[Contribution for the Department of Chemistry of the University of Washington]

Concerning the Baker-Nathan Effect

W. M. SCHUBERT and W. A. SWEENEY

Received October 5, 1955

A critical review has been made of facts pertaining to the concept of C—H hyperconjugation as a predominant mode of electron release by alkyl groups when attached to an electron-demanding aromatic system. Existing data has been reinterpreted and apparent contradictions between physical and chemical data have been resolved in terms of the role of the solvent. It has been suggested that C—H hyperconjugation is relatively less important as a mode of electron release than hitherto generally presumed.

The view that C—H hyperconjugation is the predominant mode of electron release by alkyl groups when attached to a highly electron-demanding system has been seriously questioned recently.[1,2] The concept has been advanced, originally by Baker and Nathan,[3] as an explanation of certain rate and equilibrium data. Physical evidence, on the other hand, does not give support to this concept, and indeed, appears to contradict it. The authors have extended the idea of steric hindrance to solvation to explain the chemical data and make it consistent with the physical data.[1] Shiner[4] has suggested that the role of the solvent in the rate and equilibrium studies may be to enhance C—H hyperconjugation over C—C hyperconjugation (by hydrogen bonding of the solvent with the *alpha* hydrogens). Burawoy and Spinner have chosen to neglect the role of the solvent and consider the alkyl group as releasing electrons by an inductive mechanism only.[2] The Baker-Nathan effect then is ascribed to steric hindrance to bond shortening, which should be greater for *tert*-butyl than methyl.

There are several reviews on the subject of hyperconjugation.[5-8] In general, discussion here will be confined to aromatic systems, for which the C—H hyperconjugation and inductive effects are opposite in order.

PHYSICAL EVIDENCE

Bond lengths and resonance energies. Measured resonance energies are subject to too great an error to allow a distinction to be made between the stabilizing influence of various alkyl groups attached to an aromatic or unsaturated system.[8] The bond shortening found between methyl and unsaturated systems such as —C≡C— and —C≡N is attributable at least in part to a change in the hybridization of the bond between methyl and the unsaturated linkage (see ref. 8, p. 21). Unfortunately, the bond length to an unsaturated system has been measured only for methyl; hence, no comparison between alkyl groups is possible.

Dipole moments. The dipole of the alkylbenzenes are in the inductive order; Baker concludes that the inductive effect predominates here but feels that the spread between μ values is reduced by hyperconjugation.[8] That the inductive effect is predominant in this system is ascribed to the absence of a large demand for electron release by alkyl. Thus C—H hyperconjugative electron release is presumed to increase more rapidly with electron demand than inductive electron release, and finally become predominant. Other dipole moment studies are unfortunately too incomplete to allow definite conclusions.[8,9]

Ionization potentials. To quote Baker (ref. 8, p. 30), "it is therefore probable that the most abundant and trustworthy physical evidence for hyperconjugation would be found in phenomena which involve electron transitions from one state to another," *i.e.*, in ionization potential and UV spectral data. The first ionization potential of A is a measure of the energy of the reaction, A (gas) $\rightleftarrows$ A^+ (gas) + e. The ionization potential of benzene is lowered by the introduction of an alkyl substituent. Thus, an alkyl substituent stabilizes the excited state more than the ground state. According to the Baker viewpoint, C—H hyperconjugation should be the predominant effect in stabilizing a highly electron-demanding excited state, II, over the corresponding ground state, I. Yet the ionization potentials of Table I[10] are clearly in the inductive

TABLE I

Ionization Potentials of C_6H_5R

R	I (e.v.)
H	9.24
CH_3	8.92
CH_3CH_2	8.75
i-Pr	8.6
tert-Bu	8.5

---

(1) Sweeney and Schubert, *J. Am. Chem. Soc.*, **76**, 4625 (1954).

(2) Burawoy and Spinner, *J. Chem. Soc.*, 3752 (1954).

(3) Baker and Nathan, *J. Chem. Soc.*, 1844 (1935).

(4) Shiner, *J. Am. Chem. Soc.*, **76**, 1603 (1954).

(5) Crawford, *Quart. Revs.*, **3**, 226 (1949).

(6) Becker, *Angew. Chem.*, **65**, 97 (1953).

(7) Becker, *Fortschr. chem. Forsch.*, **3**, 187 (1955).

(8) Baker, *Hyperconjugation*, Oxford University Press, London, 1953.

(9) Hurdis and Smythe, *J. Am. Chem. Soc.*, **65**, 89 (1943).

(10) Price, *Chem. Revs.*, **41**, 257 (1947).

order. This order is confirmed by Walsh, *et al.*[11]

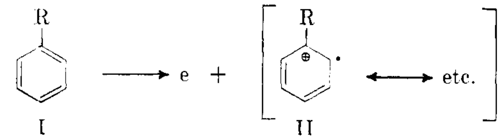
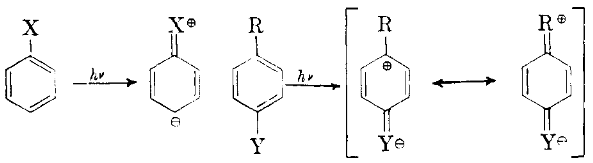

I II

TABLE II
POSITIONS IN Å OF 0,0 BAND OF C_6H_5R

R →	H	CH_3	Et	*i*-Pr	*tert*-Bu
0,0-band (Å)	2625	2663	2659	2653	2650

Absorption spectra. A slight decrease in wave length in proceeding from toluene to *tert*-butylbenzene is observed for the 0,0-band in the low intensity "B-band" region as shown in Table II.[12] This has been attributed to predominant C—H hyperconjugation controlling the energy of absorption[12,8] in this region. Objections have been raised to this interpretation by several authors.[11,13,14] Thus, Braude[14] points out that hyperconjugation "would not be expected to exert a dominant influence in the case of the B-bands which are due to almost non-polar transitions."[15] They refer to an alternative explanation by Walsh, *et al.*[11]

The ultraviolet absorption band referred to by Braude as the "E-band" (around 2100 Å for alkylbenzenes and 2500 Å for benzene substituted by NH_2, COR, NO_2, etc.) is due to excitation to a state with an increased contribution of dipolar structures, as symbolized by IV (see *e.g.*, ref. 14). There is a regular movement of the E-band to longer wave lengths as the ability of the substituents to displace electrons increases;[16] *i.e.*, the excited state is stabilized more than the ground state by increased conjugation power of X, and thus the excitation energy is decreased and the E-band wave length increased.[14] The location of the E-bands of toluene, ethylbenzene,[11,13] isopropylbenzene,[11] and *tert*-butylbenzene[14] are practically identical. If any trend is discernible it is toward higher wave length absorption for ethylbenzene than for toluene.[11,14] Thus, for a system in which a fairly large demand for electron release by alkyl is created, there is no evidence that this release is in the order expected for primary C—H hyperconjugation. According to Braude[14] this may indicate C—C hyperconjugation is as important as C—H hyperconjugation here, although he does not favor this point of view.


III IV V VI

The shift of the E-band to longer wave lengths is enhanced in *para* di-substituted benzenes in which one group is electron-attracting and the other electron-repelling.[16] Thus, the substitution of an electron-demanding group Y *para* to an alkyl group should increase the electron demand on the alkyl group in the excited state (VI), over that in the ground state (V). With the neutral compounds of type V in Table III, the trend is toward a slightly lower excitation energy (*i.e.*, increased λ_{max}) for *tert*-butyl as compared to methyl.[17] Moreover, for the positive ions of Table III, in which there is greatly increased demand in the excited state for electron release by alkyl, the excitation energies, instead of showing a Baker-Nathan effect, show a pronounced inductive *order*. Use of a wave-length scale rather than an energy scale (cm^{-1}) somewhat exaggerates the increased spread between methyl and *tert*-butyl observed with the positive ions.

CHEMICAL EVIDENCE

For the sake of clarity and brevity, attention will be confined to cases in which an activating effect clearly in the hyperconjugative *order* has been shown. There are actually few such clear cut examples. Most often cited are S_N 1 solvolysis reactions of benzhydryl halides and aromatic bromination and chlorination. Other examples of solvolysis reactions are quoted by Burawoy and Spinner.[2]

The hydrolysis of *p*-alkylbenzhydryl chlorides in 80% acetone shows a definite Baker-Nathan effect (Table IV).[18] In this reaction the electron demand in the transition state is large compared to that of the ground state. According to the Baker view, maximum opportunity for predominant hyperconjugation is afforded. Both the rates and activation energies are in the order expected for this effect. The entropies of activation were not calculated or discussed.[8,18]

A definite trend with ring size was found by Arnold[19,20] and by Baddeley[21] in the solvolysis of the compounds listed in Table V.

---

(11) Hammond, Price, Teegan, and Walsh, *Discussions Faraday Soc.*, **9**, 53 (1950).

(12) Matsen, Robertson and Choake, *Chem. Revs.*, **41**, 273 (1947).

(13) Platt and Klevens, *Chem. Revs.*, **41**, 301 (1947).

(14) Bowden and Braude, *J. Chem. Soc.*, 1068 (1952).

(15) This view is shared by Dr. W. T. Simpson of these laboratories (personal communication). For a theoretical description of the 2600 Å transition in benzene see Albrecht and Simpson, *J. Chem. Phys.*, **21**, 940 (1953).

(16) Doub and Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947); *J. Am. Chem. Soc.*, **71**, 2414 (1949).

(17) After this manuscript was submitted, an article by Burawoy and Spinner, *J. Chem. Soc.*, 2085 (1955), which confirms this trend, appeared.

(18) Hughes, Ingold and Taher, *J. Chem. Soc.*, 950 (1940).

(19) Arnold and Truett, *J. Am. Chem. Soc.*, **73**, 5508 (1951).

(20) Arnold, Dodson and Murai, *J. Am. Chem. Soc.*, **72**, 4193 (1950).

(21) Baddeley and Gordon, *J. Chem. Soc.*, 2190 (1952).

TABLE III

λ_{max} VALUES FOR E-BAND ABSORPTION; $pK_{R^\oplus}$ VALUES FOR ARYLCARBINOLS

Compound	λ_{max} mμ	ε
Nitrobenzene	260.0	8160
p-Methylnitrobenzene	274.6[a]	9400
p-tert-Butylnitrobenzene	274.7	9950
Acetophenone	242.0	13100
p-Methylacetophenone	253.0	14100
p-Isopropylacetophenone	253.5	15600
p-tert-Butylacetophenone	253.0	16600
Benzoic Acid	228.0	11830
p-Methylbenzoic Acid	236.5	14620
p-tert-Butylbenzoic Acid	237.5	16290
6-Acetylindan	258.0	13200
7-Acetylindan	258.5	13400
2-Acetyltetrahydrocycloheptabenzene	258.5	14400
2-Acetylhexahydrocyclooctabenzene	258.5	14400

Conjugate Acid of:	λ_{max} mμ	ε
p-Methylnitrobenzene	375.5	–
p-tert-Butylnitrobenzene	380.5	–
Acetophenone	295.5	21500
p-Methylacetophenone	312.5	24500
p-Isopropylacetophenone	315.0	24500
p-tert-Butylacetophenone	315.5	27100
Carbonium Ions	λ_{max}[b] mμ	$pK_{R^\oplus}$[b c]
$(C_6H_5)_3C^\oplus$	431	−6.63
$(p\text{-}CH_3C_6H_4)_3C^\oplus$	452	−3.56
$(p\text{-}i\text{-}PrC_6H_4)_3C^\oplus$	456	−6.54
$(p\text{-}tert\text{-}BuC_6H_4)_3C^\oplus$	458	−6.5[d]
$(C_6H_5)_2CH^\oplus$	442	−13.3[d]
$(p\text{-}CH_3C_6H_4)_2CH^\oplus$	472	−10.4[d]
$(p\text{-}tert\text{-}BuC_6H_4)_2CH^\oplus$	480	−13.2[d]
$p\text{-}CH_3C_6H_4C^\oplus(C_6H_5)_2$	450	−5.24
$p\text{-}tert\text{-}BuC_6H_4C^\oplus(C_6H_5)_2$	458	−6.1[d]

[a] The λ_{max} values for the alkyl nitrobenzenes, measured by the method used by Bayliss and Hulme, *Australian J. Chem.*, **6,** 257 (1953), are considered accurate within ±0.2 mμ. The other λ_{max} values (except for the arylcarbonium ions) are considered accurate within ±0.5 mμ. They were determined by inspection (1). [b] Data taken from Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, **19,** 155 (1954); Deno, Jaruzelski, and Schriesheim, *J. Am. Chem. Soc.*, **77,** 3044 (1955). [c] These values are for the equilibrium, $R^\oplus + H_2O \rightleftharpoons ROH + H^\oplus$ (Deno, *et al.*, *loc. cit.*). [d] Considered less accurate (Deno, *et al.*, *loc. cit.*).

TABLE IV

HYDROLYSIS OF $p\text{-}RC_6H_4CH(C_6H_5)Cl$ IN 80% ACETONE[a]

R →	H	Me	Et	*i*-Pr	*tert*-Bu
$10^1 k_1$ sec.$^{-1}$ (0°)	2.82	83.5	62.6	45.95	35.9
E_A (kCal)	21.0	18.9	19.4	19.8	20.05
$\Delta S\ddagger$	−8.9	−9.8	−8.6	−7.7	−5.6

[a] Hughes, Ingold, and Taher, *J. Chem. Soc.*, 950 (1940).

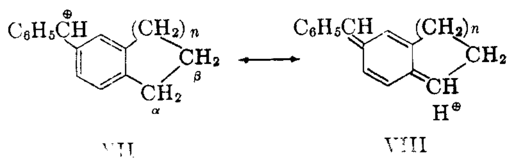
TABLE V

SOLVOLYSIS RATES AT 0° OF $C_6H_5CHClAr$

	In Ethanol[21]			In 80% Acetone[19]		
Derivative	10^5k^a (sec.$^{-1}$)	E_A (kCal)	$\Delta S^\ddagger$	10^6k^b (sec.$^{-1}$)	E_A (kCal)	$\Delta S^\ddagger$
A. 3,4-Dimethyl	18.0	17.0	−15.4	—	—	—
B. 3,4-Diethyl	11.4	18.9	− 9.3	—	—	—
C. 3,4-Cyclopento	23.3	17.3	−13.8	214	18.94	−8.0
D. 3,4-Cyclohexeno	17.9	18.1	−11.5	147	18.87	−9.0
E. 3,4-Cyclohepteno	15.1	18.2	− 9.3	105	19.40	−7.7

[a] Also determined at 20°. [b] Also determined at 25°.

Both workers interpreted their data in terms of steric inhibition of C—H hyperconjugation; *i.e.*, stabilization of the excited state (in which the ion VII is incipiently formed) by C—H hyperconjugative structures (VIII) is greater the nearer the coplanarity of the β-carbon and the aromatic nucleus. It is not quite clear how this view of the steric requirements of C—H hyperconjugation is reconciled with the view that hyperconjugation should be at a maximum when an *alpha* C—H bond lies perpendicular to the plane of the benzene ring.[22] It appears, from molecular models, that an *alpha* C—H should lie closest to a position perpendicular to the aromatic ring in compound D. No interpretation was made of the entropy data.[21]



VII VIII

Aromatic chlorination and bromination (Table VI) also show a pronounced spread between methyl and *tert*-butyl in the order of the number of *alpha* C—H bonds.[23,24] The data listed are for total

---

(22) Coulson, *Quart. Reviews*, **1,** 144 (1946).

(23) de la Mare and Robertson, *J. Chem. Soc.*, 279 (1943).

(24) Berliner and Bondhus, *J. Am. Chem. Soc.*, **68,**

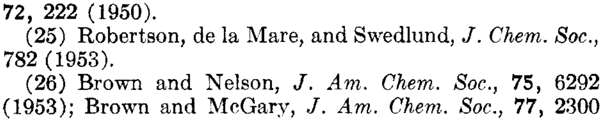
halogenation. However, since the relative rate of *para* bromination of toluene to *tert*-butylbenzene is 100:31,[25] the *para* halogenation rates no doubt also would show a definite Baker-Nathan effect. There is much less spread in rate constants for nitration of alkylbenzenes (ref. 8, p. 50). The partial rate factors for *para* nitration of toluene *vs.* *tert*-butylbenzene are 42/58, in opposition to the hyperconjugative order. This has been explained as due to a lesser electron demand in nitration than in bromination, thus reducing the relative importance of the C—H hyperconjugative effect to the point where the inductive effect predominates.[8] For a discussion of the relative "activities" of nitrating, brominating and other substituting species, [see 26,27].

ROLE OF THE SOLVENT

The apparent contradication between physical and chemical data can be resolved if the role of solvent stabilization is taken into account. The ionization potentials of the alkylbenzenes (Table I) were measured in the gas phase. A salient feature of the E-band spectral measurements (Table III) is that here again solvent influences are at a minimum. This is because there can be no reorientation of solvent molecules to minimize the energy of the excited state, VI, according to the Frank-Condon principles ([see *e.g.* 28]). This principle states that there is no movement of nuclei in the time of excitation by light.

By contrast, solvent stabilization probably plays a large role in affecting reaction rates in solution, since there is time for solvent re-orientation in going from ground to transition states. Changes in solvent stabilization in progressing from ground to transition state would be most pronounced when there is a change in charge and should be subject to steric hindrance.

Steric interference with solvent stabilization has been invoked in other studies. For example, Price and Lincoln[29] have suggested that one of the factors responsible for the rate of saponification of



IX

para- and especially *meta-tert*-butylbenzoate being slower than that of the corresponding methyl compound is a decrease in solvent stabilization of the ionic intermediate IX due to the bulk of *tert*-butyl as compared to methyl. It was also suggested that such a solvation effect may account for the similar influence of *tert*-butyl and neopentyl groups on the rates of bromination of alkyl benzenes.[29] Recently, Price has studied this effect in the saponification of *m*- and *p*-dialkylaminobenzoates.[30] Deno has suggested that the deviations found for tri-*p*-isopropyl and *tert*-butylphenyl carbinols in a plot of $pK_{R^\oplus}$ against the Hammett function *sigma* can be accounted for on the basis of steric hindrance to solvation.[31]

Solvolysis reactions of benzhydryl halides in polar solvent media should be sensitive to steric hindrance to solvation. Polarization of the ground state of the halides is small relative to the excited state, hence solvent orientation and stabilization is at the minimum. In the transition state, ionization to a carbonium ion is nearly complete. The positive charge is distributed, of course, throughout the molecule and *into the solvent* as well. That there is solvation at the benzhydryl carbon (as well as of the halide ion) is well accepted. However, only a portion of the plus charge of the transition state is centered there, the rest being distributed to the benzene rings (particularly to *o* and *p* positions) and to some extent to the alkyl substituent. Thus, it is certainly not inconceivable that orientation of solvent molecules toward the positive centers in the benzene rings may take place and have a measurable effect on the reaction. Solvation near the site of attachment of the alkyl substituent would be greatest for methyl and least for *tert*-butyl, because of greater steric interference with solvation in the latter. The effect of solvation would then be to increase the activation energy in the hydrolysis reaction of Table IV, for instance, in the order Me < Et < *i*-Pr < *tert*-Bu. Since solvent orientation would not be as great in the transition state of the *tert*-butyl as in the methyl compound, the entropy of activation due to solvation should decrease in the order *tert*-Bu > CH_3 (compare Table IV). Whereas the solvation energy would act to give the rate order, CH_3 > *tert*-Bu, the solvation entropy would act in the opposite direction. Therefore, changes of E_A/RT in the Eyring equation, $k = \frac{ekT}{h} e^{\Delta S^{\ddagger}/R} e^{-E_A/RT}$, must be greater than of $\Delta S^{\ddagger}/R$ for k to be decreasing in the order of E_A.

The magnitude of this solvation effect is difficult to predict, and there are, of course, many factors that contribute to the activation energy and entropy, hence also rate, differences of Table IV. However, steric hindrance to ring solvation would

---

2355 (1946); Berliner and Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949); Berliner and Berliner, *J. Am. Chem. Soc.*, **72**, 222 (1950).

(25) Robertson, de la Mare, and Swedlund, *J. Chem. Soc.*, 782 (1953).

(26) Brown and Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953); Brown and McGary, *J. Am. Chem. Soc.*, **77**, 2300 (1955).

(27) de la Mare, *J. Chem. Soc.*, 4450 (1954).

(28) Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(29) Price and Lincoln, *J. Am. Chem. Soc.*, **73**, 5836 (1951).

(30) Price and Belanger, *J. Am. Chem. Soc.*, **76**, 2682 (1954).

(31) Deno, Jaruzelski and Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

account nicely for the data. The Shiner view that hydrogen bonding of the solvent with the α-hydrogen of the alkyl group enhances C—H over C—C hyperconjugation[4] is equally attractive. However, it would appear difficult to account for the activation entropy differences on the basis of the explanation of Burawoy and Spinner.[2]

A consistent picture in terms of the solvation factor playing an important role can likewise be found for the data of Table V. In progressing from C to D to E and B, increased activation energy may be explained either on the basis of the steric requirements for C—H hyperconjugation or steric hindrance to ring solvation. The corresponding increase in activation entropy, however, appears to be unexplained by the former theory but agrees with the latter one. The Shiner view could also be applied here if it is assumed that as the ring size is increased, either the α-hydrogens become less exposed for hydrogen bonding with the solvent, or that the conformation for this sort of solvated conjugation becomes less favorable. From molecular models it appears that while one *alpha*-H becomes less exposed as the ring size is increased, the other alpha-H (the "equatorial" one) remains exposed to about the same degree. The *k* data of Arnold (Table V) also fit in with the concept of steric hindrance to solvation, although the E_A and $\Delta S^{\ddagger}$ values show no clear cut trend, either in terms of predominant C—H hyperconjugation or solvation. It is to be noted in Table III that the change in λ_{max} in proceeding from 6-acetylindan to 2-acetylhexahydrocyclooctabenzene is not in the direction expected according to the view of Baddeley or Arnold.

TABLE VI

RELATIVE RATES[23] OF (a) CHLORINATION AND (b) BROMINATION OF C_6H_5R IN 15% AQUEOUS ACETIC ACID AT 24°

R →	H	Me	Et	*i*-Pr	*tert*-Bu
(a)	0.29	100	84	51	32
(b)[a]	—	100	76	44	23

[a] The data of Berliner,[24] on a time of 10% reaction basis, are in close agreement.

TABLE VII

SOLVOLYSIS[33] OF *m*-ALKYLPHENYLDIMETHYLCARBINYL CHLORIDES IN 90% ACETONE AT 25°

R	$k \times 10^5$ sec.$^{-1}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H	12.4	18.8	−12.4
CH_3	24.8	18.6	−11.8
Et	24.1	19.2	−10.6
i-Pr	23.2	19.4	−10.2
tert-Bu	23.0	19.3	−10.6
p-CH_3	322	17.3	−12.0

Table VII lists some interesting data that may have a bearing on the steric hindrance to solvation idea.[32,33] Although the alkyl groups are *meta*, a mild Baker-Nathan effect is observed. Brown[34] and Berliner[35] feel that this is the result of a transmission to the *meta* position, in the highly electron-demanding transition state, of the C—H hyperconjugation effect. Operation of the normal inductive effect coupled with steric hindrance to solvation of the ring (*ortho* to the alkyl substituent) explains the rate data equally well. However, because of the slight activating effect of alkyl and the very small spread between alkyl groups, any conclusion may be unwarranted. Furthermore, the heats and entropies of activation for the various alkyl compounds are too close (*i.e.*, within experimental error) to allow interpretation.

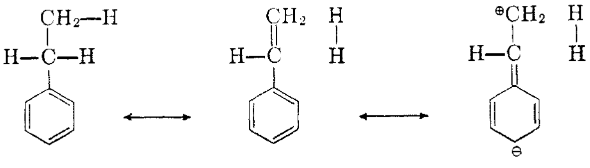
TABLE VIII

RELATIVE RATES OF BROMINATION OF ALKYLBENZENES[24]

R	Series I C_6H_5R	Series II $C_6H_5CH_2R$	Series III $C_6H_5CHRCH_3$
Me	100	100	100
Et	70	80	80
i-Pr	40	53	(71)
tert-Bu	18	30	—

The $pK_{R^{\oplus}}$ values for the ionization equilibrium between the triarylmethylcarbonium ions of Table III and the corresponding carbinols show a pronounced Baker-Nathan effect, although the λ_{max} values of the carbonium ions show the opposite order (Table III). In the carbonium ion as compared to the carbinol, there is a greatly increased demand for distribution of charge throughout the substrate molecule and into solvent molecules. The apparently contradictory $pK_{R^{\oplus}}$ and spectral results also are explainable in terms of steric hindrance to solvation.

Turning attention to the halogenation of alkyl benzenes, again the data fit the concept of a major role of solvation (Table VI). The solvation idea also is consistent with the data found for the bromination of ϕCH_2R (Table VIII) and other higher alkyl benzenes. The order in Series II of Table VIII, in which there is nearly as wide a spread in relative rates as in Series I, has been explained by Berliner on the basis of a "second-order" hyperconjugation effect illustrated by structures XI



X XI XII

---

(32) This data was kindly furnished by Dr. H. C. Brown prior to publication.

(33) Brown, *Fourth Conference on Reaction Mechanisms*, Bryn Mawr College, September, 1952.

(34) H. C. Brown, personal communication.

(35) Berliner and Berliner, *J. Am. Chem. Soc.*, **76**, 6179 (1954).

and XII.[24] From examination of Fisher-Taylor-Hirschfelder models, it appears that the solvent shielding effect of —CH_2R would be comparable to that of R. For example, while *tert*-butyl partially shields both sides of the benzene ring in the neighborhood of the alkyl group, the neopentyl group, while keeping one side relatively exposed, very effectively shields the other side. The α-hydrogens of the neopentyl group, on the other hand, appear to be relatively unshielded. Much of the rate data on bromination of higher alkyl benzenes could also be interpreted with the aid of the solvation idea, but since these systems are so complex, further speculation may be unwarranted.

A small isotope effect has been found in the rate of acetolysis of *p*-$CD_3C_6H_5CHClCH_3$ *vs.* the corresponding hydrogen compound, with $k_D = 1.04 \times 10^{-4}$ and $k_H = 1.14 \times 10^{-4}$ at 50°.[36] While indicating that CH_3 releases electrons better than CD_3, this result does not contribute to a solution of the problem of the inherent electron release tendencies of methyl *vs.* ethyl, isopropyl and *tert*-butyl.

It has been assumed that solvent stabilization plays a minimum role in determining the energy of the E-band transitions of the compounds of Table III. This assumption appears valid for at least the neutral compounds of type V, since solvent stabilization of the ground state would surely be principally around the functional group and hence not much influenced by the *para* alkyl group. On the other hand, solvent stabilization at ring positions of the ground state of the positive ions of Table III should be more important, since much of the charge would be distributed to the ring. The ground state of the *para* methyl compounds should therefore be stabilized more by solvation than that of the *tert*-butyl compounds. In the time of excitation by light, solvent nuclei do not move, although electronic polarization of the solvent is allowed. However, solvent molecules in a position to solvate the partial plus charge at or near the alkyl group in the ground state will still be in a position (though not the most favorable one) to solvate the *increased* positive charge in the neighborhood of the alkyl group in the excited state. Thus the solvent near the alkyl group may stabilize the excited state more than the ground state. Steric hindrance to solvation would then act to decrease the spread in λ_{max} between the methyl and *tert*-butyl compounds, provided that solvation by basic species in the neighborhood of the alkyl group is of any importance in the highly acidic media used.

MODES OF ELECTRON RELEASE BY ALKYL

It should be made clear that the position being taken is not that C—H hyperconjugation is necessarily of no consequence, although the concept is not needed to explain the data cited here. The viewpoint is simply this: if the role of the solvent as discussed is of importance then other modes of electron release by alkyl in the order *tert*-Bu > Me may be relatively more important, even when alkyl is attached to an electron-demanding system. Whether this would mean that the inductive effect, C—C hyperconjugation, or some other mode of interaction[37] in the *inductive* order has a greater relative role cannot be said.

SEATTLE 5, WASH.

---

[36] Lewis and Coppinger, *J. Am. Chem. Soc.*, **76**, 4495 (1954).

[37] Dr. W. T. Simpson of these laboratories has suggested that internal dispersion forces might qualitatively account for the inherent effects of alkyl substituents. For a discussion of such forces see Simpson, *J. Am. Chem. Soc.*, **73**, 5363 (1951).