the growing importance of the triplet reaction as the pressure is lowered.

The present rationalization of methylene reactivity in terms of the two electronic states implies the presence of an inert gas should increase the triplet character of the reaction by increasing the ratio of singlet–triplet transition to singlet–hydrocarbon reaction. This implication is supported by the formation of cis-1,2-dimethylcyclopropane in the photolysis of diazomethane–trans-butene-2 mixtures in the presence of 1–2 atmospheres of nitrogen or argon.[17,21] The formation of radicals,

most reasonably triplet methylene, under somewhat similar conditions was clearly demonstrated by Doering and Prinzbach.[12]

Acknowledgment.—We gratefully acknowledge the experimental assistance of Mr. L. M. Taylor. We are indebted to Dr. H. W. Anderson and Dr. S. H. Levin of this Laboratory and to Prof. E. S. Lewis of Rice University for helpful comments.

(21) Anet, et al. [F. A. L. Anet, R. F. W. Bader and A. M. van der Auwera, J. Am. Chem Soc., **82**, 3217 (1960)], have extended these observations of Frey and concluded from the results that the ground state of methylene is triplet.

Rates and Isomer Distributions in the Chlorination of Benzene, Toluene and t-Butylbenzene in Aqueous Acetic Acid Solvents. The Influence of Solvent on the Reaction and the Baker–Nathan Effect

BY LEON M. STOCK AND ALBERT HIMOE[1]

The rates, relative rates and isomer distributions for the non-catalytic chlorination of benzene, toluene and t-butylbenzene have been obtained in five aqueous acetic acid solvents. The addition of water to acetic acid provided a large rate acceleration in the chlorination of these hydrocarbons. However, the relative rates and partial rate factors, o_f^{Me}, p_f^{Me} and p_f^{t-Bu}, for chlorination are quite insensitive to the variation in absolute rate. The o_f^{t-Bu} value exhibits a major change. The activation parameters determined for two aqueous acetic acid solvents revealed the rate variations were a consequence of changes in the enthalpy of activation. The large increase in the rate is attributed to the modification of the dielectric and increased solvation of the electron-deficient transition state. The ratio $\log p_f^{Me}/\log p_f^{t-Bu}$ obtained for six solvent compositions is 1.11 ± 0.02. Under the conditions of these experiments the absolute rate of chlorination of benzene is altered by a factor of 6.5×10^3. The large influence of solvent on the rate and its negligible influence on relative reactivity suggests the Baker–Nathan effect does not have its origin in solvation phenomena.

Introduction

In recent years considerable effort has been directed toward a fuller understanding of the origin of the Baker–Nathan effect.[2] Many of the early experimental studies and the more recent contributions have been reviewed.[3] In brief, three alternative ideas have been presented to account for the Baker–Nathan sequence. The concept of hyperconjugation was introduced several years ago and has been amplified in recent discussions.[4] Two other recently expressed viewpoints contend that hyperconjugation is not significant, and suggest the predominant mode of electron release from alkyl groups is through an inductive mechanism. These interpretations differ, however, with respect to the factor responsible for the inverted sequence. Schubert and his co-workers have argued for the importance of a differential energy of solvation. According to this view, the steric requirements of the bulky t-butyl group hinder solvation and are responsible for the inversion.[5] Burawoy postulated that the Baker–Nathan sequence resulted from the repulsive energy

attendant to the contraction of an alkyl carbon–aryl carbon bond under the stress of inductive electron demand.[6]

Much chemical evidence suggesting the reality of the effect has been provided through studies of substituted benzenes. Both typical Hammett side-chain reactions and reactions yielding highly electron deficient transition states have been examined. Unfortunately, the Hammett side-chain reactions exhibit only minor differences in reactivity between the alkyl substituted and parent compounds.[7] The electron deficient side-chain reactions have provided the best experimental evidence for the effect.[8] However, these reactions also exhibit small values for the reaction constant. Selective electrophilic substitution reactions, e.g., halogenation or Friedel–Crafts acylation, have large reaction constants, but a detailed study of the influence of solvent has not been attempted. Accordingly, it appeared desirable to weigh the alternative interpretations for the Baker–Nathan order through an experimental investigation of the influence of solvent on a highly selective substitution process.

(1) Research Corporation Fellow, 1959–1961.

(2) For clarity, the Baker–Nathan effect is identified with the experimental observation: Me > t-Bu. Interpretations for this observation are distinguished by other terminology.

(3) See Tetrahedron, **5**, 107 (1959).

(4) R. S. Mulliken, C. A. Rieke and W. G. Brown, J. Am. Chem. Soc., **63**, 41 (1941); R. S. Mulliken, Tetrahedron, **5**, 253 (1959); R. S. Mulliken, ibid., **6**, 68 (1959).

(5) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, ibid., **5**, 194 (1959); W. M. Schubert, J. Robins and J. L. Haun, J. Am. Chem. Soc., **79**, 910 (1957); W. M. Schubert and W. A. Sweeney, J. Org. Chem., **21**, 119 (1956).

(6) A. Burawoy and E. Spinner, J. Chem. Soc., 3752 (1954); 2557 (1955); E. Spinner, ibid., 1590 (1956).

(7) Indeed, the major portion of Baker's monograph is devoted to the discussion of typical Hammett side-chain reactions. Rho, the reaction constant, for these reactions rarely exceeds ±3. See J. W. Baker, "Hyperconjugation," Oxford University Press, 1952.

(8) Solvolytic reactions of benzhydryl- and phenyldimethylcarbinyl chloride are in the order: p-Me > p-t-Bu ≫ H. The inductive order has never been observed for these substituents in solvolytic reactions. For a summary of the available data see E. Berliner, Tetrahedron, **5**, 202 (1959).

For the purpose of this study, it was important to consider several factors in the selection of a reaction. A primary consideration was that the reaction rate exhibit a significant dependence on substituent groups and involve an electron-deficient transition state. It was also desirable to select a reaction with an established mechanism. Finally, it was essential to choose a reaction with a large rate dependence on solvent. Of the several available selective substitution reactions, the non-catalytic chlorination reaction fulfills all these requirements. The partial rate factors for chlorination of the alkyl substituted benzenes in dry acetic acid[9,10] are p-methyl, 817; p-t-butyl, 400; m-t-butyl, 6.0; m-methyl, 4.95; and hydrogen, 1.0. The reaction constant based on these data and the assigned σ^+-constants[11,12] is -10.0. The reaction is clearly selective. The extensive researches of Robertson, de la Mare, Keefer and Andrews and their associates demonstrate that the mechanism of the reaction is not unduly complex.[13] The kinetics are fortunately simple. Reports in the literature suggested the rate of chlorination in acetic acid would be dependent on the concentration of water. Lauer and Oda found a large increase in the rate of bromination of benzene in water over that determined in acetic acid.[14] The accelerating influence of water is evident in both bromination and chlorination in 85% aqueous acid.[15] A recent investigation of the bromination of anisole in these solvents demonstrated the large influence of water.[16]

On the basis of these reports, the chlorination reaction was selected for investigation. The first efforts were directed toward an examination of the influence of mixed solvents of acetic acid and water on the reactivity and relative reactivity of benzene, toluene and t-butylbenzene. The chlorination of these compounds in other pure solvents will be considered in a subsequent article.

Results and Discussion

Kinetic Observations.—Preliminary experiments were undertaken to evaluate the chlorination reaction as a tool for the investigation of solvent effects on the Baker–Nathan effect. As has been observed,[14,16] the addition of water to acetic acid resulted in a large increase in the rate of chlorination. A spurious observation made in the course of these preliminary studies suggested the importance of chloronium ion[17] as an intermediate in the aqueous solvents. Subsequent work revealed this process to be unimportant under the conditions adopted for this study. However, to ensure the elimination of this reaction path all aqueous sol-

(9) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

(10) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5615 (1959).

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

(12) L. M. Stock and H. C. Brown, *ibid.*, **81**, 5623 (1959).

(13) This work has been reviewed: P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, Chapter 9.

(14) K. Lauer and R. Oda, *Ber.*, **69**, 851 (1936).

(15) P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 276 (1943).

(16) L. M. Yeddanapalli and N. S. Gnanapragasam, *J. Indian Chem. Soc.*, **36**, 745 (1959).

(17) P. B. D. de la Mare, J. T. Harvey, M. Hassan and S. Varma, *J. Chem. Soc.*, 2756 (1958).

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE NON-CATALYTIC CHLORINATION OF BENZENE, TOLUENE AND t-BUTYLBENZENE IN AQUEOUS ACETIC ACID SOLVENTS

Compound	Composition of reaction mixture, M				$10^3 k_1$, l. mole^{-1} sec.$^{-1}$	Relative rate
	[H$_2$O]	[HCl]	[ArH]	[Cl$_2$]		
Solvent A at 25°						
Benzene	4.13	1.15	0.250	0.0170	0.0141	1.0
			.250	.0361	0.0142	
Toluene			.235	.0244	3.81	280
			.235	.0136	3.81	
t-Butylbenzene			.179	.0188	1.30	92.5
Solvent B at 35°						
Benzene	4.10	1.11	0.282	0.0188	0.0302	1.0
			.282	.0184	0.0306	
Toluene			.235	.0161	7.40	244
			.220	.0141	7.40	
t-Butylbenzene			.161	.0264	2.05	67
			.161	.0260	2.05	
Solvent B at 25°						
Benzene	4.10	1.11	0.282	0.0202	0.0142	1.0
			.282	.0206	0.0143	
Toluene			.229	.0108	4.10	292
			.222	.0244	4.18	
t-Butylbenzene			.159	.0148	1.07	77.5
			.159	.0148	1.12	
Solvent B at 10°						
Benzene	4.10	1.11	0.282	0.0330	0.00354	1.0
			.282	.0333	0.00337	
Toluene			.230	.0330	1.41	410
			.230	.0322	1.36	
t-Butylbenzene			.160	.0242	0.310	98
			.160	.0228	0.350	
Solvent C at 25°						
Benzene	9.78	1.19	0.250	0.0355	0.0624	1.0
			.250	.0304	0.0603	
Toluene			.0184	.00949	19.0	314
			.0178	.00879	19.6	
t-Butylbenzene			.0202	.0117	5.32	90.5
			.0203	.0132	5.75	
Solvent D at 25°						
Benzene	15.3	1.19	0.250	0.0280	0.184	1.0
			.250	.0267	0.170	
Toluene			.0219	.00880	55.3	318
			.0215	.00842	60.5	
t-Butylbenzene			.0193	.00726	16.6	91.0
			.0200	.00702	15.6	
Solvent E at 25°						
Benzene	20.8	1.19	0.205	0.0254	0.465	1.0
			.205	.0231	0.440	
Toluene			.00545	.00497	145	320
t-Butylbenzene			.00410	.00410	47.2	101
			.00458	.00377	44.5	
Solvent F at 25°						
Benzene	27.6	1.18	0.0563	0.00365	1.02	1.0
			.110	.0108	0.96	
Toluene			.00396	.00214	270	270
			.00627	.00391	270	
t-Butylbenzene			.00894	.00406	100	95
			.00833	.00353	90.9	
Solvent F at 0°						
Benzene	27.6	1.18	0.113	0.00824	0.141	1.0
			.113	.00775	0.111	
Toluene			.00627	.00443	59.0	490
			.00627	.00400	64.0	
t-Butylbenzene			.00826	.00505	18.0	134
			.00730	.00392	15.6	

vents were prepared with molar concentrations of hydrogen chloride.

Five water–acetic acid solvents were selected for kinetic investigation. The concentration of water was limited by the solubility of the aromatics and the very rapid reaction rates obtained. From the results, it is apparent that further increases in the water concentration will have considerably less influence on the rate. The kinetic data for the

chlorination of benzene, toluene and t-butylbenzene were obtained by conventional iodometric procedures.[9,15] In most experiments, the reaction was followed to 70–85% completion. As in other studies of the chlorination reaction,[13] the results obeyed second-order kinetics over the full extent of reaction. The second-order behavior was further examined in the more aqueous solvents in reactions with aromatic to chlorine ratios of near unity. To test the reproducibility of the preparation of solvent and the measurements, a new batch of one solvent was prepared and the measurements repeated, solvents A and B. The second-order rate constants, concentrations employed and relative rates determined are summarized in Table I.

The test of the procedure and methods was provided by a reinvestigation of the solvent approximately 4.1 M in water (solvents A and B in Table I). The agreement in the second-order rate constants for benzene in the two independently prepared solvents is probably fortuitous. In the authors' view the 8% error observed for the alkylbenzenes in these solvents is a more reliable measure of the reproducibility of the preparation of the solvent and kinetic measurements. The results obtained in kinetic experiments in the more aqueous solvents are less precise. Two factors contribute to this situation. For each hydrocarbon in each solvent, the experiments were carried out at random employing different solutions of chlorine and in some cases aromatic. Thus, although the precision appears low in certain instances, the accuracy of the measurements is probably good. Further difficulties were encountered in the more aqueous solvents because of the large reaction velocities. Accordingly, the relative rates derived from kinetic measurements have an experimental uncertainty of about 10%.

The chlorination reaction is greatly accelerated in the aqueous media. The absolute rate of reaction of benzene with chlorine in solvent F at 25° is 6.5×10^8 more rapid than the reaction in dry acetic acid; Table I. Among the solvents examined in this study, the largest single change, a factor of 92, occurs upon the introduction of water to provide a solution 4.1 M in that component.[18] Another factor of 70 is introduced upon variation of the water concentration from 4.1 to 27.6 M. Inspection of the results indicates that increasing the water content alters the rate by progressively smaller increments in the highly aqueous solvents.

It seemed important to establish the rate enhancement was not the result of a change in the electrophilic reagent in the more aqueous media. Adopting the viewpoint that the only important chlorination paths are through chlorine molecule and more positive halogen species, e.g., chloronium ion,[17] the problem was approached through a consideration of the influence of added chloride ion, acid and base.[19] For convenience, the study of the influence of electrolytes on the reaction rate was carried out in solvent D containing 15.3 M

(18) This observation confirms the view, often expressed, that different values for the rate of halogenation in acetic acid are the consequence of small variations in water content.

(19) P. W. Robertson, J. Chem. Soc., 1267 (1954).

TABLE II

EXPERIMENTS RELATING TO THE INFLUENCE OF ADDED ELECTROLYTES ON THE CHLORINATION OF BENZENE IN ACETIC ACID CONTAINING 15.3 M WATER AT 25°

| Added electrolyte | Molar concentration | | | $10^4 k_2$, |
	[MX]	[C$_6$H$_6$]	[Cl$_2$]	1. mole^{-1} sec.$^{-1}$
HCl	0.000	0.264	0.0213	10.3
	.056	.264	.0253	11.1
	.056	.264	.0234	11.4
	.112	.264	.0120	12.3
	.112	.264	.0356	12.4
	.420	.264	.0387	15.1
	1.19	.250	.0280	18.4
	1.19	.250	.0267	17.0
NaCl	0.100	.264	.0332	11.9
NaOAc	0.100	.264	.0216	10.8

water. The kinetic observations are summarized in Table II.

In addition to simple kinetic behavior, Robertson utilized the contrasting influences of electrolytes on the reactions of molecular chlorine and positive halogens to examine the nature of the electrophilic reagent.[19] Based on the small positive catalytic influence of added electrolytes, Robertson concluded molecular chlorine and bromine served as the reagents in acetic acid. Similar experiments, Table II, revealed hydrogen chloride, sodium chloride and sodium acetate exhibited only minor influences on the rate in aqueous acid. Molar quantities of hydrogen chloride provided only a twofold increase in rate. A study of several concentrations of the acid failed to reveal any type of simple kinetic dependence.[20] Moreover, equivalent amounts of hydrogen chloride or sodium chloride have almost identical catalytic influence. Sodium acetate also exhibits an accelerating effect. These facts cannot be reconciled with a mechanism involving positive halogen carriers.

Other evidence indicating the reagent to be unchanged is provided by the constancy of the relative rates, Table I, and the minor variation in the product distributions, Table IV. Finally, the partial rate factors for chlorination, Table V, are in sharp contrast with the results obtained for the acid-catalyzed reaction of hypochlorous acid with toluene,[17] o_f^{Me} 134, m_f^{Me} 4.0, p_f^{Me} 82. Clearly, the electrophilic reagent is little altered in glacial and aqueous acetic acid and presumably is the chlorine molecule.

In other studies of the relative rates of substitution of aromatics, it has occasionally been found that kinetic and competitive procedures provided significantly different values for the relative rates. For example, in the deuterium exchange reactions of toluene and t-butylbenzene in trifluoroacetic acid, the small difference in relative rate determined kinetically was not substantiated in competitive measurements.[21] To test this possibility, toluene and t-butylbenzene were allowed to react competitively with insufficient chlorine. The results for two experiments carried out in solvent A containing 4.13 M water and analyzed by vapor phase chromatography are summarized in Table III.

(20) Similar behavior has been found in the reaction of mesitylene and bromine in acetic acid with hydrogen bromide; ref. 19.

(21) W. M. Lauer, G. M. Matson and G. Stedman, J. Am. Chem. Soc., 80, 6433, 6437 (1958).

TABLE III

COMPETITIVE DETERMINATION OF THE RELATIVE RATE OF CHLORINATION OF TOLUENE AND t-BUTYLBENZENE IN ACETIC ACID WITH 4.13 M H$_2$O AND 1.15 M HCl AT 25°[a]

Compound	Concentration, M Initial	Final[b]	Relative rate[c] $k_{Tol}/k_{t\text{-}BuBz}$
Toluene	0.200	0.108	3.14
t-Butylbenzene	.200	.164	
Chlorine	.128	.000	
Toluene	.200	.106	3.33
t-Butylbenzene	.200	.166	
Chlorine	.128	.000	
Kinetic value[a]			3.02

[a] Solvent A in Table I. [b] Final composition determined by analysis of chloro compounds through vapor phase chromatography. [c] Calculated from the expression derived by C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

The comparison provided by the results summarized in Table III indicates that the kinetic procedure provides a reliable estimate of the relative rates of chlorination. Accordingly, within the limits of error associated with the kinetic procedures, the results may be discussed with some confidence.

Isomer Distributions.—In order to evaluate the positional rates of substitution in toluene and t-butylbenzene, the products of reactions carried out under kinetic conditions were analyzed by vapor phase chromatography or infrared spectroscopy. Each method was examined for reproducibility and accuracy by the analysis of known mixtures prepared from pure compounds demonstrated to be free (99 ± 1%) of isomeric impurities by vapor phase analysis. The experimental procedures and results for representative analytical tests are summarized in the Experimental Part.

Under the conditions employed side-chain substitution was unimportant. The careful inspection of several chromatograms for benzyl alcohol resulting from the hydrolysis of benzyl chloride in the reaction and workup revealed only trace concentrations (less than 2%). The products of the chlorination reaction were also shown to be free of dichloroalkylbenzenes by the chromatographic method. In this investigation, no attempt was made to establish the % *meta* substitution. Previous work had shown m-chlorotoluene was produced in 0.5% yield[9] while m-chloro-t-butylbenzene had been obtained as 2.3% of the chlorination products.[10] In the toluene case, the extent of *meta* substitution is smaller than the uncertainty in the predominant isomers. On this basis, the minor product was ignored. However, for t-butylbenzene, the m-isomer was evident in the vapor phase chromatograms and in the infrared spectra of the products. Some determinations of the concentration of this product are summarized in the Experimental Part. The observations indicated the degree of m-substitution to be small and showed little variation in the aqueous solvents from that obtained in dry acid. Rather than undertake the extensive experimental work required to establish the concentration, it was selected to adopt the previous value of 2.3% m- and to normalize the o- to p-chloro-t-butylbenzene ratio

on this basis. The results are summarized in Table IV.

The product distributions for the halogenation reaction, Table IV, were obtained under conditions similar to those employed in the kinetic investigation. The experimental limits of uncertainty are presented in that table. Based on the excellent agreement obtained in the analysis of known mixtures and the reliability of the methods, the small variation in the isomer distribution between anhydrous and highly aqueous acetic acid solvents is believed to be real. For each hydrocarbon the increase in water content of the reaction media leads to increased substitution in the o-position. With toluene this effect is rather small; in the case of t-butylbenzene it is readily measurable. This result is in accord with the fact that the chlorination of toluene in water with 5 M hydrochloric acid under heterogeneous conditions leads to 69% o-chlorotoluene just slightly greater than the amount obtained in 27.6 M water in acetic acid.[22]

Partial Rate Factors.—The positional relative rate data evaluated from the kinetic results and the isomer distributions are summarized in Table V.

The partial rate factors, Table V, are derived from the kinetic observations reported in Table I and the normalized product distributions summarized in Table IV. In view of the experimental uncertainties discussed in the preceding paragraphs some caution must be exercised in the assignment of differences to real causes. The small decrease in the partial rate factors in aqueous acetic acid from those observed for chlorination in anhydrous acid is presumably beyond the limit of experimental doubt. However, the variations in o_f^{Me}, p_f^{Me} and $p_f^{t\text{-}Bu}$ are not significantly different. The small change for % o-chlorotoluene among these solvents is not sufficiently large to be reflected in the value for o_f^{Me}. The much larger variation in % o-chloro-t-butylbenzene is readily apparent in $o_f^{t\text{-}Bu}$.

Activation Parameters.—The consequences of variation in solvation and other factors influencing additivity relationships and relative reactivity have been recently discussed.[23,24] In view of these discussions and general interest in the role of entropy in electrophilic substitution reactions,[25,26] data were obtained for the evaluation of the activation parameters for the non-catalytic chlorination. Solvents designated as B and F, the least and most aqueous media investigated, were adopted for the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the chlorination of benzene, toluene and t-butylbenzene. The activation parameters were derived from the thermal dependence of rate and product distribution as summarized in Tables I and IV. The results are presented in Table VI together with earlier results for chlorination in dry acid.

The uncertainty in the reaction velocity in the more aqueous media introduces an experimental

(22) L. M. Stock and A. Himoe, *Tetrahedron Letters*, No. 13, p. 9 (1960).

(23) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959).

(24) K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1725 (1959).

(25) W. J. LeNoble and G. W. Wheland, *J. Am. Chem. Soc.*, **80**, 5397 (1958).

(26) H. C. Brown and M. Dubeck, *ibid.*, **81**, 5608 (1959).

TABLE IV

ISOMER DISTRIBUTIONS IN THE NON-CATALYTIC CHLORINATION OF TOLUENE AND *t*-BUTYLBENZENE IN AQUEOUS ACETIC ACID AT 25°

Compound	Chloroalkylbenzenes, %			Number[a]	
	ortho-	meta-	para-	Expts.	Anal.
Dry acetic acid at 25°					
Toluene[b]	59.8 ± 0.4	0.5 ± 0.05	39.7 ± 0.4	5	8
t-Butylbenzene[b]	21.5 ± 1.8	2.3 ± 0.2	76.2 ± 1.3	3	4
Solvent B[c] at 35°					
Toluene[d]	63.7 ± 2.0		36.3 ± 2.0	2	3
t-Butylbenzene[e]	28.6 ± 0.6		69.1 ± 0.6	2	4
Solvent B[c] at 25°					
Toluene[d]	62.0 ± 2.0		38.0 ± 2.0	3	6
t-Butylbenzene[e]	28.4 ± 0.6		69.3 ± 0.6	2	4
Solvent B[c] at 10°					
Toluene[d]	61.2 ± 2.0		38.8 ± 2.0	2	2
t-Butylbenzene[e]	26.6 ± 1.1		71.2 ± 1.1	2	4
Solvent C[c] at 25°					
Toluene[d]	60.5 ± 1.2		39.5 ± 1.2	1	4
t-Butylbenzene[d]	30.6 ± 1.2		67.1 ± 1.2	2	4
Solvent D[c] at 25°					
Toluene[d]	61.0 ± 0.4		39.0 ± 0.4	1	3
t-Butylbenzene[d]	30.8 ± 2.3		67.0 ± 2.3	2	4
Solvent E[c] at 25°					
Toluene[d]	63.3 ± 0.6		36.7 ± 0.6	1	2
t-Butylbenzene[d]	33.0 ± 1.1		64.7 ± 1.1	3	6
Solvent F[c] at 25°					
Toluene[d]	65.9 ± 1.0		34.1 ± 1.0	2	4
t-Butylbenzene[e]	37.9 ± 1.2		59.8 ± 1.2	2	4
Solvent F[c] at 0°					
Toluene[d]	66.0 ± 0.3		34.0 ± 0.3	2	4
t-Butylbenzene[e]	35.5 ± 2.3		62.1 ± 2.3	2	4

[a] Number of independent experiments and total number of analyses. [b] Results for dry acetic acid taken from refs. 9 and 10. [c] See Table I for composition of the solvent. [d] Analysis based on vapor phase chromatography. [e] Analyses based on infrared spectroscopy.

TABLE V

PARTIAL RATE FACTORS FOR THE NON-CATALYTIC CHLORINATION OF TOLUENE AND *t*-BUTYLBENZENE IN ACETIC ACID SOLVENTS

Solvent[a]	Partial rate factors[b]			
	Toluene		*t*-Butylbenzene	
	o_f^{Me}	p_f^{Me}	o_f^{t-Bu}	p_f^{t-Bu}
At 25°				
Acetic acid	617	820	56.6	401
Solvent A	521	638	78.8	385
B	543	666	66.0	322
C	570	744	83.1	364
D	582	744	84	366
E	608	705	100	392
F	534	552	108	341
At 35°				
Solvent B	448	531	57.5	278
At 10°				
Solvent B	753	954	78.2	419
At 0°				
Solvent F	970	1000	169	499

[a] See Table I for the composition of each solvent. [b] The rate in a selected position of the alkylbenzene compared to a single position in benzene.

error of approximately 10% in $\Delta S^{\ddagger}$. The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the less aqueous media (solvent B) are on a firm basis as demonstrated by the excellent linear relationships utilized for the determination of these parameters.

The activation parameters have been measured for the chlorination reaction in dry acetic acid in several laboratories. Unfortunately, the results are not in good agreement. In an early investigation, de la Mare and Robertson[15] examined the chlorination of benzene in 99% acetic acid and obtained activation parameters of 17 kcal. and −30 cal. deg.$^{-1}$. Mason has recently reported $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for benzene and biphenyl.[27] In particular, the $\Delta S^{\ddagger}$ values for these hydrocarbons were −23.4 and −24.6 cal. deg.$^{-1}$, respectively. Andrews and Keefer have examined the chlorination of toluene and *m*-xylene.[28] The activation entropies found were −30.4 and −30.6 cal. deg.$^{-1}$. In each investigation the $\Delta S^{\ddagger}$ values have been determined to be constant within the experimental uncertainty for the aromatics under examination. On the other hand, a discrepancy, approximately six entropy units, exists between the results of the two studies.[29] Values obtained in the current work for the reactions in aqueous acetic acid are very nearly the same as found in toluene in dry acetic acid by Andrews and Keefer.[28] The activation parameters, Table VI, indicate the increase

(27) S. F. Mason, *J. Chem. Soc.*, 1233 (1959).

(28) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 1063 (1959).

(29) A possible source for the discrepancy is the different procedures employed; Andrews and Keefer[28] examined the reaction at 25 and 45°; Mason[27] investigated the reaction at 15, 20, 25 and 30°.

TABLE VI

ACTIVATION PARAMETERS FOR NON-CATALYTIC CHLORINA-
TION OF AROMATICS IN ACETIC ACID SOLVENTS

Compound	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, cal. deg.$^{-1}$	Reference
For reacn. in dry acetic acid			
Benzene[a,b]	17	−30	15
Benzene[a,c]	19.6	−23.4	27
o-Methyl[a,d]	13	−30	28
p-Methyl[d]	13	−31.6	28

For reacn. in acetic acid with 4.11 M H$_2$O and 1.11 M HCl, solv. B

Benzene[a]	14.7	−30.3	
o-Methyl[a]	11.4	−29.0	
p-Methyl	10.6	−30.9	
o-t-Butyl[a]	12.7	−28.7	
p-t-Butyl	12.0	−27.6	

For reacn. in acetic acid with 27.6 M H$_2$O and 1.18 M HCl, solv. F

Benzene[a]	13.0	−27.6	
o-Methyl[a]	8.9	−29.0	
p-Methyl	8.8	−29.0	
o-t-Butyl[a]	10.5	−27.7	
p-t-Butyl	10.3	−25.3	

[a] The value for $\Delta S^{\ddagger}$ is based on rate data statistically corrected for a single equivalent position. [b] Measurements in 99% acetic acid at two temperatures. [c] Four kinetic observations over 15° temperature range. [d] Positional values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ based on a temperature independent isomer ratio of 60% o- and 40% p-; rate measurements were made at 25° and 45°.

in the rate of chlorination from solvent B to solvent F, a factor of 70, is the consequence of a variation in $\Delta H^{\ddagger}$. The entropy factor remains constant within the limits of experimental error for these solvents. Because of the differences in the $\Delta S^{\ddagger}$ values obtained for dry acid,[15,27,28] it is not possible to assign the rate increase observed for aqueous media exclusively to the enthalpy.

Role of the Solvent.—This investigation was conceived as an examination of solvent influences on the Baker–Nathan effect through a study of the highly selective chlorination reaction. It was hoped that the experimental observations of rates, relative rates and product distributions could provide decisive information concerning the solvent as a factor modifying the degree and character of electron release from alkyl groups. Prior to a discussion of this question, it is appropriate to consider the other consequences of the solvent effects.

In summary, the principal findings of this investigation have been: (1) the rate of chlorination of aromatics is greatly accelerated in aqueous acetic acid in contrast to the rate in dry acid; (2) the activation parameters indicate the change in absolute rate is reflected in $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ is constant among the different solvents and different positions substituted; (3) the rate of chlorination of toluene or t-butylbenzene relative to benzene is only moderately affected by the change in absolute rate; (4) the partial rate factors are slightly smaller for reaction in aqueous media than in dry acid; (5) among the aqueous solvents o_f^{Me}, p_f^{Me} and $p_f^{t\text{-Bu}}$ are essentially constant; (6) surprisingly, a pronounced variation in relative rate is observed for o-substitution in t-butylbenzene increasing as the absolute rate increases.

The solvent effect manifest in the increase in reaction velocity in the aqueous media has frequently been observed.[30] Thus, the rate of chlorination of benzene exhibits a good correlation with $\Delta H^{\ddagger}$ or $\Delta F^{\ddagger}$ for the solvolysis of t-butyl chloride in acetic acid–water mixtures[31] over the range of composition studied. The influence of water may be attributed in part to a large modification in the dielectric properties of the solvent. An influence of this nature is apparent in the conductance of solutions of sodium perchlorate in aqueous acetic acid solvents as contrasted with dry acid.[32,33] This interpretation is possibly satisfactory for aqueous acetic acid; however, it will not be sufficient to account for solvent effects on the rate of chlorination in general. For example, the chlorination of aromatics in trifluoroacetic acid is very rapid[34] (comparable to the reaction rate in solvent F). Trifluoroacetic acid has a moderate dielectric constant,[35,36] 8.5, and is not a good solvent for salts.[37] Solvolytic reactions in this medium are very rapid.[38] At present, the dependence of the reaction velocity on the nature of the solvent is not satisfactorily defined for the chlorination reaction. Clearly, the influence of the medium is large and is perhaps best described as related to the ionizing power[39] of the solvent.

The solvation enhancement of the reaction is reflected in $\Delta H^{\ddagger}$ for the reaction in aqueous solvents. As had been found in other studies of activation parameters for electrophilic substitution,[25,26] the entropy of activation was observed to be invariant among the available positions; Table VI. Further, the differences in $T\Delta S^{\ddagger}$ among the two aqueous solvents are negligibly small compared to $\Delta H^{\ddagger}$. Accordingly, the substituent and solvent effects found for the chlorination reaction in aqueous acetic acid solvents are reflected exclusively in $\Delta H^{\ddagger}$.[40] Certain previous observations, Table VI, suggest the enthalpy of activation is also the dominant factor in the change in rate in dry and aqueous media.

(30) The rate changes are identified with a solvent effect rather than with a change in mechanism on the basis of the experiments designed to test the importance of positive halogen carriers as discussed above.

(31) S. Winstein and A. H. Fainberg, J. Am. Chem. Soc., 79, 5937 (1957).

(32) K. B. Wiberg and R. J. Evans, ibid., 80, 3019 (1958).

(33) I. M. Kolthoff and A. Williams, ibid., 56, 1007 (1934).

(34) L. J. Andrews and R. M. Keefer, ibid., 79, 1412, 5169 (1957).

(35) W. Dannhauser and R. H. Cole, ibid., 74, 6105 (1952).

(36) F. E. Harris and C. T. O'Konski, ibid., 76, 4317 (1954).

(37) G. S. Fujioka and G. H. Cady, ibid., 79, 2451 (1957).

(38) P. E. Peterson, Abstracts 137th Meeting American Chemical Society, Cleveland, Ohio, April, 1960, p. 49-O.

(39) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

(40) Laidler, ref. 24, has recently presented a theory for the assignment of the origin of polar, steric and solvent effects to ΔH_0, ΔS_0 and ΔC_p. Steric factors are predicted to modify all three thermodynamic functions. With reference to aromatic substitution, this view argues for random variation in $T\Delta S^{\ddagger}$ for steric effects operative at the o-position in contrast to the unhindered m- and p-sites. The study of nitration,[25] mercuration[26] and chlorination of several aromatics, however, has demonstrated that the value for $\Delta S^{\ddagger}$ among the available positions is constant within experimental error. It does not seem satisfactory to ascribe this behavior to a fortuitous cancellation of the factors determining $\Delta S^{\ddagger}$, i.e., $\Delta S_0^{\ddagger}$ and $\Delta C_p^{\ddagger}$, in the three different reations. Curiously, the steric factor operative in the o-position is reflected exclusively in $\Delta H^{\ddagger}$.

The partial rate factors, summarized in Table V, are not subject to major changes over an extended range of total reaction rate. Variation in relative reactivity are observed, but contrasted with the large increase in absolute rate the changes are minor. Such behavior has customarily been interpreted as evidence for common or very similar electrophilic reagents.[41] The chlorination reaction exhibits behavior characteristic of the same phenomenon. At this time, the effective electrophilic reagent is best described as a chlorine molecule whose electrophilic properties are slightly modified by interaction with acetic acid or water,[42] while the small decrease in the value for the partial rate factors o_f^{Me}, p_f^{Me} and p_f^{t-Bu} in aqueous media is most reasonably attributed to a slightly greater electrophilic reactivity of the chlorine–water species as contrasted to the chlorine–acetic acid reagent.[43]

Solvent Interaction and Baker–Nathan Effect.— As discussed in the preceding sections, evidence has been presented to indicate that increased solvation of the electron-deficient transition state provides for an enhanced rate of chlorination in aqueous solvents. Under the diverse conditions of these experiments, the partial rate factors are essentially unaltered. The relative rate data are summarized in Table VII.

TABLE VII

RATE RATIOS FOR CHLORINATION OF AROMATICS IN ACETIC ACID SOLVENTS AT 25°

Solvent[a]	Relative rate for benzene[b]	$\dfrac{k_{p-Me}}{k_{p-t-Bu}}$	$\dfrac{k_{o-Me}}{k_{o-t-Bu}}$	$\dfrac{\log p_f^{Me}}{\log p_f^{t-Bu}}$
Dry acid	1.00	2.0	10.9	1.12
Solvent B	93	2.1	8.3	1.13
C	398	2.0	6.9	1.12
D	1150	2.0	6.9	1.12
E	2940	1.8	6.1	1.10
F	6430	1.6	4.9	1.08

[a] See Table I for composition. [b] Relative rate for benzene in dry acetic acid, ref. 9, adopted as 1.00.

The results, Table VII, demonstrate k_{p-Me}/k_{p-t-Bu} is little altered in these systems. Although the experimental uncertainty in the results for reaction in the most aqueous solvent is not minor, the decrease in the ratio for this solvent appears to be significant. As presented above, the halogenation reagent is less selective in the more aqueous media, and two species are important. In this situation, it is necessary to treat the results on a more formal basis. A linear free energy relationship for substitution in the p-position of each hydrocarbon yields the relation[12]

$$\frac{\log p_f^{Me}}{\log p_f^{t-Bu}} = \frac{\sigma^+_{p-Me}}{\sigma^+_{p-t-Bu}} = \text{constant}$$

Values for the logarithmic ratio are summarized in the table. No significant differences are observed. Accordingly, in a reaction subject to large change in rate because of variation in the

(41) Examples are the nitration reaction (E. D. Hughes, C. K. Ingold and R. I. Reed, *J. Chem. Soc.*, 2400 (1950)), and the acetylation reaction (F. R. Jensen and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 3039 (1958)).

(42) L. M. Stock and A. Himoe, Abstracts 138th A.C.S. Meeting, New York, September, 1960, p. 1-P.

(43) This problem is under investigation in this Laboratory.

degree of solvation, the electronic properties of p-methyl and p-t-butyl groups are not altered. Although these results are not decisive, the failure to detect a major variation in relative reactivity of the p-alkyl group suggests the Baker–Nathan effect does not have its origin in solvation phenomena.

In contrast, the ratio o_f^{Me}/o_f^{t-Bu} is subject to variation well beyond the limits of experimental error. The quantity $\log o_f^{Me}/\log o_f^{t-Bu}$ alters by 25% in the extreme solvents reflecting the greater ease of substitution *ortho* to a t-butyl group in the more aqueous media. The degree of o-substitution in toluene is also slightly enhanced in the aqueous solvents. The greater sensitivity of the o-t-butyl group is indicative of a steric effect. Although the origin of this steric effect is obscure, it is most reasonably attributed to the reduced steric requirements of the water-associated chlorine reagent in contrast to the electrophile present in acetic acid.[22]

Experimental Part

Materials.—Commercial benzene (thiophene free) and toluene (J. T. Baker analytical grade) were fractionated and dried. t-Butylbenzene (Phillips research grade) was dried but not otherwise treated. The chlorotoluenes (Eastman Kodak Co.) were fractionated and dried. p-Chloro-t-butylbenzene was prepared by the method of Lerer and Fabre[44] and was recrystallized from acetone; m.p. 24°. The o- and m-isomers were available from an earlier study.[10] The principal criteria of purity adopted for the aromatic hydrocarbons was kinetic behavior during early portions of the reaction. The absence of a rapid decrease in the halogen concentration indicated freedom from reactive impurities. The purity of the aryl chlorides was established by vapor phase chromatography. The chromatograms indicated that all compounds were at least 99% pure. Hydrogen chloride and chlorine (Matheson) were employed without further purification. In some cases the solvent was prepared from aqueous concentrated hydrochloric acid (Baker and Adamson). The concentrations of hydrochloric acid were established by the Volhard procedure. The solvent mixtures employed for kinetic measurements were examined for the rate of halogen consumption. A typical series of observations for the disappearance of chlorine is presented in Table VIII.

TABLE VIII

DATA FOR THE DISAPPEARANCE OF CHLORINE FROM SOLVENT ACETIC ACID CONTAINING 9.78 M WATER AND 1.19 M HYDROGEN CHLORIDE AT 25°

Time, sec.	Chlorine concn., M
0	0.0284
4800	.0281
7500	.0281
90,300	.0262

Kinetic Experiments.—The procedures utilized for the determination of second-order rate constants were similar to those employed in earlier studies.[9,10] The presence of high acid concentrations in the reaction solvent required a dilute (3%) potassium iodide quench solution and prompt titration. Several check experiments employing V.P.C. indicated the formation of benzyl chloride (as benzyl alcohol) was very small and that disubstitution did not occur under the conditions of the experiment. Data for a typical run are presented in Table IX.

Competitive Determination of the Relative Rate.— Toluene, 9.222 g., and t-butylbenzene, 13.431 g., were dissolved in 250 ml. of acetic acid containing 4.13 M water and 1.18 M hydrogen chloride in acetic acid. Another solution 0.256 M in chlorine was prepared. Equal volumes were mixed and the reaction allowed to proceed to completion.

(44) M. Lerer and C. Fabre, *Bull. soc. chim.*, [5] 198 (1956).

TABLE IX

KINETIC OBSERVATIONS FOR THE CHLORINATION OF TOLU-
ENE IN ACETIC ACID CONTAINING 9.78 M WATER AND 1.19 M
HYDROGEN CHLORIDE AT 25°

t, sec.	[Cl$_2$]	[Toluene]	$10^4 k_2$, 1. mole^{-1} sec.$^{-1}$
0	0.00879	0.0178	
70	.00707	.0160	185
125	.00592	.0149	196
190	.00496	.0139	194
260	.00399	.0129	204
358	.00319	.0121	198
441	.00259	.0116	200

The vapor phase chromatogram indicated a clean reaction in each of two experiments. It was established that a relationship existed between the observed areas for the chlorotoluenes and chloro-t-butylbenzenes and the true relative mole concentrations. On the basis of the absence of side-products, the relative rate was calculated on an assumed 100% yield. The formula of Ingold and Shaw was employed.[45] The results are summarized in Table III.

Isomer Distributions.—The product ratios were determined by vapor phase chromatographic analyses or infrared spectroscopy of reaction mixtures carried out under kinetic conditions. The aromatic to chlorine ratio was maintained large through all experiments in order to prevent disubstitution. In a typical experiment, solutions of the aromatic (0.5 M) and chlorine (0.1 M) were mixed and the reaction allowed to proceed to completion. The concentrations of aromatic and halogen varied greatly depending on the solubility in the reaction solvent.

The solution was then transferred to a separatory funnel, water added and the organic materials extracted into carbon tetrachloride. The extraction was repeated several times. All extracts were combined and dried over calcium sulfate. The excess solvent was then removed by careful fractionation. In a few cases, the aqueous phase was again extracted and the carbon tetrachloride extract examined for products. None were detected by V.P.C. The latter fractions of the distillation were also found to be free of products. The solution remaining in the distillation flask was then examined for the product distribution by V.P.C. Analyses were carried out with a Hallikainen chromatograph, Shell Development Design, equipped with a 24' × ¹/₄'' copper column packed with 25% tricresyl phosphate on firebrick. The column was operated at 120° with an inlet pressure of 20 p.s.i. and a flow of 80 ml. He min.$^{-1}$. Under these conditions, the retention times for o- and p-chlorotoluene were 67 and 72 min., respectively. A complete resolution was achieved. The analysis of known mixtures indicated a small correction was necessary to relate the mechanically integrated area to the mole fraction of the isomeric chlorotoluenes. Products from competitive reactions were examined under the same conditions. The retention times for t-butylbenzene, m-, o- and p-chloro-t-butylbenzene were 60, 185, 205 and 225 min., respectively. The peaks for the chloro-t-butylbenzenes were broad and not satisfactory for the evaluation of the isomer distribution. The analyses for the isomer distribution in t-butylbenzene were more conveniently performed at 155° with a flow of 100 ml. He

(45) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

min.$^{-1}$ on the same column.[46] The retention times observed under these conditions were 93, 103 and 112 min. for the m-, o- and p-isomers. In this case a correction was necessary to relate the integrated area to the true composition. The resolution of the m-isomer from the o- and p-products was complete. However, in order to achieve a good resolution of the major products it was necessary to employ a small sample. Accordingly, a rather large error was introduced into the area evaluated for the m-isomer. In a series of experiments the area % *meta* determined was 4.0, 1.3, 2.3, 3.0, 2.9, 1.3, 2.9, 2.9, 2.2, 2.0 and 3.0 for samples obtained in solvents B, C, D and E, Table I. The values obtained are within experimental error of the more reliable spectroscopic result,[10] 2.3%. This value was adopted for all solvents and the isomer distribution obtained by normalization of the observed *ortho/para* ratio. The results are summarized in Table IV.

The chromatograms were examined for the products anticipated for chloro-de-t-butylation, side-chain attack and disubstitution. It is possible that chlorobenzene was present in the reaction products since a very small area appeared at a retention time compatible with that for chlorobenzene. The amount was so small, however, that analysis was not possible. Side-chain attack also was small (1.2%) and disubstitution products were absent.

The duration of the V.P.C. analysis for the chloro-t-butylbenzenes led to a deterioration of the column packing over the course of these experiments. Accordingly, it proved more convenient and more accurate to adopt V.P.C. for the rapid separation of the chlorohydrocarbons from the concentrated reaction mixture and infrared analysis of the trapped products as the analytical method. The experimental techniques provided equivalent results. The experimental results for known mixtures are summarized in Table X.

TABLE X

ANALYSIS OF KNOWN MIXTURES OF o- AND p-CHLORO-t-BUTYLBENZENES BY VAPOR PHASE CHROMATOGRAPHY AND INFRARED SPECTROSCOPY

Known		Found by V.P.C.[a]		Found by infrared	
o-	p-	o-	p-	o-	p-
19.0	81.0	18.5	81.5	19.5	80.5
19.0	81.0	19.1	80.9	19.3	80.7
25.3	74.7	26.1	73.9	24.3	75.7
25.3	74.7	24.6	75.4		
31.2	68.8	30.0	70.0	31.0	69.0
31.2	68.8	32.3	67.8	31.6	68.4

[a] Corrected to value reported on basis of relationship between observed arch and mole %.

(46) The effective lifetime of the TCP column was reduced by operation at the higher temperature and its replacement was necessary after a month of continual operation. Moreover, the exact duplication of the column packing proved to be extremely difficult and considerable variation in the effectiveness was observed with columns presumably prepared and operated in an identical fashion.