Solvent Effects in the Bromination of Neopentylbenzene, *t*-Butylbenzene, Toluene, and Benzene in Aqueous Trifluoroacetic Acid[1]

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Abstract: It is concluded that the step $ArH + Br_2 \rightarrow ArHBr^+ + Br^-$ is rate controlling in the molecular bromination of neopentylbenzene, *t*-butylbenzene, and toluene in 78.3, 86.1, and 93.3% trifluoroacetic acid, and benzene in 93.3% trifluoroacetic acid. By contrast, reversal of this step is significant in the bromination of benzene in 78.3 and 86.1% trifluoroacetic acid. In the former instances, the reaction is cleanly first order in bromine ($[Br_2]_0 \sim 10^{-3}$ *M*, $[ArH] \sim 10^{-1}$ *M*) and is practically unchanged by added sodium bromide (10^{-2} *M*). In the latter instances, the kinetic behavior in the absence of added excess bromide ion is complex (apparent contribution of kinetic terms higher than first order in bromine); added excess sodium bromide reduces the dependence on bromine to solely first order, and suppresses the rate without significantly reducing the concentration of molecular bromine. The value of p_f^{Me} reached a maximum, in 93.3% trifluoroacetic acid, of 42,400, which is by far the largest rate-enhancing effect of a *p*-methyl substituent yet encountered. The extreme selectivity of the bromination also was reflected in the failure to detect any *ortho* bromination of *t*-butylbenzene or *meta* bromination of any of the alkylbenzenes. Between 78.3 and 93.3% trifluoroacetic acid, $k_{p\text{-}t\text{-}Bu}/k_{p\text{-}Me}$ increased from 1.06 to 1.40, $k_{p\text{-}Neop}/k_{p\text{-}Me}$ from 0.82 to 1.07, and $k_{o\text{-}Neop}/k_{o\text{-}Me}$ from 0.13 to 0.21. The behavior of the relative rates is in contradiction to the Baker–Nathan hypothesis, and serves to illustrate once again the important role of solvation in governing the relative kinetic parameters of alkyl-substituted compounds. In the Discussion, the alkyl-substituent effects on ground- and transition-state solvation are considered explicitly and in some detail. The conclusion reached is that the Schubert–Sweeney hypothesis of steric hindrance to specific nucleophilic solvation near bulky alkyl substituents provides a reasonable rationalization of the results, but is not unique in this respect.

Studies of the effect of the neopentyl substituent in electron-demanding reactions are few in number. In reactions 1–5 of Table I, the rate constant for the neopentyl compound is less than that of the corresponding methyl compound, and comparable to that of the *t*-butyl compound in those instances in which the rate of the *t*-butyl compound was determined. In reaction 5, direct steric hindrance by the alkyl substituent may be a factor. However, in reactions 1–4,[3] the substituent is removed from the immediate site of the reaction. In such instances, the relatively small "activating" effect of the neopentyl substituent has been attributed variously to the inability to participate in second-order hyperconjugation,[4] steric hindrance to bond shortening,[5] steric interference with solvent enhancement of C–H hyperconjugation,[6] steric inhibition of hyperconjugation,[7,8a,9] or steric hindrance to solvation near the substituent.[10,11]

According to molecular models, rotation about the bond between the neopentyl substituent and a trigonal carbon is restricted. Consequently, the substituent may be constrained to a conformation in which neither α-C–H bond is in position for maximum overlap with the adjacent p or π orbital (Figure 1), and possible C–H hyperconjugative interaction may be partially reduced.[13]

In some elegant and very accurate work, Shiner has found a number of examples in which the β-deuterium isotope effect in SN1 reactions shows a conformational dependence.[15] Such results are consistent with an important chemical role for C–H hyperconjugation,[16] although some doubt of a correlation between the magnitude of C–H hyperconjugation and the magnitude of

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[2] Petroleum Research Fund Fellow, 1964–1965.

[3] In reaction 4, the order of *para*-substitution rates corresponds to the order of total rates.[4]

[4] E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, 72, 222 (1950).

[5] A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

[6] V. J. Shiner, Jr., and C. J. Verbanic, *J. Am. Chem. Soc.*, 79, 369, 373 (1957).

[7] R. T. Arnold, R. M. Dodson, and K. Murai, *ibid.*, 72, 4193 (1950); R. T. Arnold and W. L. Truett, *ibid.*, 73, 5508 (1951).

[8] (a) G. Baddeley and M. Gordon, *J. Chem. Soc.*, 2191 (1952); (b) G. Baddeley and M. Gordon, *ibid.*, 4379 (1958); (c) G. Baddeley, S. Varma, and M. Gordon, *ibid.*, 3171 (1958).

[9] V. J. Shiner, Jr., *J. Am. Chem. Soc.*, 78, 2654 (1956).

[10] (a) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, 21, 119 (1956); (b) W. M. Schubert and J. Robins, *J. Am. Chem. Soc.*, 80, 559 (1958); (c) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, 17, 199 (1962); (d) W. M. Schubert and R. G. Minton, *J. Am. Chem. Soc.*, 82, 6188 (1960).

[11] The ascribing of a rate constant order for alkyl compounds to such factors involves the assumption that orders of free energy of activation correspond to potential energy orders. Such an assumption can be risky, especially in view of the small differences in free energies of activation being dealt with (see, *e.g.*, ref 10d and 12).

[12] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, Chapter 9; J. E. Leffler, *J. Org. Chem.*, 20, 1202 (1955).

[13] Since there is partial overlap with both α-C–H bonds, possible C–H hyperconjugation is not completely inhibited. If the neopentyl group is constrained to the conformation shown in Figure 1 and the extent of C–H hyperconjugation depends on $\cos^2 \theta$,[14] where θ is the angle between either C–H bond and the plane of the adjacent trigonal carbon, then the interaction is reduced to 0.5 the maximum value.

[14] L. M. Stock and J. Suzuki, *J. Am. Chem. Soc.*, 87, 3909 (1965).

[15] (a) V. J. Shiner, Jr., *Tetrahedron*, 5, 243 (1959); (b) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, 83, 240 (1961); (c) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *ibid.*, 85, 2413 (1963); (d) V. J. Shiner, Jr., and J. S. Humphrey, *ibid.*, 85, 2416 (1963); (e) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, 87, 1382, 1384 (1965).

[16] Stock and Suzuki have found a similar conformational dependence of the delocalization of electron spin density of semiquinones.[14]

Table I. Neopentyl Substituent Effects

Reaction	Neop	*t*-Bu	Me	H	Ref
1. *p*-$RC_6H_4CHPhCl$, k[a] "67%" acetone, 0°	502	470	1217	37.9	6
2. *p*-$RC_6H_4CHPhCl$, k[a] "80%" acetone, 0°	40.1	38.7	86.2	2.6	6
3. *p*-$RC_6H_4CHPhCl$, k[a] EtOH, 0°	0.393	...	0.612	0.0188	8c
4. $PhR + Br_2$, k[b] "85%" HOAc, 25°	1	0.85	4.83	...	4
5. $RCH{=}CH_2 + Br_2$, k_2[c] HOAc, 25°	0.10	0.70	*d*	...	*g*
6. *p*-$RC_6H_4C(Ph)_2Cl$, K[e] SO_2, 0°	10.1	8.78	7.86	0.42	*h*
7. *p*-$C_6H_4NO_2$, relative ν,[f] gas phase	0	270	480	2330	10[b]

[a] Units are 10^{-3} sec^{-1}. [b] Based on times of 10% reaction for total bromination.[3] [c] Units are 10^{-3} l. mol^{-1} sec^{-1}. [d] For *n*-$BuCH{=}CH_2$, the value is 1.05. [e] $K \times 10^4$ for dissociation to separated ions. The values of K for reaction 6 are for dissociation to separated ions; *i.e.*, $K = K_1K_2$ for $Ar_3CCl \rightleftharpoons Ar_3C^+Cl^-$ (ion pair) $\rightleftharpoons Ar_3C^+ + Cl^-$. [f] Values of $\nu_R - \nu_{Neop}$ (±20 cm^{-1}) for the principal electronic transition. For neopentyl, ν_{max} is 39,490 cm^{-1}. [g] P. W. Robertson, J. K. Hayes, and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952). [h] N. N. Lichtin, P. E. Rowe, and M. S. Puar, *J. Am. Chem. Soc.*, **84**, 4259 (1962).

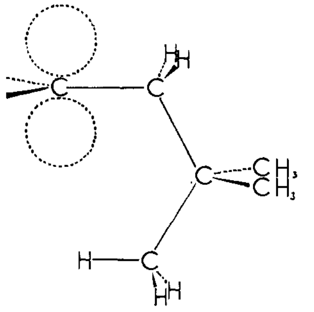

Figure 1.

secondary deuterium isotope effects has been expressed.[17,18] The secondary deuterium isotope effect apparently also is subject to substituent electronic effects,[15a,17] and instances of its solvent dependence have been encountered.[9,15a,19]

The *total* hyperconjugative interaction of the neopentyl substituent may not be greatly affected by the conformational restraint depicted in Figure 1.[20] In this conformation, C–H hyperconjugation would be reduced only partially, and C–C hyperconjugation would be at a maximum. Whether the total hyperconjugative effect is subdued or enhanced would depend on the relative importance of C–H and C–C hyperconjugation. It has been postulated that C–H hyperconjugation is slightly less important than C–C (ref 14 and references cited therein). However, Baddeley, who was among the first to postulate inhibition of C–H hyperconjugation,[8a] later concluded that a comparison of kinetic parameters for the solvolysis of 4-alkylbenzhydryl chlorides and their 3,5-dimethyl derivatives "does not provide evidence for the view that the hyperconjugative effect of primary alkyl groups is affected by torsional rotation of the group about the bond attaching it to the benzene ring."[8c]

The conformation represented in Figure 1 also is one in which the neopentyl substituent strongly shields one side of the adjacent trigonal carbon.[21] According to the Schubert–Sweeney hypothesis,[10] such shielding will interfere with specific nucleophilic solvation of this site. This factor should be more important in the more electron-deficient state of the two states of a chemical transition. Thus, say for a reaction proceeding to a highly electron-deficient transition state, the effect would be to increase the enthalpy of activation, and presumably also the free energy of activation.[11,22]

Most of the observations of comparative alkyl substituent effects on chemical reactions can be rationalized in terms either of the Baker–Nathan hypothesis[23] or the Schubert–Sweeney hypothesis. For example, consider reactions 1–4 of Table I. In terms of the former hypothesis, it can be argued that the electron demand on the *p*-alkyl substituent is sufficiently large for the C–H hyperconjugative effect of the methyl substituent to become predominant. However, a large electron demand on the *para* substituent implies a large electron deficiency in the neighborhood of the substituent, *i.e.*, a large demand for basic solvation. Since the solvent is reasonably basic it can be argued, in terms of the Schubert–Sweeney hypothesis, that steric hindrance to specific solvation of the transition state near the bulkier alkyl substituents acts to invert an intrinsic inductive order of rate constants.[24] The latter hypothesis appears to be more compatible than the former with the increase in k_{Neop}/k_{Me} and $k_{t\text{-Bu}}/k_{Me}$ with decreasing water con-

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(17) C. G. Swain, T. E. C. Knee, and A. J. Kresge, *J. Am. Chem. Soc.*, 79, 505 (1957).

(18) L. S. Bartell, *ibid.*, 83, 3567 (1961).

(19) E. S. Lewis, *Tetrahedron*, 5, 143 (1959).

(20) H. H. Jaffé and J. L. Roberts, *J. Am. Chem. Soc.*, 79, 391 (1957).

(21) The *t*-butyl substituent, on the other hand, partially shields both sides of an attached trigonal carbon, and a model in which this trigonal carbon is solvated bears a formal resemblance to the strained transition state of an SN2 substitution of neopentyl halide.

(22) Steric hindrance to solvation of the transition state also would act to increase the entropy of activation, and thus a "compensation effect"[12] would be exerted on the free energy of activation. Such compensation effects have been found in the influence of changing solvent on the kinetic parameters for alkyl compounds.[10d]

(23) The term Baker–Nathan effect refers to experimental observation. The explanation of such an effect in terms of C–H hyperconjugation is termed the Baker–Nathan hypothesis.

(24) The Schubert–Sweeney hypothesis does not directly concern itself with the nature of the electronic interactions. It does not negate an imporant role for C–H hyperconjugation, but does assume that the net intrinsic electronic effect of Me and *t*-Bu, etc., is in the inductive *order*, regardless of the electron demand.

tent of the solvent in the solvolysis of *p*-alkylbenzhydryl chlorides, reactions 1–3. The absence of a Baker–Nathan Effect[23] in the *K* values[25] of reaction 6 also is consistent with either hypothesis. In terms of the former hypothesis, it can be argued that the electron demand on the substituent is sufficiently low in this instance[26] to allow inductive and C–C hyperconjugative electron release to predominate over C–H hyperconjugation. In terms of the latter hypothesis it can be argued that a somewhat lower demand for basic solvation coupled with the fact that the solvent is weakly basic lessens the effect of steric hindrance to solvation near the substituent.

In contrast to reactions 1–4, "reaction" 7, the principal electronic transition of *p*-alkylnitrobenzenes, which is very strongly electron demanding on the substituent, shows the energy order Neop < *t*-Bu < *i*-Pr < Et < Me ≪ H in the gas phase, *i.e.*, opposite to a Baker–Nathan Effect. In basic solvents, the excitation energy spread between neopentyl and methyl, and *t*-butyl and methyl compounds is reduced, in agreement with the Schubert–Sweeney hypothesis.[10b,c,27] Insofar as electronic and chemical transitions may be treated in the same vein, it appears that the Schubert–Sweeney hypothesis reconciles results in both areas better than the Baker–Nathan hypothesis. Indeed, it was the apparent contradiction between the results of chemical measurements and physical measurements in general, when viewed in terms of the Baker–Nathan hypothesis, that first led to the consideration of a role of the solvent in alkyl substituent effects.[10]

As regards the neopentyl substituent, it is of course possible that both solvation and conformational effects on hyperconjugation are important in its total effect on reactions in solution. If steric hindrance to solvation is a factor, then rate ratios for neopentyl (as well as *t*-butyl) *vs.* methyl compounds should be solvent dependent in a specific way. That is, $k_{\mathrm{Neop}}/k_{\mathrm{Me}}$ should increase with decreasing basicity of the solvent provided there is no compensatory increase in demand for basic solvation.[11] To test this, we have studied the bromination of neopentylbenzene, *t*-butylbenzene, toluene, and benzene in trifluoroacetic acid containing varying amounts of water. Trifluoroacetic acid was chosen because of its weakly basic character, and because it was felt that in this solvent the demand on the substituent would be large. While this work was in progress a similar and extensive study of solvent effects on electrophilic aromatic substitution reactions of *t*-butylbenzene, toluene, and benzene was being made by Stock and Himoe[28] and results on bromination of toluene and *t*-butylbenzene in 100% trifluoroacetic acid have been reported by Brown and Wirkkala.[29]

Experimental Section

Materials. Neopentylbenzene, *t*-butylbenzene, and toluene were shaken with concentrated sulfuric acid, then thoroughly washed with water, dried over barium oxide, and fractionated through a 20-plate metal helix column. Each compound showed only one vpc peak (Aerograph A-90, Silicone SF 96 column).

Trifluoroacetic acid (Matheson) was distilled from phosphorus pentoxide,[30] then redistilled. Large batches of mixed solvent were prepared by weighing appropriate amounts of the individual solvents. Weight percentages were checked by titration against standardized sodium hydroxide.

Rate Measurements. Rate constants were determined by means of the ultraviolet spectrophotometric method. The reactions were run in 1-cm quartz Beckman cells which were placed in a water-thermostated cell compartment that was fitted between the monochromator and photocell compartments of a Model DU Beckman spectrophotometer. Temperature control to 0.03° was maintained by means of a Sargent Thermoniter regulating unit.

Initial kinetic solutions contained excess sodium bromide (about 10^{-2} *M*) as well as bromine (about 10^{-3} *M*) and excess aromatic hydrocarbon (0.02 to 0.10 *M*). The decrease in optical density at 280–300 mμ, a region of absorption by Br_3^-, was followed as a function of time. In later runs, sodium bromide was not added and the decrease in optical density at 410–420 mμ, a region of absorption by molecular bromine, then was followed.

The Bromine–Tribromide Equilibrium. The ultraviolet spectra of bromine–bromide solutions, measured in a Cary Model 14 instrument, were used to obtain values of the concentration equilibrium constant, K_4, for the equilibrium of eq 4. It was found that preparing bromine–bromide solutions by transferring aliquots of bromine solution led to loss of bromine due to volatilization.[31] Consequently, solutions of known stoichiometric concentration in bromine and bromide ion were prepared by mixing aliquots of stock solutions of potassium bromate and sodium bromide (excess) and diluting to a given volume. This procedure has the further advantage that the salts used are very pure and can be easily handled and accurately weighed. Also to avoid loss of bromine, the final solution was neither poured nor pipetted into the Cary cell. Instead, the solution was "pushed" by means of the positive pressure of a slight amount of air through a tube extending to the bottom of the Cary cell and allowed to overflow the cell before the cell was stoppered. Trial experiments established that no bromine was lost in the transfer. Equation 1 was then applied in a region of the spectrum (250–280 mμ) in which tribromide ion absorbs strongly and $\epsilon_{\mathrm{Br_2}}$ is insignificant. The value of $\lambda_{\max}$ for tribromide ion was 260 mμ, and $\epsilon_{\max}$ was assumed to be 5.5×10^4.[32]

$$[\mathrm{Br_2}]/[\mathrm{Br_2}]_{\mathrm{stoich}} = (\epsilon_{\mathrm{Br_3^-}} - \epsilon)/(\epsilon_{\mathrm{Br_3^-}} - \epsilon_{\mathrm{Br_2}}) \qquad (1)$$

$$= 1/(1 + K_4[\mathrm{Br^-}]) \qquad (2)$$

The value of K_4 in 78.3% trifluoroacetic acid was 5 ± 1. More approximate values in 86.1 and 93.3% trifluoroacetic acid were 3.0 and 0.7, respectively.

Isomer Distributions. Reactions for product analysis were carried out under conditions that paralleled as closely as possible conditions prevailing in the kinetic runs, except that the concentrations of bromine, aromatic hydrocarbon, and sodium bromide were about threefold that used in kinetic runs. After completion of the reaction in the dark at constant temperature, the reaction solution (50 ml) was diluted with water (100 ml), then extracted with carbon disulfide (four 15-ml portions). The extract was dried over barium oxide, and then the drying agent was removed by gravity filtration and washed with 10 ml of carbon disulfide.

For neopentylbenzene and *t*-butylbenzene, the combined carbon

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[25] See footnote *e*, Table I.

[26] The ratio $K_{\mathrm{Me}}/K_{\mathrm{H}}$, which can be considered as a measure of the demand on the *para* substituent, has a value of 18.7. For reactions 1, 2, and 3, which show the Baker–Nathan Effect, the values of $k_{\mathrm{Me}}/k_{\mathrm{H}}$ are 32.1, 33.2, and 32.6, respectively.

[27] The Schubert–Sweeney hypothesis accounts for the much rarer occurrence of the Baker–Nathan effect in electronic as compared to chemical transitions. The Franck–Condon principle applies to electronic transitions. That is, solvent orientation to the excited state is practically the same as to the ground state and thus the solvent is only weakly oriented near the alkyl substituent in the excited state. Hence steric hindrance to specific solvation would have a milder effect on the energy of the electronically excited states than on the energy of electron-deficient transition states, to which the solvent is maximally oriented.

[28] A. Himoe and L. M. Stock, *J. Am. Chem. Soc.*, 91, 1452 (1969). We are indebted to Professor Stock for making the results known to us before publication.

[29] H. C. Brown and R. A. Wirkkala, *ibid.*, 88, 1447, 1459 (1966).

[30] W. Dannhauser and R. H. Cole, *ibid.*, 74, 6105 (1952).

[31] The absorbance of solutions of bromine (3×10^{-3} *M*) in 78.3% trifluoroacetic acid decreased by as much as 15–20% when the solutions were simply poured from a Cary cell into a beaker and then back into the cell.

[32] A. I. Popov and R. F. Swenson, *J. Am. Chem. Soc.*, 77, 3724 (1955), report an $\epsilon_{\max}$ of 5.5×10^4 in acetonitrile (269 mμ) and 5.4×10^4 in ethylene dichloride (273 mμ).

disulfide extract was analyzed by vpc in an Aerograph Hyfi, Model 600 (5 ft × 1/8 in. Carbowax 20 column at 138°). Relative areas of vpc peaks were measured by the triangulation method.[33,34] Two well-separated and symmetrical peaks, corresponding to *ortho* and *para* isomers, were obtained for bromoneopentylbenzene. The absence of *meta* isomer was confirmed by nmr. Only one peak, that for *para* isomer, was obtained for bromo-*t*-butylbenzene, although known mixtures of *ortho* and *para* isomers were resolved. The absence of *ortho* or *meta* isomer was verified by nmr and infrared analysis. Similar procedures were applied in the analysis of isomer distributions obtained in other substitutions.[35]

Analysis of the bromination products of toluene was made by nmr since the vpc peaks were not completely resolved. Carbon disulfide extracts, obtained as above, were concentrated by distillation through a glass-helices column until the solution was about 20% by weight of bromotoluenes and the nmr spectrum taken in a Varian A-60 instrument. No *m*-bromotoluene could be detected, either in the aromatic- or methyl-proton region of the spectrum. By examination of the nmr spectrum of control mixtures in the region of τ 3.02, where the *meta* isomer showed its fairly isolated most intense aromatic-proton signal, it is estimated that as much as 2–3% *meta* isomer could have escaped detection. Ratios of *o*- to *p*-bromotoluene were determined by means of the resolved sharp singlet methyl-proton signals at τ 7.69 and 7.81, respectively. This region of the spectrum was expanded by use of a sweep width of 100 cycles and the relative areas determined by the method of peak height times half-width. This method was found to check within 2% for known mixtures of *o*- and *p*-bromotoluene.

Results

Most of the substitution products of neopentylbenzene were unknown before this work. Their preparation, isolation, and identification is described elsewhere.[35]

Bromination Rates. Use of the ultraviolet spectrophotometric method to determine bromination rate constants offers the advantages of allowing the reaction to be carried out under first-order conditions (hydrocarbon concentration in large excess of bromine concentration), ensuring that the concentrations of the reactants are sufficiently low so as not to change the reaction medium, and eliminating the necessity of knowing accurately the initial bromine concentration.

Furthermore, the low initial bromine concentration, *ca.* 10^{-3} *M*, minimizes the possible contribution of any kinetic terms higher than first order in bromine concentration.[36–39]

In brominations in acetic acid and aqueous acetic acid, apparent kinetic terms higher than first order in bromine have been encountered. Such terms have been suppressed by the use of low initial concentrations of bromine and the addition of sodium bromide.[36–39] Sodium bromide, in about tenfold excess over initial bromine concentration, also was added in many of the kinetic runs made in this work. The change in absorbancy of Br_3^-, which has a very large extinction coefficient[32] and arises in small amount from the equilibrium of eq 4, afforded a convenient method of following the reaction rate.[39] Readings of the optical density at 280–300 mμ were taken for at least two half-lives, and the stable final readings (D_∞) taken around ten half-lives. Values of k_{obsd}, duplicable to better than 2%, were extracted from the visual slopes of the first-order plots of log ($D - D_\infty$) against time, which were linear for at least two half-lives. Values of k_2, the second-order rate coefficient, were obtained by applying the equation $k_{\text{obsd}} = k_2[\text{ArH}]_0/(1 + K_4[\text{Br}^-])$. Under the conditions used, only a small fraction of the stoichiometric bromine was tied up in the form of tribromide ion (eq 4). In most runs in which sodium bromide was added, the initial concentration of bromine was less than 10^{-3} *M*, and the sodium bromide concentration was 7.29×10^{-3} *M*, 7.09×10^{-3} *M*, and 1.53×10^{-2} *M*, in 78.3, 86.1, and 93.3% trifluoroacetic acid, respectively. Under these conditions, the correction term $[\text{Br}_2]/\text{Br}_2]_{\text{stoich}} = 1/(1 + K_4[\text{Br}^-])$ was 0.965, 0.98, and 0.99 in 78.3, 86.1, and 93.3% trifluoroacetic acid, respectively.[40]

In later kinetic runs, sodium bromide was omitted and the initial bromine concentration was maintained sufficiently high (up to 3.8×10^{-3} *M*) so as to enable the following of a significant change in bromine absorption ($\lambda_{\max}$ 410 mμ (ϵ 160)). Under these conditions, a negligible proportion of the stoichiometric bromine was in the form of tribromide ion.[40] First-order plots of log ($D - D_\infty$) against time were linear for at least two half-lives for toluene, *t*-butylbenzene, and neopentylbenzene in 78.3, 86.1, and 93.3% trifluoroacetic acid, and for benzene in 93.3% trifluoroacetic acid. Furthermore, the values of k_2 were within 2% of the values of k_2 for the corresponding kinetic runs in which excess sodium bromide had been added. Average values of k_2, obtained by both methods, are given in Table II.

Table II. Values of $k_2 \times 10^4$ (l. mol^{-1} sec^{-1}) for Total Monobromination of RC_6H_5 at 25°[a–c]

CF_3CO_2H, wt %	H	Me	*t*-Bu	Neop
78.3	0.110[d] (0.5)[e]	433	377	302
86.1[f]	0.0504[g] (0.1)[e]	395	398	327
93.3	0.0356	303	352	281

[a] Average values of $k_2 = k_{\text{obsd}}[\text{ArH}]_0/(1 + K_4[\text{Br}^-])$, duplicable to 2% or better. At least two determinations were made in presence of sodium bromide, at least one in absence of sodium bromide. [b] Except for benzene in 78.3 and 86.1% trifluoroacetic acid, the same k_2 values were obtained with bromine alone ($\sim 3 \times 10^{-3}$ *M*) as with sodium bromide ($\sim 10^{-2}$ *M*) and bromine ($\sim 10^{-3}$ *M*). [c] Hydrocarbon molarities: benzene, 0.1; alkylbenzenes, 0.03. [d] Value in presence of 7.29×10^{-3} *M* sodium bromide, with $[\text{Br}_2]_0 = 7 \times 10^{-4}$ *M*. When 3.2×10^{-2} *M* sodium bromide was used, the value decreased to 0.060. [e] Value in parentheses is initial k_2 in the absence of added sodium bromide, with $[\text{Br}_2]_0 \sim 3 \times 10^{-3}$ *M*. [f] Reported values of $k_2 \times 10^4$ in 87% trifluoroacetic acid, obtained titrimetrically and in the absence of added bromide ion are: benzene, 0.144; toluene, 363.[29] [g] Value in presence of 7.09×10^{-3} *M* sodium bromide, with $[\text{Br}_2]_0 = 5 \times 10^{-4}$ *M*. When 3.1×10^{-2} *M* sodium bromide was used, the value decreased to 0.045.

In the bromination of benzene in 78.3 and 86.1% trifluoroacetic acid in the absence of added sodium bro-

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(33) M. Krejci and J. Janak, *Chemie* (Prague), 10, 264 (1958).

(34) J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

(35) D. F. Gurka and W. M. Schubert, *J. Org. Chem.*, 31, 3146 (1966).

(36) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, England, 1959, Chapter 9.

(37) V. P. Zimmerman and E. Berliner, *J. Am. Chem. Soc.*, 84, 3953 (1962).

(38) E. Grovenstein, Jr., and U. V. Henderson, Jr., *ibid.*, 78, 569 (1956).

(39) E. M. Arnett and G. B. Klingsmith, *ibid.*, 87, 1032 (1965).

(40) In the kinetic runs in which sodium bromide was not added, the term $[\text{Br}_2]/[\text{Br}_2]_{\text{stoich}} = 1/(1 + K_4[\text{Br}^-])$ could be neglected. Based on the maximum initial concentration of bromine used in any of the runs (3.8×10^{-3} *M*) and $K_4 = 5$, the minimum value of $1/(1 + K_4[\text{Br}^-])$ at one half-life in 78.3% trifluoroacetic acid was greater than 0.99. In 86.1 and 93.3% trifluoroacetic acid, K_4 is smaller, and hence an even smaller fraction of stoichiometric bromine was in the form of tribromide ion.

mide, kinetic complexities were encountered. The first-order rate plots (C_6H_6 = 0.1 *M*, $[Br_2]_0 \sim 3 \times 10^{-3}$ *M*) were badly curved (decreasing apparent k_{obsd}), more so in 78.3% trifluoroacetic acid. On the other hand, when excess sodium bromide was added, the first-order plots were linear over the entire period the reaction was followed, two to two and one-half half-lives. Moreover, the values of k_2 obtained in the presence of excess sodium bromide were less than the initial values of k_2 (*ca.* 10% reaction) obtained in the absence of sodium bromide, especially in 78.3% trifluoroacetic acid. Also, the k_2 values decreased on addition of more sodium bromide, more so in 78.3% than in 86.1% trifluoroacetic acid (see Table II for values). No such effects were encountered in the bromination of benzene in 93.3% trifluoroacetic acid, or in the brominations of the alkylbenzenes in any of the three solvents.

Due to a slow volatilization of bromine, it was necessary to carry out the brominations of the very slowly reacting benzene in sealed rather than stoppered Beckman cells. In tightly stoppered cells, blank solutions of bromine or bromine and sodium bromide in 78.3 to 93.3% trifluoroacetic acid lost as much as 10% in absorbancy over a period of a week.[31] In *sealed* cells, there was no change in absorbancy of the blank solutions throughout the wavelength scale over a period of 3 months at 25°. The use of stoppered cells, though of no consequence in the relatively fast brominations of the alkylbenzenes (half-lives of about 15 min) would constitute a serious source of error in the bromination of benzene, which has a half-life of 23 days in 93% trifluoroacetic acid. For the brominations of benzene carried out in sealed cells, readings of the optical density were made for at least two half-lives. It was assumed that $D_\infty = 0$ at the wavelengths used since (1) neither the excess benzene (0.1 *M*) nor the bromobenzene ($[ArBr]_\infty \sim 10^{-3}$ *M*) had any absorbancy at these wavelengths, and (2) in the faster runs on alkylbenzenes, the optical density at ten half-lives reached a value corresponding to the excess alkylbenzene absorbance, which was very low at 280–330 mμ and zero at 400–420 mμ. The resulting linear plots of log $(D - D_\infty)$ against time for each of the wavelengths were parallel and k_{obsd} checked within 2% on duplicate runs.

Photocatalytic bromination, absent in other instances,[29,39,41,42] also was shown to be absent here. Rate constants for the bromination of toluene were the same when the reaction cell was exposed to the ultraviolet light beam during the entire kinetic run as when the light beam was on only during the brief times of reading the optical density.

Isomer Ratios. Isomer distributions obtained in halogenations are listed in Table III. Duplicate analyses were carried out on each product mixture, and in trifluoroacetic acid, two brominations were carried out on each compound.

Table III. Isomer Distributions in the Bromination of RC_6H_5 at 25° [a,b]

Solvent	R	% *ortho*	% *para*
78.3% TFA[c,d]	Me	18.2 ± 0.5	81.8 ± 0.5
	t-Bu[e]	0	100
	Neop	3.3 ± 0.2	96.7 ± 0.2
93.3% TFA[c]	Me	17.0 ± 0.4	83.0 ± 0.4
	t-Bu[e]	0	100
	Neop	3.9 ± 0.4	96.1 ± 0.4
100% TFA[f]	Me	17.6	82.4
	t-Bu	0	100
85% HOAc	Me[g]	32.9	66.8
	t-Bu[g]	1.2	97.4
	Neop	8.5 ± 0.2	91.5 ± 0.2
100% HOAc, Fe catalyst	Neop	8.9 ± 0.2	91.1 ± 0.2
100% HOAc, $ZnCl_2$ catalyst	Neop	8.8 ± 0.4	91.2 ± 0.4

[a] Except where noted, the values were obtained in these laboratories and the quoted experimental errors are maximum deviations from the average. The values in 78.3 and 93.3% trifluoroacetic acid are averages of four determinations, two on each of two separate reaction mixtures. The value for neopentylbenzene in the acetic acid solvents are averages of two determinations on one reaction mixture. [b] No detectable *meta* isomer except where noted. [c] Approximate molarities: Br_2, 0.03; NaBr, 0.09; ArH, 0.10. [d] Reported values for toluene in 87% trifluoroacetic acid are 17.5% *ortho* and 82.5% *para*.[29] [e] No detectable *ortho* or *meta* isomer by nmr, vpc, and ir. [f] Literature values.[29] [g] Literature values: *m*-bromotoluene, 0.3%; *m*-bromo-*t*-butylbenzene, 1.4%.[48]

Discussion

Kinetics and Mechanism of Bromination. In all three solvents, 78.3, 86.1, and 93.3% trifluoroacetic acid, bromination of the alkylbenzenes was cleanly first order in bromine, regardless of whether excess sodium bromide was added or not. Furthermore, for each alkylbenzene, the values of the second-order rate coefficient, k_2, were the same, within 2%, either in the presence or absence of added sodium bromide. It can be concluded that the electrophilic species is probably molecular bromine and that the rate-controlling step is formation of the arenonium ion (eq 2). The same conclusion can be made for the bromination of benzene in 93.3% trifluoroacetic acid, since here also the bromination was cleanly first order in bromine in either the presence or absence of added sodium bromide, and the values of k_2 obtained under the two conditions were identical.

The velocity expression for rate-controlling arenonium ion formation is given by eq 6. Equation 6 is a simplification, under the condition $k_3 \gg k_{-2}[Br^-]$, of the more general expression of eq 5. Equation 5 is derived on the basis of assuming a steady-state concentration for the intermediate arenonium ion. Both equations contain the term $1/(1 + K_4[Br^-])$ which corrects for any significant reduction, *via* equilibrium 4, in the relative concentration of molecular bromine. Under the conditions used herein, this term was near unity for the brominations carried out in the presence of excess sodium bromide, and was practically unity for the brominations carried out in the absence of added bromide ion.[40]

$$ArH + Br_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArHBr^+ + Br^- \qquad (2)$$

$$ArHBr^+ + \text{solvent bases} \xrightarrow{k_3} ArBr \qquad (3)$$

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

$$K_4 = [Br_3^-]/[Br_2][Br^-] \qquad (4)$$

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(41) R. M. Keefer, J. H. Blake, and L. J. Andrews, *J. Am. Chem. Soc.*, **76**, 3062 (1954).

(42) R. F. W. Ciecіuch and F. H. Westheimer, *ibid.*, **85**, 2591 (1963).

$$-\mathrm{d}[\mathrm{Br}_2]_{\mathrm{stoich}}/\mathrm{d}t = \frac{1}{1 + K_4[\mathrm{Br}^-]}\,\frac{k_2\,k_3[\mathrm{ArH}][\mathrm{Br}_2]}{k_{-2}[\mathrm{Br}^-] + k_3} \quad (5)$$

when $v_3 \gg v_{-2}$

$$-\mathrm{d}[\mathrm{Br}_2]_{\mathrm{stoich}}/\mathrm{d}t = \frac{1}{1 + K_4[\mathrm{Br}^-]}k_2[\mathrm{ArH}][\mathrm{Br}_2] \quad (6)$$

$$-\mathrm{d}[\mathrm{Br}_2]_{\mathrm{stoich}}/\mathrm{d}t = \frac{1}{1 + K_4[\mathrm{Br}^-]}(k_{\mathrm{I}}[\mathrm{Br}_2] + k_{\mathrm{II}}[\mathrm{Br}_2]^2 + k_{\mathrm{III}}[\mathrm{Br}_2]^3 + \ldots) \quad (7)$$

Only the bromination of benzene in 78.3 and 86.1% trifluoroacetic acid in the absence of sodium bromide showed kinetic complications. In the presence of about a tenfold excess of added sodium bromide over initial bromine and with the benzene concentration in large excess of the initial bromine concentration, the first-order rate plot was linear for the entire time that the reaction was followed (two to two and one-half half-lives). However, in the absence of added sodium bromide, the first-order plots were badly curved upwards, particularly in 78.3% trifluoroacetic acid. Furthermore, with the same concentration of excess benzene, the initial slopes of the latter plots exceeded the slopes of the first-order plots obtained in the presence of excess sodium bromide, by a factor of about 5 in 78.3% trifluoroacetic acid and about two in 86.1% trifluoroacetic acid (Table II). In other words, the initial apparent reaction order was greater than one and decreased as bromination proceeded. The behavior of benzene in these solvents is consistent with the mechanism of eq 2 and 3, and the rate expression 5, provided that there is significant reversal of the step of arenonium ion formation.

A priori, there are three conceivable explanations for the complex behavior, in the absence of added sodium bromide, of the bromination of benzene in 78.3 and 86.1% trifluoroacetic acid. These are: (1) a significant decrease during reaction in $[\mathrm{Br}_2]/[\mathrm{Br}_2]_{\mathrm{stoich}} = 1/(1+ K_4[\mathrm{Br}^-])$, due to the buildup in bromide ion concentration; or (2) the significant formation of transition states containing the elements of more than one bromine molecule; or (3) a significant reversal, as bromide ion is being formed, of the arenonium ion formation process represented by eq 2. Neither of the first two explanations appear to apply.

The first possibility, that of a significant decline in $1/(1 + K_4[\mathrm{Br}^-])$ during bromination in the absence of added excess sodium bromide, is ruled out by the fact that $K_4[\mathrm{Br}^-]$ remains very small with respect to unity throughout.[40] In other words, since the initial bromine concentration was very small ($\sim 3 \times 10^{-3}$ *M*) and the experimentally determined equilibrium constant, K_4, has a relatively small value in the trifluoroacetic acid solutions, a negligible fraction of stoichiometric bromine was in the form of tribromide ion during a kinetic run. Furthermore, under identical conditions (excess ArH, no added sodium bromide), the brominations of the alkylbenzenes were cleanly first order for at least two half-lives.

Kinetic complexity of the sort found here for benzene, *i.e.*, apparent decreasing reaction order during a kinetic run, has frequently been encountered in molecular brominations of aromatic compounds in other solvents. This has been ascribed to higher kinetic terms in the concentration of molecular bromine, as expressed in eq 7. The literal interpretation has been that bromination proceeds through various competing transition states, one containing the elements of one bromine molecule, another the elements of two bromine molecules, and so on (see ref 36 and 37, and references cited therein). Such an interpretation does not appear to be applicable to the bromination of benzene in 78.3 and 86.1% trifluoroacetic acid. Since the equilibrium constant for tribromide ion formation is small in these solvents, it was possible to add a tenfold excess of sodium bromide over bromine and still maintain the initial concentration of free molecular bromine relatively high.[40] In 78.3% trifluoroacetic acid containing tenfold excess sodium bromide, the kinetics was clearly first order when the initial concentration of free molecular bromine was as great as 3.4×10^{-3} *M*. In the absence of added sodium bromide, curvature of the first-order plots was very pronounced even when the initial molecular bromine concentration was somewhat lower than this (3.0×10^{-3} *M*). Thus, if the kinetic complications in the absence of sodium bromide had been due to reactions in which the transition state contains the elements of more than one molecule of bromine, one would not have expected the apparent higher order kinetic terms to have been suppressed by the addition of excess sodium bromide.[43]

The simple two-step mechanism of eq 2 and 3 accounts reasonably for the kinetic behavior of the brominations of benzene, with and without added sodium bromide. In the absence of excess sodium bromide, the term $k_{-2}[\mathrm{Br}^-]$ in eq 5 is increasing during the course of bromination. Provided the value of this term grows to significance relative to k_3, a curvature of the rate plots in the absence of added excess bromide ion would be expected. The relative constancy of this term in the presence of added excess sodium bromide, of course accounts both for the first-order kinetics and the decreased initial rate under the latter conditions. Finally, it can be shown that eq 5, with $k_{-1}[\mathrm{Br}^-]$ a variable, can be converted to an equation of the form of 7, with k_{I}, k_{II}, etc. being equal to complex constants.[44] Indeed, the fact that eq 5 and 7 are equivalent raises the question of whether or not the simple mechanism of eq 2 and 3, with $k_{-2}[\mathrm{Br}^-]$ becoming significant relative to k_3 as bromination proceeds, applies to at least some of the previously encountered instances of complex aromatic bromination kinetics.[45]

Selectivity of the Bromination. Values of p_f^{Me}, derived from the rate constants of Table II and the isomer distributions of Table III, are listed in Table IV. The single p_f^{Me} value listed for 93.3% trifluoroacetic acid is

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(43) This argument assumes that there is no inordinate salt effect by sodium bromide acting to greatly decrease rate constants for formation of transition states containing more than one bromine molecule relative to the rate constant for forming a transition state containing just one molecule of bromine.

(44) The term $1/(k_2[\mathrm{Br}^-] + k_3)$ of eq 5 can be converted to the form $(C_1 - C_2[\mathrm{Br}_2])^{-1}$, by expressing $[\mathrm{Br}^-]$ in terms of $[\mathrm{Br}_2]$ as the only variable. Since $(C_1 - C_2[\mathrm{Br}_2])^{-1}$ expands to give a power series in $[\mathrm{Br}_2]$, eq 5 is equivalent to eq 7.

(45) This possibility is being actively explored in these laboratories.

Table IV. Values of p_f^{Me} and Relative Rate Constants for *ortho* and *para* Bromination at 25°[a]

CF_3CO_2H, wt %	p_f^{Me}	$k_{p\text{-Neop}}/k_{p\text{-Me}}$	$k_{p\text{-}t\text{-Bu}}/k_{p\text{-Me}}$	$k_{o\text{-Neop}}/k_{o\text{-Me}}$
78.3	19,300 (4000)[b]	0.82	1.06	0.13
86.1[c]	38,700 (19,000)[b,d]	0.97	1.22	0.07
93.3	42,400	1.07	1.40	0.21
100[e]	12,700	...	1.52	...

[a] All values except p_f^{Me} in 78.3 and 86.1% trifluoroacetic acid are independent of whether or not sodium bromide was added (see footnote *b* of Table II). [b] The first value of p_f^{Me} in this solvent is based on the first-order k_{obsd} for benzene in the presence of excess sodium bromide (see footnotes *d* and *g* of Table II). The second, approximate, value in parentheses, is based on the initial k_{obsd} for benzene in the absence of sodium bromide (see footnote *e* of Table II). [c] Relative rates based on assumption that isomer distributions are half-way between those found in 78.3 and 93.3% trifluoroacetic acid. [d] Reported value in 87% trifluoroacetic acid, no added bromide ion, is 12,400.[29] [e] Data of ref 29.

for rate-controlling arenonium ion formation (eq 2). In 78.3 and 86.1% trifluoroacetic acid, the value of k_2 for benzene ($k_2 = k_{obsd}/[C_6H_6]$), but not for any of the alkylbenzenes, depended on whether or not excess sodium bromide had been present. Consequently, two values of p_f^{Me} are listed for these solvents. The latter value, in parentheses, is only approximate. It is based on the initial slope of the curved first-order plot for bromination of benzene in the absence of sodium bromide (benzene concentration in excess). However, the latter value probably more nearly represents p_f^{Me} for rate-controlling arenonium ion formation (see the preceding section of the Discussion). In either event, it is clear that p_f^{Me} is very large and increases at least somewhat between 78.3 and 93.3% trifluoroacetic acid. In fact, the unambiguous value of 42,400 in 93.3% trifluoroacetic acid is by far the largest rate-enhancing effect of a *p*-methyl substituent that has been reported.[46]

High selectivity between substitution on toluene and *para* substitution on benzene is generally associated with high selectivity between *para*, *ortho*, and *meta* positions.[47] This also is true here. Thus, there was no detectable *meta* bromination of any of the alkylbenzenes. Furthermore, there was no detectable *ortho* bromination of *t*-butylbenzene, although in 85% acetic acid, a detectable amount (1.2%) occurs.[48] Also, the percentage of *ortho* bromination of toluene and neopentylbenzene is appreciably less in trifluoroacetic acid solution than in acetic acid solutions (Table III). This very high selectivity indicates that the transition state lies relatively close to the arenonium ion intermediate, *i.e.*, that the positive character in the ring moiety of the transition state is relatively large. This may be in part due to the ability of the highly acidic solvent to stabilize, by hydrogen bonding, the developing bromide ion of the transition state.[49] The implication of the high selectivity is that both the electron demand on the substituent and the demand for nucleophilic solvation of the ring moiety are relatively high in the transition state.

Relative Partial Rate Factors. Rate constants for *ortho* and *para* bromination of neopentylbenzene and for *para* bromination of *t*-butylbenzene, relative to those for toluene, are listed in Table IV. Values of $k_{o\text{-}t\text{-Bu}}/k_{o\text{-Me}}$ as well as $k_{m\text{-}t\text{-Bu}}/k_{m\text{-Me}}$ and $k_{m\text{-Neop}}/k_{m\text{-Me}}$ could not be obtained because *ortho* bromination of *t*-butylbenzene and *meta* bromination of *t*-butylbenzene and neopentylbenzene could not be detected. The main features of the relative rate data are: (1) the absence of a Baker–Nathan effect in any of the trifluoroacetic acid solutions; (2) the increase in both $k_{p\text{-}t\text{-Bu}}/k_{p\text{-Me}}$ and $k_{p\text{-Neop}}/k_{p\text{-Me}}$ with decreasing water content of the solvent; and (3) the corresponding increase in $k_{o\text{-Neop}}/k_{o\text{-Me}}$. These results are not only contradictory to the Baker–Nathan hypothesis,[23] but illustrate once again the importance of solvent in modifying the relative kinetic parameters of alkyl compounds.

When the transition state places a high electron demand on the substituent, the prediction of the Baker–Nathan hypothesis is that the methyl compound should have the largest rate constant.[11] In other words, the hypothesis requires that α-C–H hyperconjugation, when not sterically inhibited, increase more than other modes of electronic stabilization as the electron demand on the alkyl substituent is increased, and to be dominant when this demand is large. For the brominations in the trifluoroacetic acid solutions, the values of p_f^{Me}, which are a measure of the electron demand on the substituent are orders of magnitude greater than for many other reactions in which the Baker–Nathan effect is observed.[26] Thus, the finding that $k_{p\text{-}t\text{-Bu}}$ is greater than $k_{p\text{-Me}}$ in these brominations is unexpected in terms of the Baker–Nathan hypothesis. Also unexpected in terms of this hypothesis, is the fact that $k_{p\text{-Neop}}$ is comparable to $k_{p\text{-Me}}$ despite possible inhibition of C–H hyperconjugation in the neopentyl substituent.

The effect on the relative partial rate factors of varying the water content of the trifluoroacetic acid solutions is even less consistent with the Baker–Nathan hypothesis. In proceeding from 78.1 to 93.3% trifluoroacetic acid, the electron demand on the substituent, as measured by p_f^{Me}, increases somewhat. Yet $k_{p\text{-}t\text{-Bu}}/k_{p\text{-Me}}$ and $k_{p\text{-Neop}}/k_{p\text{-Me}}$ show a steady increase, in contradiction to the Baker–Nathan hypothesis.

It is evident that the behavior of the relative rates for *para* bromination requires that the role of the solvent be given specific consideration. The results are consistent with the solvent role that is assigned in the Schubert–Sweeney hypothesis.[24] According to this hypothesis, specific nucleophilic solvation near the alkyl substituent is subject to steric hindrance by bulky alkyl substituents such as *t*-butyl and neopentyl. Since in aromatic bromination, the ring moiety is much more electron deficient in the transition state than in the ground state, this presumably would act in the direction of increasing the relative free energy of activation for *t*-butylbenzene and neopentylbenzene.[11] Thus, in terms of this hypothesis, the increase in $k_{p\text{-Neop}}/k_{p\text{-Me}}$ and $k_{p\text{-}t\text{-Bu}}/k_{p\text{-Me}}$ as the water content of the solvent is decreased is a reflection of the decrease in the ability of the

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(46) By way of contrast, the value of p_f^{Me} for molecular bromination in 85% acetic acid at 25° is 2420,[28] previously considered to be a rather large value. Substantially smaller rate enhancements by *p*-methyl are found in solvolysis reactions, which generally exhibit a Baker–Nathan effect[26] (*e.g.*, see Table I).

(47) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(48) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5615 (1959)

(49) Solvent stabilization of bromide ion relative to tribromide ion also could account for the much smaller value in trifluoroacetic acid than in acetic acid of K_4 (eq 4) for formation of tribromide ions.

solvent to participate in nucleophilic solvation.[50]

The highest reported value of $k_{p\text{-}t\text{-Bu}}/k_{p\text{-Me}}$ for aromatic bromination, 1.52, was obtained in anhydrous trifluoroacetic acid.[29] This could be considered as reflecting more closely the inherent electronic effects of the *t*-butyl and methyl substituents since nucleophilic solvation of the transition state should be least important in this very acidic solvent. The fact that the Baker–Nathan effect is not found even in 78.3% trifluoroacetic acid would indicate that this solvent is still weakly basic.[51] The stoichiometric molar ratio of water to trifluoroacetic acid is small, 1.76. Furthermore, the degree of protonation of water is probably extensive, and hydration of the hydronium ion further reduces the availability of water for nucleophilic solvation of the transition state.

A very low value of $k_{p\text{-}t\text{-Bu}}/k_{p\text{-Me}}$, 0.33, has been found at 25° in the much more basic solvent, 85% acetic acid.[28] This observation also is consistent with the Schubert–Sweeney hypothesis, assuming that the greater ability of this solvent to participate in nucleophilic solvation is not offset by the decrease in demand for such solvation, as reflected by the smaller value, 2420, of p_f^{Me}.

If steric hindrance to specific solvation of electron-deficient sites adjacent to the neopentyl or *t*-butyl substituent is a factor in *para* bromination, then it also should be a factor in *ortho* bromination. Indeed *ortho* bromination could be more sensitive to this factor insofar as an electrophile entering the *ortho* position could more than additively contribute to solvent shielding near the substituent. In agreement with this, the ratio $k_{o\text{-Neop}}/k_{o\text{-Me}}$ increases appreciably with decreasing water content of the solvent (Table IV). Furthermore, the steepness of this increase in $k_{o\text{-Neop}}/k_{o\text{-Me}}$ exceeds that of $k_{p\text{-Neop}}/k_{p\text{-Me}}$. However, the values of $k_{o\text{-Neop}}/k_{o\text{-Me}}$ are not as reliable simply because of the inevitably larger *percentage* error in measuring the small extent of *ortho* bromination, especially for neopentylbenzene which gives only 3–4% *o*-bromo product. Thus, not too much significance should be attached to the fact that the recorded values for $k_{o\text{-Neop}}/k_{o\text{-Me}}$ increase to a greater extent than those for $k_{p\text{-Neop}}/k_{p\text{-Me}}$, although the extra increase is just outside of the maximum experimental deviation.

While the bromination results are entirely consistent with the Schubert–Sweeney hypothesis, it is to be emphasized that steric hindrance to nucleophilic solvation does not provide a unique rationalization of the results. Thus the postulate by Shiner that nucleophilic solvation of α-hydrogens acts to enhance C–H over C–C hyperconjugation[6] is equally applicable here, although perhaps not as satisfactory in other instances.[10b,d] Indeed, one can rationalize the particular results reported here without invoking either steric hindrance to nucleophilic solvation or solvent enhancement of C–H hyperconjugation. For example, *assume* that the transition states of the *t*-butyl and neopentyl compounds lie closer to the intermediate arenonium ion and bromide ion than does the transition state of the methyl compound. Assume further that the propensity of the solvent to stabilize the transition state by electrophilic solvation of the developing bromide ion increases with increasing per cent trifluoroacetic acid. This would then act in the direction of the experimental findings. Any nucleophilic solvation, in the absence of steric hindrance to nucleophilic solvation, would act in the opposite direction.

Transition-State *vs.* Ground-State Solvation. In placing emphasis, in this instance, on steric hindrance to *specific* nucleophilic solvation stabilization of the polar transition state *vs.* the nonpolar ground state, the Schubert–Sweeney hypothesis is not to be construed as requiring that the *total* enthalpy of solution of the transition state of the *t*-butyl compound be greater, in the algebraic sense, than that of the methyl compound. Nor does it require that the total differential enthalpy of solution of the transition states, $\Delta\bar{H}_s(t\text{-Bu}^{\ddagger}) - \Delta\bar{H}_s(\text{Me}^{\ddagger})$, increase as the solvent is changed to one in which there is a greater propensity for specific nucleophilic solvation of the electron-deficient transition state. The hypothesis does not, indeed can not, place restrictions on the behavior *per se* of either the differential enthalpies of the transition states or the ground states, *i.e.*, these quantities, or their change with solvent, can be positive or negative, large or small. All and everything that the hypothesis requires is that the *difference*, partial molal enthalpy of solution of the transition states less that of the ground states, be positive in any particular nucleophilic solvent; and, that this difference become greater, algebraically, as the solvent is changed to one in which there is a greater propensity for specific nucleophilic solvation. Nevertheless, it would be of interest to examine the behavior of enthalpies of solution of ground and transition states separately.

In principle, values in any particular solvent of differential enthalpies (or free energies or entropies) of solution of transition states cannot be determined by experiment, at least in the absence of gas phase data. However, the *change* in such quantities brought about by solvent change can be determined through measurements of both differential enthalpies of activation and differential partial molal heats of solution of the groundstates (*cf.* ref 53–55).[56] No direct data for alkyl compounds is presently available. However, Arnett has measured the relative partial molal *enthalpies* of solution of toluene and *t*-butylbenzene in both acetic acid and trifluoroacetic acid, and Stock and Himoe have measured the *free energies* of activation for *para* and *ortho* chlorination of these compounds in the same

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(50) The hypothesis that specific nucleophilic solvation near the substituent is important in governing the relative rate ratios of alkyl compounds does not deny the important role of specific electrophilic solvation, *e.g.*, of the developing bromide ion, in the over-all stabilization of the transition state. Indeed, if the transition states for say *t*-butylbenzene and toluene bromination lie at significantly different "distances" along the reaction coordinate, a changing extent of electrophilic solvation also could act to change the rate ratios.

(51) The value of the acidity function, H_0, is −1.3 in 78% trifluoroacetic acid, corresponding to that of about 27% perchloric acid. Furthermore, the H_0 value decreases only very gradually with decreasing per cent water.[52]

(52) J. E. B. Randles and J. M. Tedder, *J. Chem. Soc.*, 1218 (1955).

(53) R. A. Clement, J. N. Naghizadeh, and M. R. Rice, *J. Am. Chem. Soc.*, 82, 2449 (1960).

(54) S. Winstein and A. H. Fainberg, *ibid.*, 79, 5937 (1957).

(55) (a) E. M. Arnett, P. McC. Duggleby, and J. J. Burke, *ibid.*, 85, 1350 (1953); (b) E. M. Arnett and D. R. McKelvey, *ibid.*, 87, 1393 (1965); (c) E. M. Arnett, W. C. Bentrude, J. J. Burke, and P. McC. Duggleby, *ibid.*, 87, 1541 (1965); (d) E. M. Arnett, W. G. Bentrude, and P. McC. Duggleby, *ibid.*, 87, 2048 (1965).

(56) The treatment assumes that the internal structure of the transition states (bonding, charge distribution) is unaltered by the solvent change.

Table V. Relative Partial Molal Enthalpies of Solution of Toluene and *t*-Butylbenzene and Relative Free Energies of Activation for Chlorination[a]

	100% CF_3CO_2H	100% CH_3CO_2H
$\Delta\bar{H}_s(t\text{-Bu})^b$	1920 ± 20	540 ± 10
$\Delta\bar{H}_s(\text{Me})^b$	1130 ± 20	350 ± 10
$\Delta F^{\mp}_{p\text{-}t\text{-Bu}} - \Delta F^{\mp}_{p\text{-Me}}{}^c$	−227	425
$\Delta F^{\mp}_{o\text{-}t\text{-Bu}} - \Delta F^{\mp}_{o\text{-Me}}{}^c$	510	1410

[a] In calories per mole at 25°. [b] Arnett's values of partial molal enthalpies of solution.[55] [c] Values of Himoe and Stock for free energies of chlorination.[28]

two solvents. The data are reproduced in Table V.[57]

Strictly, free energy differences cannot be compared with enthalpy differences. However, one can use the data of Table V to calculate a probable lower limit of the change in differential enthalpy of solution of the transition states, by making the limiting assumption that the change in the differential enthalpy of activation is equal to the measured change in differential free energy of activation.[58a] On the basis of this assumption, the value of $\Delta\bar{H}_s(t\text{-Bu}^{\mp}) - \Delta\bar{H}_s(\text{Me}^{\mp})$ for *para* chlorination would be 52 cal/mol greater (lower limit) in acetic acid than in trifluoroacetic acid; for *ortho* chlorination, 300 cal/mol.[59] The happenstance that the (lower limiting) values of the differential partial molal heats of solution of the transition states change little with solvent might lead one to the superficial, and incorrect, conclusion that ground-state solvent effects alone are largely responsible for the Baker–Nathan effect[28] that arises in proceeding from trifluoroacetic to acetic acid. This would amount to considering the transition states as if they were in a vacuum. Instead, one is still forced to consider why the solvent effect on the transition states is so much different than on the ground states. In other words, in the final analysis, any reactivity postulate must account for the "fact" that the partial molal enthalpies of solution of the transition states increase substantially *relative to* those of the ground states. As a matter of interest, one can of course first examine the behavior of the differential enthalpies of solution of transition and ground states separately before considering the difference between the behaviors.

Consider firstly the nonpolar ground states. Arnett has presented ample evidence that the partial molal enthalpy of solution of nonpolar solutes in organic solvents largely represents heat required to break up ordered solvent structure in order to create a hole for the solute molecule; further, that the extent of disruption of solvent structure increases with the size of the solute and the orderdness of the solvent.[55] Thus, the greater relative partial molal heat of solution of *t*-butylbenzene than of toluene, in either solvent, is due to its greater volume. The larger value of $\Delta\bar{H}_s(t\text{-Bu}) - \Delta\bar{H}_s(\text{Me})$ in trifluoroacetic acid implies that introducing an inert solute causes a greater disruption of solvent structure in this solvent than in acetic acid.[58b]

Consider next the relative solute behavior of the transition states. Since the substituents are remote from the reaction center, the difference between the effective volumes of the two transition states is the same as that between the ground states (neglecting slight volume differences that may arise as the result of different extents of bond making and breaking). Thus, if the transition states were relatively inert bodies, as are presumably the ground states, one would expect the differential enthalpy of solution to change to practically the same extent as for the ground states, *i.e.*, one would expect to observe little solvent effect on the differential enthalpy of activation. Clearly then, some other solvation factor or factors must assume increased importance in the transition states, *and be largely responsible for the change in differential enthalpy of activation.* The most obvious factor is specific solvation, since the most obvious difference between the nature of the transition states and ground states is the much greater polarity of the former. In other words, *specific solvation* is logically largely responsible for relatively greater net stabilization (or lesser net destabilization) of the methyl transition state in the more nucleophilic solvent, acetic acid.[60] This is in complete accord with the Schubert–Sweeney hypothesis. However, as pointed out in the previous section of the Discussion, the hypothesis is not unique in being able to account for the greater relative specific solvent stabilization, in the more nucleophilic solvent, of the transition state of the methyl compound. Shiner's hypothesis of specific nucleophilic solvation of hyperconjugating α-hydrogens also is applicable here, as is the possibility of greater relative specific electrophilic solvation stabilization in trifluoroacetic acid of the transition state of the *t*-butyl compound. In any event, however, the conclusion is inescapable that the relative effect of alkyl substituents on experimental parameters of solution reactions is strongly a function of solvent effects *per se;* further, that the relative degree of *specific solvation*, especially of the more polar of the two states of a chemical transition, may play a decisive role.

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(57) The authors are indebted to Professors E. M. Arnett and L. M. Stock for making the data of Table V available to them.

(58) (a) It is likely that the change in differential enthalpy of activation is in the same direction as the change in differential free energy of activation, but of a greater magnitude, due to compensation effects.[10,12] Similarly, the differential partial molal free energy of solution would probably change less than the differential partial molal enthalpy.[55c,58b] (b) By the same token, this should lead to a greater differential partial molal entropy of solution in trifluoroacetic acid than in acetic acid, exerting a compensating effect on the partial molal free energy of solution.[55]

(59) For *ortho* as compared to *para* halogenation, the measured change in differential free energy of activation is less reliable due to the smaller fraction of *ortho* substitution.

(60) One may picture the enthalpy of solution of the transition states as the sum of enthalpies for two arbitrary thermodynamic processes: (1) disruption of solvent structure to create a hole for the solute and (2) reorientation of the solvent shell toward polar sites of the solute. The effect of the former on the change with solvent of the differential partial molal enthalpy of the transition states (comparable to that of the ground states) is, in this instance, approximately counterbalanced by the effect of the latter. This simplified picture is consistent with the observed smaller (less endothermic) relative partial molal enthalpy of solution of ionic compounds as compared to neutral solutes of comparable size.[55]