes from Indenes. III.[1] Substituted Methanes as Carbene Precursors
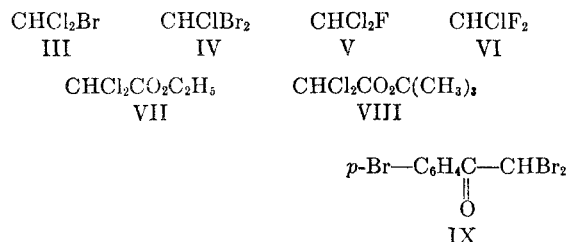
WILLIAM E. PARHAM[2] AND ROBERT R. TWELVES[3]

Seven substituted methanes have been examined as possible carbene precursors in reactions with potassium t-butoxide and indene. Dichlorobromomethane (III) gives principally the adduct of dichlorocarbene, and the apparent tendency for bromide ion to be eliminated from the anion of III is at least six times greater than for chloride ion. The thermally unstable adduct obtained from reactions employing dibromochloromethane (IV) was converted in high over-all yield to an approximately equimolar mixture of 2-chloro and 2-bromonaphthalene. Thus, there appears to be far less apparent selectivity of the halogen eliminated from the cyclopropane intermediates, than from the anions of the haloforms. Data obtained from reactions with dichlorofluoromethane (V) furnish direct evidence for the existence of chlorofluorocarbene, and indirect evidence to support the conclusion that the cyclopropane derived from this carbene and indene is more stable than other analogs studied. If carbene intermediates are involved in reactions of the substituted methanes VI–IX, they do not add appreciably to indene.

We have previously described a synthesis of 2-halonaphthalene[1,4] which involves the reaction of indene, or a substituted indene, with chloroform or bromoform and base.

$$CHX_3 + B^- \longrightarrow CX_2 + X^- + HB$$
$$I$$

$$II$$
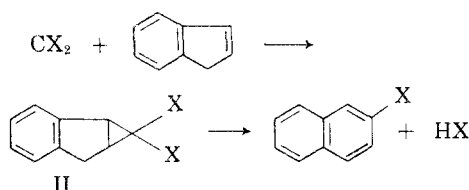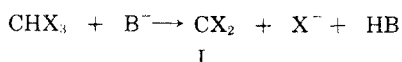
The principal product of this reaction is a dihalocyclopropyl compound (II), which loses hydrogen halide quantitatively, by a unimolecular process in polar solvents, to give 2-halonaphthalene. It is apparent[1,4] that dihalocarbenes (I) are intermediates in these reactions, and the existence of such in-

termediates has been more conclusively established by the work of Hine,[5] Doering,[6] Skell,[7] and their coworkers. The purpose of this study was to evaluate the substituted methanes III–IX as carbene precursors in the reaction of indene, substituted methane, and base.

CHCl$_2$Br	CHClBr$_2$	CHCl$_2$F	CHClF$_2$
III	IV	V	VI

CHCl$_2$CO$_2$C$_2$H$_5$	CHCl$_2$CO$_2$C(CH$_3$)$_3$
VII	VIII

$$p\text{-Br}—C_6H_4\overset{O}{\overset{\|}{C}}—CHBr_2$$
$$IX$$

(1) Preceding paper, W. E. Parham, H. E. Reiff, and P. Swartzentruber, J. Am. Chem. Soc., 78, 1437 (1956).

(2) This work was supported in part by a grant (NSF-G2163) from the National Science Foundation.

(3) Parke, Davis and Co. fellow (1955–56), E. I. du Pont de Nemours fellow (summer 1955).

(4) W. E. Parham and H. E. Reiff, J. Am. Chem. Soc., 77, 1177 (1955).

(5) (a) J. Hine, J. Am. Chem. Soc., 72, 2438 (1950); (b) J. Hine and A. M. Dowell, Jr., J. Am. Chem. Soc., 76, 2688 (1954); (c) J. Hine, P. C. Peek, Jr., and B. D. Oakes, J. Am. Chem. Soc., 76, 6162 (1954); (d) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., J. Am. Chem. Soc., 78, 479 (1956); (e) J. Hine and N. W. Burske, J. Am. Chem. Soc., 78, 3337 (1956).

(6) (a) W. von E. Doering and A. Hoffman, J. Am. Chem. Soc., 76, 6162 (1954); (b) W. von E. Doering and P. LaFlamme, J. Am. Chem. Soc., 78, 5448 (1956).

(7) (a) P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 3409 (1956); (b) P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 5430 (1956); (c) P. S. Skell and R. C. Woodworth, J. Am. Chem. Soc., 78, 4496 (1956).