Rates and Relative Rates of Chlorination of Benzene, Toluene, and *t*-Butylbenzene in Carboxylic Acid Solvents. The Influence of Solvent on the Baker–Nathan Effect[1]

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Abstract: Rates, relative rates, and isomer distributions are reported for the noncatalytic chlorination of benzene, toluene, and *t*-butylbenzene in carboxylic acid solvents. The reaction solvent influences both the absolute and relative rates for chlorination. The rate ratio, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$, is 2.8 in pivalic acid, 1.8 in propionic acid, 2.0 in acetic acid, 1.1 in formic acid, and 0.69 in trifluoroacetic acid; $k_{m\text{-Me}}/k_{m\text{-}t\text{-Bu}}$ is 0.84 in acetic acid, 0.45 in formic acid, and 0.18 in trifluoroacetic acid. Added nucleophilic cosolvents have a modest influence on $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$. The values 0.84 and 1.05 were determined for chlorination in trifluoroacetic acid–22 *M* water and 51.5% trifluoroacetic acid–acetic acid, respectively. The influence of reagent selectivity on the rate ratio was examined by study of the ferric chloride catalyzed chlorination of the hydrocarbons in nitromethane. The relative rate, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$, is 1.3 for this reaction in accord with the expected dependence on reagent selectivity. Ground-state solvation effects appear significant. The partial molal heats of solution of toluene and *t*-butylbenzene in acetic acid and in trifluoroacetic acid (determined by Arnett and Douty) differ significantly. These results are discussed with reference to the interpretations advanced for the Baker–Nathan effect.

The experimental observation that the order of reactivity of alkyl substituted compounds is altered from the "normal inductive order" of *t*-Bu > *i*-Pr > Et > Me is known as the Baker–Nathan effect.[3] Interpretations emphasizing the importance of hyperconjugation[4] or of a polar effect in the inductive order coupled with steric hindrance to solvation[5] are well known. A third, less familiar idea is that the Baker–Nathan effect originates in steric hindrance to bond contraction.[6] The evidence for the effect and the relative merits of these viewpoints have been thoroughly discussed.[7–9] The apparent conclusion reached in these critical reviews is that the rate sequence for electrophilic substitution of the alkylbenzenes (*p*-Me > *p*-*t*-Bu ≫ *m*-*t*-Bu > *m*-Me > H) would offer secure evidence for the somewhat greater importance of C–H hyperconjugation relative to C–C hyperconjugation if other factors, in particular solvent–transition-state interactions, could be excluded.[7,8]

The suggestion that the reaction medium plays a major role in the origin of the Baker–Nathan effect[5] prompted our investigations[10] of solvent effects on the nuclear, noncatalytic chlorination of the alkylbenzenes. Chlorination was chosen for study because, among other reasons,[10] the arenonium ions formed in the course of this reaction fulfill the requirement for isovalent, nonsacrificial hyperconjugation.[11] We measured the rates and relative rates for chlorination and used eq 1

$$\frac{\log p_f^{\text{Me}}}{\log p_f^{t\text{-Bu}}} = \frac{\sigma^+_{p\text{-Me}}}{\sigma^+_{p\text{-}t\text{-Bu}}} = \text{constant} \qquad (1)$$

where p_f^{Me} and $p_f^{t\text{-Bu}}$, the *para* partial rate factors, are defined by the rate constants for substitution in the *para* position, $k_{p\text{-Me}}$ and $k_{p\text{-}t\text{-Bu}}$, relative to one position in benzene, to assess the variations in the substituent effects of the alkyl groups in different solvents. An approach of this kind is essential because the simple rate ratio, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$, depends on the selectivity of the reagent, that is, on the reaction constant, ρ. Presumably, ρ measures the charge deficiency in the aryl fragment of the transition state. This charge deficiency is, according to current thought, determined by the electrophilic properties of the reagent and by the degree of nucleophilic solvation in the transition state. Reagent electrophilicity is, in turn, solvent dependent. The fact that a linear free energy relationship correlates electrophilic substitution data implies that the contributions of the alkyl groups, *i.e.*, the σ^+ values, should not depend on reagent electrophilicity. Thus, substituent effects originating in important variations in the nucleophilic solvation of differently substituted transition states and manifest in the relative free energy of solvation of ground and transition state should be revealed by solvent dependent values of $\log p_f^{\text{Me}}/\log p_f^{t\text{-Bu}}$.

We first examined the chlorination of benzene, toluene, and *t*-butylbenzene in six aqueous acetic acid

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(2) Fellow of the Petroleum Research Fund, 1961–1963.

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Table I. Second-Order Rate Constants for Chlorination in Carboxylic Acid Solvents at 25°

	Rate constant,[a] 10^2k_2, M^{-1} sec^{-1}		
Acid solvent	C_6H_6	$C_6H_5CH_3$	$C_6H_5C(CH_3)_3$
Pivalic[b,c]	...	0.0007 ± 0.0001	
Propionic[b]	...	0.0024 ± 0.0004	
Formic[d]	0.60 ± 0.03	160 ± 5	75 ± 1
Trifluoroacetic[d]	0.751 ± 0.02	330 ± 50	227 ± 27
1.3 M H_2O[d]	1.62 ± 0.30		
5.6 M H_2O[d]	5.17 ± 0.17		
11.1 M H_2O[d]	7.40 ± 0.30		
22.0 M H_2O[d]	10.2 ± 0.10		
49.5% HOAc[d,e]	0.0149 ± 0.0004	7.96 ± 0.14	3.95 ± 0.20

[a] Average of several observations. [b] Concentration range: toluene, 0.5 M; chlorine, 10^{-2}–10^{-3} M. [c] At 35°. [d] Concentration range: alkylbenzene, 10^{-2}–10^{-3} M; benzene, 10^{-1} M; chlorine, 10^{-2}–10^{-3} M. [e] Mole %.

solvents (0–27.6 M water).[10a] Water has a large influence on the reaction rate. The rate constant for the reaction in the most aqueous solvent is about 10^4 greater than the rate constant for the same reaction in dry acetic acid. The values of log p_f^{Me}/log $p_f^{t\text{-Bu}}$ for the reaction in dry acid and in the most aqueous solvent are 1.12 and 1.08, respectively. We extended the investigation to five aprotic solvents.[10b]. Reagent selectivity is much larger in these media (p_f^{Me} is 9500 in nitromethane and 6250 in acetonitrile). The Baker–Nathan effect is observed in each case with log p_f^{Me}/log $p_f^{t\text{-Bu}}$ equal to 1.15 in nitromethane and 1.08 in acetonitrile. The variations in the logarithmic ratio are very small in view of the enormous variations in solvent nucleophilicity and steric properties. The results of these two studies seem most compatible with the view that the solvent plays a minor role in the origin of the Baker–Nathan effect. This conclusion depends on the notion that the incipient *p*-methyl- and *p*-*t*-butylbenzenonium ions would experience different solvation if the steric interactions between the alkyl groups and the solvent were actually significant. The small observed difference in log p_f^{Me}/log $p_f^{t\text{-Bu}}$ may, indeed, reflect small differences in nucleophilic solvation of the transition states. Accordingly, the possibility remained that less nucleophilic solvents would have a larger influence on the logarithmic ratio diminishing the ratio to unity or less.

Several investigations have established that the influences of alkyl groups on electrophilic substitution reactions do depend on the solvent. Smith and his associates report that log p_f^{Me}/log $p_f^{t\text{-Bu}}$ is 0.86 for the pyrolysis of 1-arylethyl acetates in the vapor phase at 600°K, a reaction that apparently proceeds *via* an electron-deficient transition state as shown by an excellent σ^+ correlation.[12] Further, rate data for deuterium and tritium exchange[13] of the alkylbenzenes indicate log p_f^{Me}/log $p_f^{t\text{-Bu}}$ alters when the solvent is changed falling to 0.97 for tritium exchange in trifluoroacetic acid.[13c] Moreover, log p_f^{Me}/log $p_f^{t\text{-Bu}}$ is 0.96 for bromination in trifluoroacetic acid compared to 1.16 for bromination in aqueous acetic acid.[9,14] These observations prompted us to study the chlorination of the alkylbenzenes in other carboxylic acids and to examine other aspects of the reaction in trifluoroacetic acid rich solvents. We also studied the ferric chloride catalyzed chlorination of the hydrocarbons in nitromethane, and ground-state solvation effects to provide a firmer basis for a discussion of the results.

Results

The chlorination reaction was examined in propionic, pivalic, formic, and trifluoroacetic acid. In addition, the influence of added nucleophilic cosolvents, water and acetic acid, on the reaction in trifluoroacetic acid was studied. The rate data were obtained by the experimental procedures described previously.[10] The reaction obeyed a simple second-order rate law in each solvent. The second-order rate constants for nuclear chlorination are presented in Table I.

The reaction is very slow in propionic and pivalic acid. Rate data could not be obtained for benzene in these solvents because the halogen is slowly consumed by the solvent. The rate constants for the more rapid chlorination of benzene in formic and trifluoroacetic acids and the mixed solvents were measured with precision. The chlorination of toluene and *t*-butylbenzene in 49.5% acetic acid–trifluoroacetic acid also proceeded at a convenient rate and the rate constants are known with some confidence. The far faster reactions of the alkylbenzenes in formic and trifluoroacetic acids could be followed, but the large rate constants for *t*-butylbenzene and toluene are less precise (±15%) than the other rate data. No attempt was made to obtain rate data for the alkylbenzenes in aqueous trifluoroacetic acid.

The modestly imprecise kinetic parameters for chlorination in trifluoroacetic acid suggest $k_{\mathrm{T}}/k_{t\text{-Bu}}$ is about 1.5. Rather than relying on this result, we also determined the rate ratio by competitive experiment. The more precise, and presumably more accurate, value measured in five experiments is 1.25. Toluene to *t*-butylbenzene rate ratios were also measured for aqueous trifluoroacetic acid solvents and propionic and pivalic acids by competitive experiments. In addition, we determined the *o*- and *p*-xylenes to toluene rate ratio by competitive technique to assess m_f^{Me}. The results for replicate experiments are presented in Table II.

Isomer distributions were determined for each solvent. The amount of *o*- and *p*-chlorotoluenes was assessed by vpc. The isomer distribution for *t*-butylbenzene was determined by vpc or by infrared analysis of the chloro-

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Table II. Relative Rates of Chlorination Determined by Competitive Measurement at 25°

Acid solvent	Relative rate[a] $k_T/k_{t\text{-Bu}}$	$k_{o\text{-xylene}}/k_T$	$k_{p\text{-xylene}}/k_T$
Pivalic[b]	5.93 ± 0.40	...	...
Propionic	3.82 ± 0.14	...	...
Formic	...	5.93 ± 0.67[d]	4.88 ± 0.49
Trifluoroacetic	1.25 ± 0.05	6.90 ± 0.67[d]	8.63 ± 0.50
1.3 *M* H_2O	1.12 ± 0.12	...	...
5.6 *M* H_2O	1.45 ± 0.07	...	...
11.1 *M* H_2O	1.56 ± 0.01	...	...
22.0 *M* H_2O	1.60 ± 0.08	...	...
49.5% HOAc[c]	...	6.46 ± 0.08[d]	7.33 ± 0.03

[a] Calculated from the equation of C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927). [b] At 35°. [c] Mole %. [d] We are indebted to Miss B. Zachery for these determinations.

Table III. Isomer Distributions for Noncatalytic Chlorination in Carboxylic Acid Solvents at 25° [a]

Acid solvent	Chlorotoluene, % *ortho*	*meta*	*para*	Chloro-*t*-butylbenzene, % *ortho*	*meta*	*para*
Pivalic[b]	64.0	...	36.0	23.0	...	77.0
Propionic	58.1	...	41.9	11.7	...	88.3
Formic	65.1	(0.5)[c]	34.9	30.4	2.5	67.2
Trifluoroacetic	66.9	0.5	33.1	36.2	3.7	60.1
22 *M* H_2O	66.0	...	34.0	35.0	...	65.0
49.5% HOAc[d]	66.0	(0.4)[c]	34.0	29.4	4.9	65.6

[a] The *ortho* and *para* concentrations are uncertain to ±3–5%. The *meta* concentrations are uncertain to ±10%. [b] At 35°. [c] Assessed by additivity approach. [d] Mole %.

t-butylbenzene fraction isolated by vpc. This latter method accurately measures the amount of *m*-chloro-*t*-butylbenzene. Spectroscopic analyses of the chlorotoluene fraction revealed <1% *meta* isomer.

A detailed infrared analysis of the chlorotoluene fraction isolated by vpc from the reaction in trifluoroacetic acid indicated 0.5 ± 0.1% *m*-chlorotoluene. The limit of error was established by replicate analyses from different reaction mixtures. In addition, we used the additivity approach to evaluate m_f^{Me} for trifluoroacetic acid, formic acid, and the trifluoroacetic acid–acetic acid solvent. This procedure is known to be quite accurate for the halogenation reactions of aromatic hydrocarbons.[15,16] Equations 2 and 3 were solved for m_f^{Me} using the values of o_f^{Me} and p_f^{Me} presented in

$$\frac{k_{p\text{-xylene}}}{k_T} = \frac{4o_f^{Me}m_f^{Me}}{2o_f^{Me} + 2m_f^{Me} + p_f^{Me}} \tag{2}$$

$$\frac{k_{o\text{-xylene}}}{k_T} = \frac{2o_f^{Me}m_f^{Me} + 2p_f^{Me}m_f^{Me}}{2o_f^{Me} + 2m_f^{Me} + p_f^{Me}} \tag{3}$$

Table VI and the relative rate data presented in Table II. The predicted amount of *meta* isomer is shown in Table III and the average calculated values of m_f^{Me} are shown in Table VI.

The isomer distributions determined in this study are summarized in Table III.

The rate data and isomer distributions reveal that $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$ decreases from 2.0 in acetic acid[10a] to 0.69 in trifluoroacetic acid. In an attempt to understand the origin of this reversal in the substituent effects, we examined several other aspects of the reaction. Control experiments with simulated reaction mixtures containing the hydrocarbons or products with hydrogen chloride established that isomerization, disproportionation, and intermolecular halogen transfer do not occur in trifluoroacetic acid under the conditions of the kinetic experiments.

Noncatalytic aromatic halogenations proceed without a primary kinetic isotope effect.[17] The inference is that 1-halobenzenonium ions form products much more rapidly than they revert to the starting materials. In this situation, only the energy barrier for the formation of the ion is kinetically significant. However, the removal of a proton from an arenonium ion may become kinetically important when bases are absent or at low concentration.[18] If the second step of the substitution reaction were kinetically significant, then the measured relative rate is not uniquely identifiable with a single energy barrier. In the exchange reaction, for example, the rate ratio for two alkyl groups reflects the set of rate constants for the formation of the benzenonium ions and for the partition of the ions to product and starting materials. The substituent effects of the alkyl groups could, in principle, be modified in such circumstances. We examined the reaction in trifluoroacetic acid for a primary kinetic isotope effect to test this explanation for the reversal of $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$. The relative rate for the competitive chlorination of toluene-4-*d* and *t*-butylbenzene is 1.26 ± 0.05, identical with the result for unlabeled material. The isomer distribution for the chlorination of toluene-4-*d*, 66% *o*- and 34% *p*-chlorotoluene, is also unchanged.[19] Thus, the reaction proceeds without a kinetic isotope effect in trifluoroacetic acid. Apparently, the benzenonium ion forms in the rate-limiting step in this weakly basic solvent as in other halogenations in other solvents.[17]

The notion that $\log p_f^{Me}/\log p_f^{t\text{-Bu}}$ may depend on the properties of the electrophilic reagent was tested by de la Mare and his students.[20] They examined the acid-catalyzed hypobromous acid bromination of the alkylbenzenes[20a,b] and contrasted the results for this reaction with the data for noncatalytic bromination.[20] The Baker–Nathan effect is observed in each reaction with $\log p_f^{Me}/\log p_f^{t\text{-Bu}}$ determined as 1.16 for molecular bromine and as 1.12 for hypobromous acid. Neither, the changing charge on the reagents ($BrOH_2^+$ and Br_2), nor the changing electron deficiency in the aromatic nucleus at the transition state (ρ for $BrOH_2^+$ is −6.2 and for Br_2 ρ is −12) alter the substituent effects of the alkyl groups significantly.[20c] These reactions were examined in 50% dioxane-water and in 85% acetic acid-water, respectively. There is a remote chance that the change in solvent may compensate for the

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(18) H. Zollinger, *Helv. Chem. Acta*, 38, 1597, 1617, 1623 (1955).

(19) A primary kinetic isotope effect of 1.25 is easily detected by this sensitive method. Exchange does not occur under the conditions of the experiment.

(20) (a) P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36 (1956); (b) *ibid.*, 131 (1957); (c) ref 15, pp 134–136.

Table IV. Partial Rate Factors for Noncatalytic and Ferric Chloride Catalyzed Chlorination in Nitromethane

Conditions	Partial rate factors o_f^{Me}	m_f^{Me}	p_f^{Me}	$o_f^{t\text{-Bu}}$	$m_f^{t\text{-Bu}}$	$p_f^{t\text{-Bu}}$
CH_3NO_2, Cl_2, 25° [a]	2420	8.3	9500	1310		2960
CH_3NO_2, Cl_2, $FeCl_3$, 0° [b]	110	3.8	100	47	5.3	75

[a] Reference 10b. [b] Reference 21.

Table V. Partial Molal Enthalpy of Solution of Toluene and *t*-Butylbenzene in Acetic and Trifluoroacetic Acid at 25°

Solute	ΔH_s,[a] kcal mol^{-1} CH_3CO_2H	 CF_3CO_2H	$\Delta\delta\bar{H}_s$, kcal mol^{-1}
Toluene	0.35 ± 0.01	1.13 ± 0.02	0.78 ± 0.03
t-Butylbenzene	0.54 ± 0.01	1.92 ± 0.02	1.38 ± 0.03

[a] The absolute values are not meaningful.

Table VI. Partial Rate Factors and Rate Ratios for Toluene and *t*-Butylbenzene

Solvent, conditions	Partial rate factors o_f^{Me}	m_f^{Me}	p_f^{Me}	$o_f^{t\text{-Bu}}$	$m_f^{t\text{-Bu}}$	$p_f^{t\text{-Bu}}$	Log ($m_f^{\mathrm{Me}}/m_f^{t\text{-Bu}}$)	Log ($p_f^{\mathrm{Me}}/p_f^{t\text{-Bu}}$)
Noncatalytic Chlorination								
$(CH_3)_3CCO_2H$, 35° [a]								(2.8)[b]
$CH_3CH_2CO_2H$, 25° [a]								(1.8)[b]
HOAc, 25° [c]	617	5.0	820	57	6.0	400	0.90	1.12
27.6 *M* H_2O, 25° [c]	534		552	108		341		1.08
HCO_2H, 25° [a]	520	4.2[i]	560	114	9.4	500	0.63	1.02
CF_3CO_2H, 25° [a,d]	780	5.8	750	330	33	1,100	0.50	0.95
22 *M* H_2O, 25° [a]								(0.84)[b]
49% HOAc, 25° [a]	1,060	5.2[i]	1,100	233	39	1,100	0.45	1.00
Noncatalytic Bromination								
85% HOAc, 15% H_2O, 25° [e]	600	5.5	2,420	5.0	6.1	806	0.94	1.16
CF_3CO_2H, 25° [f]	1,360	10	12,700			19,300		0.96
Nitration								
90% HOAc, 10% H_2O, 45° [g]	42	2.5	58	5.5	4.0	75	0.66	0.94
Tritium Exchange								
71.3% H_2SO_4, 28.7% H_2O, 25° [h]	250	5.0	250	170		180		1.06
40% H_2SO_4, 34% H_2O, 26% HOAc, 25° [h]	305	5.0	313		9.3	230	0.72	1.05
2.5% H_2SO_4, 2.2% H_2O, 95.3% CF_3CO_2H, 25° [h]	541	9.2	702		32	863	0.64	0.97
2.5% $HClO_4$, 5.5% H_2O, 92% CF_3CO_2H, 25° [h]	330	7.2	313	393	24	387	0.62	0.96
Mercuration								
HOAc, 25° [f]	5.7	2.2	23.0		3.4	17.2	0.64	1.10
CF_3CO_2H, 25° [f]	3.6	2.6	46.9		1.9	32.3	1.41	1.11

[a] This study. [b] Rate ratio, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$. [c] Reference 10. [d] Based on kinetic relative rate $k_{t\text{-Bu}}/k_{\mathrm{B}} = 300$ and the competitive rate ratio $k_{\mathrm{T}}/k_{t\text{-Bu}} = 1.25$. [e] H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79,** 1421 (1957). [f] Reference 14, see also the accompanying paper by Schubert and Gurka,[9] for a more complete discussion of this reaction. [g] H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, **169**, 291 (1952). [h] Reference 13c. [i] Average value based on eq 2 and 3.

change in reagent selectivity. Accordingly, we examined noncatalytic and ferric chloride catalyzed chlorination in a common solvent, nitromethane.[21] The partial rate factors for these reactions are compared in Table IV.

Selectivity is substantially decreased in the catalytic reaction. Yet, the Baker–Nathan order is observed in each case as found for bromination by de la Mare.[20] Quantitatively, log p_f^{Me}/log $p_f^{t\text{-Bu}}$ is 1.15 for molecular chlorination and 1.07 for the ferric chloride catalyzed reaction. The logarithmic ratios for molecular bromine and hypobromous acid show a parallel, but smaller, change. These differences are beyond the limit of experimental error. To this extent, there is a minor dependence of log p_f^{Me}/log $p_f^{t\text{-Bu}}$ on reagent selectivity. More important, the data indicate that a major variation in reagent selectivity, *i.e.*, a twofold change in ρ, produces only a very minor change in the logarithmic rate ratio for the alkyl groups. We infer that the smaller, solvent induced changes in reagent selectivity for noncatalytic chlorination could not be responsible for the changes in log p_f^{Me}/log $p_f^{t\text{-Bu}}$ in the carboxylic acid solvents.

The results suggest, see the Discussion, that all the positions of *t*-butylbenzene exhibit enhanced reactivity in trifluoroacetic acid. Important differences in the solvation of the hydrocarbons could lead to this result. To test this idea, Arnett and Douty measured the partial molal enthalpy of solution, ΔH_s, of toluene and *t*-butylbenzene in acetic and trifluoroacetic acid. Their observations are summarized in Table V.

Discussion

The results for chlorination obtained in this investigation and relative rate data for other selected substitution reactions are summarized in Table VI. The data chosen for presentation emphasize the influence of solvent with particular reference to the changing *p*-methyl/*p*-*t*-butyl ratio in trifluoroacetic acid rich solvents.[22]

Eaborn and Taylor's investigation of tritium exchange revealed that important variations in log p_f^{Me}/log $p_f^{t\text{-Bu}}$ may occur for the same electrophilic substitu-

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(21) A. Himoe, B. M. Hoffman, J. K. Housinger, and L. M. Stock unpublished results.

(22) Other substitution reactions of *t*-butylbenzene and toluene have been examined, see Tables 2 and 7 of ref 16 for a summary of this work.

tion reaction in different solvents.[13c] They conclude that the variable influences of the alkyl groups cannot be reconciled with interpretations for the Baker–Nathan effect that stress either hyperconjugation or steric hindrance to solvation and they suggest both factors are significant. The more recent results for mercuration,[14] bromination,[9,14] and chlorination are equally difficult to accommodate within the framework of one of the popular theories. To illustrate, the alkyl groups exhibit the Baker–Nathan order for mercuration in both acetic and trifluoroacetic acid. On the other hand, the inductive order of stabilization obtains for nitration in all solvents.[23] Clearly, it is not possible to categorize the reaction medium as a "Baker–Nathan solvent" or an "inductive solvent." In contrast to the unchanging role of the alkyl groups in mercuration and nitration, log p_f^{Me}/log $p_f^{t\text{-}Bu}$ for exchange,[13] bromination,[9,14] and chlorination depends on the character of the reaction medium. None of the theories advanced for the Baker–Nathan effect are sufficiently sophisticated to accommodate this array of data.

For chlorination, the control experiments, the absence of a primary kinetic isotope effect, and the negligible dependence on ρ discussed in the Results exclude interpretations based on side reactions, a change in the rate-limiting step or an important dependence on reagent selectivity alone. The kinetic parameters reflect the energy requirements for the conversion of the hydrocarbons to the transition states leading to benzenonium ions for a reaction of appreciable selectivity; ρ is about -10. The results tabulated in Table VI indicate that both log p_f^{Me}/log $p_f^{t\text{-}Bu}$ and log m_f^{Me}/log $m_f^{t\text{-}Bu}$ are inconstant. These observations are cogent evidence for the intimate involvement of solvent in the determination of alkyl group substituent effects in chlorination.

The concept of steric inhibition of solvation[5] can account for the solvent dependence of the *para* reactivities for chlorination, bromination, and tritium exchange. Weakly nucleophilic solvents, *e.g.*, formic or trifluoroacetic acid, should solvate the incipient arenonium ions less effectively than the more nucleophilic acids, *e.g.*, acetic or propionic acid. As a consequence of the decreased solvation of the ions in the less nucleophilic media, the steric effect of the *p-t*-butyl group is relatively less important with the substituent effects of the alkyl groups in the normal inductive order of electron release. In the more nucleophilic acids, on the other hand, solvation of the 4 position of 4-*t*-butylbenzenonium ion is sterically inhibited relative to the equivalent site in 4-methylbenzenonium ion with the substituent effects in the Baker–Nathan order. This explanation is also applicable to the finding that $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$ is somewhat larger in pivalic acid (2.8 compared to 2.0 for acetic acid). This result may be rationalized on the basis of the greater steric requirements of pivalic acid as a nucleophilic solvent with an increase in the energy required for the *para* substitution of *t*-butylbenzene relative to that for the *para* substitution of toluene.

While the steric interpretation offers a reasonable explanation for solvent effects on the relative rates for *para* chlorination, bromination, and tritium exchange, two lines of evidence suggest that this concept is not uniquely responsible for the solvent dependence. One clear inference of the steric argument is that added nucleophilic cosolvents should increase the rate ratio, $k_{p\text{-Me}}/k_{p\text{-}t\text{-Bu}}$. Qualitatively, this expectation is realized for chlorination in trifluoroacetic acid. The rate ratio does indeed increase from 0.69 in the anhydrous acid to 0.84 in the solvent with 22 M water and to 1.05 in the solvent with 49.5% acetic acid. The dependence on solvent nucleophilicity, however, is very small. Our intuitive, but perhaps naive,[24] expectation was that the Baker–Nathan order would be restored in these mixed solvents. The failure to detect a greater change, although certainly not sufficient cause to discount the steric explanation for the Baker–Nathan order, suggests that other factors are important.

There is a second, more serious difficulty. The steric interpretation emphasizes the selective inhibition of solvation at the site adjacent to the substituent in the 4-alkylbenzenonium ions to account for the reversal in substitution rates at the *meta* and *para* positions in nucleophilic solvents.[25] The usual view is that solvent effects are less significant for the 3-alkylbenzenonium ions because the electron-deficient sites in these molecules are more remote from the substituent. The data for chlorination, and exchange to a lesser extent, show that log m_f^{Me}/log $m_f^{t\text{-}Bu}$ is as solvent dependent as log p_f^{Me}/log $p_f^{t\text{-}Bu}$.[26] This result is apparently the consequence of the unusually large $m_f^{t\text{-}Bu}$ values which are greater than 30 for chlorination and as large as 20 for tritium exchange in trifluoroacetic acid solvents, *i.e.*, $m_f^{t\text{-}Bu}$ increases while m_f^{Me} does not change appreciably. The changes in the *meta* ratio closely parallel the changes in the *para* ratio. The activation free energy differences for chlorination in trifluoroacetic acid and acetic acid defined by eq 4 are about 600 cal mol^{-1} for R = *p*-Me,

$$2.3RT(\log (k_R/k_{R'})_{HOAc} - \log (k_R/k_{R'})_{CF_3CO_2H}) \quad (4)$$

R′ = *p-t*-Bu; about 800 cal mol^{-1} for R = *m*-Me, R′ = *m-t*-Bu; and about 900 cal mol^{-1} for R = *o*-Me, R′ = *o-t*-Bu.

The large influence of solvent on *meta*-substitution rates is not easily reconciled with the steric-inhibition theory for the Baker–Nathan effect. Eaborn and Taylor have also critically discussed the possible interpretations for solvent dependent rate ratios.[13c] Their arguments follow somewhat different lines but their conclusion is the same as that reached here: the simple theories are not adequate.

The observations for chlorination, bromination, and exchange are, we believe, much more easily understood from a quite different viewpoint. Clement and his

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[23] A typical nitration result is presented in Table VI; log p_f^{Me}/log $p_f^{t\text{-}Bu}$ is about 0.95 for a variety of solvents, see entries 25–31 in Tables 2 and 7 of ref 16 for a more complete set of data.

[24] The activity of water in aqueous trifluoroacetic acid is apparently unknown. Since water must be associated with the hydronium ion and trifluoroacetate anion, its activity and hence its capacity for nucleophilic solvation of the incipient arenonium ions may be small.

[25] Several viewpoints concerning the differences in solvation of 3- and 4-alkylbenzenonium ions are discussed by E. Berliner and M. M. Chen, *J. Am. Chem. Soc.*, 80, 343 (1958). The point is also discussed by several authors in ref 7.

[26] The value of m_f^{Me} for the reaction in trifluoroacetic acid is based on a direct determination of per cent *m*-chlorotoluene and the rate data for *o*- and *p*-xylenes. For the other solvents, m_f^{Me} is based on the rate data alone.

associates report that the free energy of solution of *p-t*-butylbenzyl chloride is 250 cal mol^{-1} more endothermic than the free energy of solution of *p*-methylbenzyl chloride in methanol.[27] The results indicate that the activity coefficient for the *t*-butyl derivative is somewhat greater than that for the methyl derivative. The relative solvolysis rates of these compounds necessarily reflect this ground-state energy difference as well as the more difficultly defined substituent and solvent effects in the transition states. The remarkably large $m_f^{t\text{-Bu}}$ values and the similar differences in activation free energy for all the positions of *t*-butylbenzene compared to toluene in trifluoroacetic acid relative to acetic acid suggest that the change in relative reactivity may simply arise from an enhanced activity coefficient for *t*-butylbenzene in trifluoroacetic acid. The partial molal enthalpy of solution of toluene and *t*-butylbenzene in acetic and trifluoroacetic acid were measured as a preliminary test of this idea. The data, Table V, reveal that the change in the heat of solution ($\delta\Delta\bar{H}_s$) of the solutes in trifluoroacetic acid relative to acetic acid is endothermic in each case, but substantially greater for *t*-butylbenzene than for toluene. The corresponding change in the entropy of solution is not known. Conservatively, it is inappropriate to conclude that the enthalpy change is necessarily reflected in the change in free energy of solution, *i.e.*, in the activity coefficients of the hydrocarbons in the ground state. It seems likely, however, that this is the case. The reduced values of both $\log p_f^{\mathrm{Me}}/\log p_f^{t\text{-Bu}}$ and $\log m_f^{\mathrm{Me}}/\log m_f^{t\text{-Bu}}$ in trifluoroacetic acid solvents may arise, at least in part, from an increased activity coefficient for *t*-butylbenzene.

The area of solvent–ground-state and solvent–transition-state interactions is under active investigation. Recent work by Arnett and his associates[28] reveals that the solvent dependent ionization rates of *t*-butyl chloride result in large part from solvent–substrate interactions. Schubert and his students find that solvent–transition-state interactions are important in the acid-catalyzed hydrolysis of certain quinoline acetals.[29] These important studies indicate that generalizations implying the unique importance of solvent–transition-state or solvent–ground-state are inappropriate and that different reactions require careful experimental attention.

In summary, the results of this investigation indicate that the solvent is important in the determination of the substituent effects of alkyl groups. Although the reactivity pattern for *para* substitution is compatible with the concept of steric inhibition of solvation, the reactivity pattern for *meta* substitution and the large value of $\delta\Delta\bar{H}_s$ suggest solvent–substrate interactions influence the rate ratio. If the view is taken that solvent–substrate interactions dominate the situation in trifluoroacetic acid rich solvents, then the results for chlorination are consistent with the view that the differential contributions[30] of C–H and C–C hyperconjugation are responsible for the Baker–Nathan effect. Until more definitive evidence is available regarding the magnitude of solvent–transition-state interactions, the concept of steric inhibition of solvation remains as an alternative. The full set of data for electrophilic substitution of the alkylbenzenes, Table VI, do not conform to a simple pattern. The results of this investigation suggest that solvent–ground-state interactions may be responsible for some of these variations. It is evident, however, that variations in solvent–transition-state interactions or the polar influences of alkyl groups themselves must be important in some cases.

Experimental Section

Materials. Benzene, toluene, *t*-butylbenzene, authentic samples of the isomeric chlorotoluenes and chloro-*t*-butylbenzenes, and anhydrous acetic acid were available from previous studies. *p*-Xylene was Phillips research grade material. Toluene-4-*d* (96 ± 1% by infrared analysis) was prepared from *p*-bromotoluene by hydrolysis of the Grignard reagent with deuterium oxide (Volk Chemical Co., 99%) by the method of Weldon and Wilson.[31] Formic acid was purified by the method of Winstein and Marshall.[32] Trifluoroacetic, propionic, and trimethylacetic acid were purified by careful fractionation in a dry atmosphere.

Experimental Procedures. The kinetic and competitive experiments were carried out as described.[10] The isomer distributions were also established by reported procedures.[10] The concentration of *m*-chloro-*t*-butylbenzene was assessed by infrared analysis of the chloro-*t*-butylbenzene fraction isolated by vpc. Absorptions at 752 and 823 cm^{-1} were employed for determination of the *ortho* to *para* ratio in about 0.1 *M* solution. The *para* to *meta* ratio was evaluated in somewhat more concentrated solution employing the absorptions at 1011 and 781 cm^{-1}. Known mixtures of the authentic isomers were employed to standardize the techniques.

Acknowledgment. We are indebted to Professor Schubert for a fruitful discussion of this problem.

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