THE INFLUENCE OF THE SOLVENT ON THE RELATIVE ELECTRON RELEASING CAPACITIES OF ALKYL GROUP

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The role that the solvent plays in shifting the balance between the two apparent mechanisms for electron release, inductive and hyperconjugative, by alkyl groups has not been explored until recently.

Hughes, Ingold, and Taher[1] found a definite Baker-Nathan order in 80% aqueous acetone and a less prominant Baker-Nathan order in ethanol in a study of the rates of solvolysis of *p*-alkyldiphenylmethyl chloride.

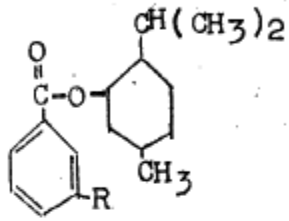
Berliner and coworkers[2] studied the alkaline hydrolysis of ethyl *p*-alkylbenzoates and found a Baker-Nathan order in 85% ethanol but an inductive effect order in 56% acetone. This was explained by Berliner as a change in mechanism of electron release due to the role of the solvent. Price and Lincoln[3] carried out a similar study in aqueous acetone and suggested that one of the factors responsible for the slower rate of saponification of *p*-t-Bu, and especially m-t-Bu compounds, than that of the corresponding methyl compound is a decrease in solvent stabilization of the ionic intermediate due to the bulk of the t-Bu group as compared to that of the methyl group.

Deno and coworkers[4] have studied the thermodynamic equilibrium constants for the reaction,

$$R^+ + H_2O \rightleftharpoons ROH + H^+$$

for twenty mono, di, and triarylcarbinols in water-sulfuric acid at 25° C and have suggested that the deviations found for tri-p-i-propylphenyl and *p*-t-butylphenyl carbinols in a plot of PK_{R^+} against the Hammett sigma function can be accounted for on the basis of steric hindrance to solvation due to the bulky alkyl group on the triarylcarbonium ions.

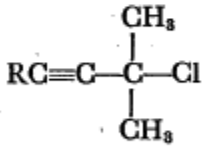
The bulky effect of large groups was also implied by Newman and Easterbrook[5] in discussing the results of their study of the rates of the sodium methoxide catalyzed methanolysis of *m*-alkyl-1-menthyl-benzoates.



(R=t-Bu, i-Pr, Et, Me, H)

The rates increased in the order H>(*m*-Me<*m*-Et<*m*-i-Pr<*m*-t-Bu), indicating a Baker-Nathan order of electron release by the alkyl groups. Newman and Easterbrook explained this as follows: when the two oxygen atoms of the ester group are coplaner with the ring, the m-t-Bu group interferes with the 1-menthyl group whereas in the m-methyl ester formed by the methanolysis this interference does not exist, so the reaction of the t-Bu ester is accompanied by release of strain. Moreover, release of strain should be greatest for the m-t-Bu ester and least for the m-methyl ester, with the result that the former would react more rapidly than the latter and, because electron release from the alkyl groups retards reaction, the hyperconjugative effect only appears to be operative, according to these authors[5].

In order to minimize such complications as the relief of the steric strain in the original halide accompanying ionization, Burawoy and Spinner[6] have studied the rates of unimolecular solvolysis and alkaline hydrolysis of 1,1-dimethylprop-2-ynyl chloride and its 3-alkyl derivatives.



(R=H, Me, Et, i-Pr, t-Bu)

The solvolysis was studied in 80% ethanol and the hydrolysis in wet formic acid. The rates of these unimolecular reactions in 80% ethanol decreased in the order R=Me>Et>i-Pr>t-Bu>>H, that is, the Baker-Nathan order. The authors' explanation is as follows: "the polarity of C-Hal bond in the original alkyl halide molecule $R{\cdot}CH_2{\cdot}Hal$ will increase and its energy of heterolytic fission will be reduced in the order of the increasing electron-donating inductive effect of the alkyl groups R (factor 1). On the other hands, in the cations $R\text{-}CH_2^+$ formed (or the transition state obtained during ionization) the contraction and stabilization of the

R-C^+ bond will be reduced by the steric repulsion, increasing with the size of the alkyl groups R (factor 2). The magnitude of the stabilization energy (and its reduction due to the steric inhibition of bond contraction) will increase as the effective nuclear charge at the C^+ atom increase. Factor 1 will facilitate ionization in the order Me<Et<i-pr<t-Bu, factor 2 in the reverse order. In the ionization of the alkyl halide, the latter factor is more important and therefore, a Baker-Nathan effect is observed[6]." The same authors felt that this idea was confirmed from a study of electronic spectra of diphenyl-acetophenone and its oxonium salt formed in conc. sulfuric acid, aniline, the phenoxide ion and some of their 4-alkyl derivatives, because of the absence in the electronic spectra of a hyperconjugative electron-release in the order t-Bu<i-Pr<Et<Me.[7,8]

Spinner[9] has studied the rates of ionization of the halides $R{\cdot}CMe_2Cl$ (R= Me, Et, i-Pr, t-Bu) in five different solvents to elucidate the nature of the Baker-Nathan effect. Spinner suggests that the difference between hyperconjugation and steric resistance to bond contraction is that the hyperconjugation effect, i.e., stabilization is obtained as the result of electric charge transfer to the positive center from the alkyl group. The bond contraction, on the other hand, is not a polar effect; increased overlap of the bonding orbitals, and hence a stronger sigma-bond, result in a gain of stabilization by bond contraction. Hence if the Baker-Nathan effect is a polar effect, or if it is due to inhibition of solvation, it should be most pronounced in solvents which solvate cations most effectively; if it is due to neither of these causes, these will be just the solvents in which the inductive effect is most prominent." His experimental results show that there is an inductive effect order of electron release by the alkyl groups when the cation-solvating power of the solvent increses. Therefore Spinner concluded that "the Baker-Nathan effect is not a polar effect, i.e., hyperconjugation, but due to steric resistance of bond contraction, and that the only true polar effects exerted by alkyl groups are of the inductive and inductomeric type."[9]

It was pointed out by Schubert, Robins, and Huan[10] that the Burawoy and Spinner interpretation is insufficient to explain the Baker-Nathan effect since it ignores the role of solvent, except possibly insofar as the solvent may change the electron demand on alkyl.[10]

Sweeney and Schubert[11,12] have suggested that "alkyl substituents release electron in the inductive order (though not necessarily by the inductive mechanism) regardless of demand and that steric hindrance to solvation of electron deficient

sites near the alkyl substituent tends to give an opposite experimentally observed order of apparent 'activation[10]'."

Schubert and Sweeney[11] used the concept of steric hindrance to solvation to reinterpret the previous work. With the solvolysis of benzhydryl halides as an example, the authors explained the role of the solvent as follows. In the ground state, solvent orientation and stabilization are at a minimum, since the polarization of the ground state is small relative to the excited state. Now, ionization to form a carbonium ion is nearly complete in the transition state, the positive charge being distributed throughout the molecule and into the solvent. It is accepted that there is solvation at the benzhydryl carbon, and orientation of solvent molecules toward the positive center, distributed over the benzene ring (particularly ***ortho*** and ***para***), may occur. From the steric consideration, solvation near the site of attachment of the alkyl group would be greatest for methyl and least for t-butyl group. The effect of solvation would then be to increase the activation energy in the hydrolysis reaction in the order Me<Et<i-Pr<t-Bu. "Since solvent orientation would not be as great in the transition state of the tert-butyl as in the methyl compond, the entropy of activation due to solvation should decrease in the order ***tert***-Bu>CH_3. 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,

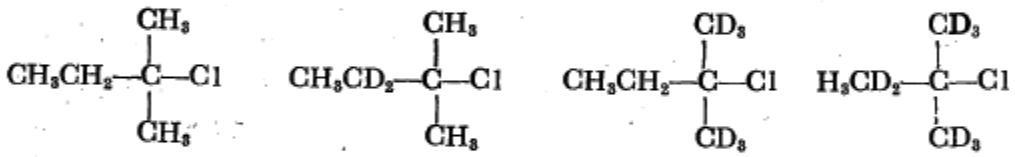
$$\text{rate} = \frac{eKT}{h} \; e^{\Delta S^{\ddagger}/R} \; e^{-E_A/RT}$$

must be greater than of $\Delta S^{\ddagger}/R$ for rate to be decreasing in the order of E_A. "The magnitude of this solvent effect on the activation energy and entropy is difficult to predict, and there are many factors contributing to the quantities. However, the authors suggeested that the concept of steric hindrance to ring solvation account nicely for the solvolysis of *p*-$RC_6H_5CH(C_6H_5)Cl$[1] and of C_6H_5CH-ClAr,[13] the chlorination and the bromination of alkylbenzenes, [14,15,16] and the ionization equilibrium between some triarylcarbonium ions and the corresponding carbinols.[17]

Schubert and Sweeney, however, make it clear that their position is not that C-H hyperconjugation is necessarily of no consequence, although they were able to explain the data cited in their article without applying the concept of hyperconjugation.[11]

Schubert, Robins, and Haun[9] have studied the ultraviolet spectrum of *p*-alkyl substituted nitrobenzene and acetophenone in the gas phase and in a wide variety of solvent. The results show that the excitation energies in the gas phase and in non-polar solvents are in the inductive effect order, but in polar solvents the order of solvent stabilization of excited over ground state is a hyperconjugative order, and that the greatest effect is exerted generally in basic solvents, and in strongly acidic solvents the excitation energies tend to revert back to the inductive effect order. The authors concluded from these results that "the solvent has a considerable influence on the apparent relative activating effect of the alkyl groups in these systems and probably in other systems as well," and "either steric hindrance to solvation or hydrogen boding to the α-hydrogens of the alkyl group can be responsible for the solvent effect."[10]

In studies on isotope effects in elimination and substitution reaction, Shiner[10] has measured the rates of solvolysis of t-amyl chloride and three of its deutero derivatives:



in 80% ethanol at 25°C and found that the rates of formation of alcohol and olefin are retarded, by an equal amount, by deuterium substitution in the methylene as well as in the β-methyl groups. This is in agreement with the S_N1-El mechanism, but since no C-H bonds are directly involved in the formation of the carbonium ion, Shiner assumed that the β-hydrogen atoms are solvated and the solvation energy relayed, by hyperconjugation, to the β-carbon atom. In the transition state there will be a partially developed double bond, and elimination type driving forces are important in the rate-determing step. To support his point of view, Shiner pointed out, from the results of a further study of the solvolysis of 2,3-dimehtyl-2-chlorobutane and its 3-deutero analog,[18]

that the degree of C-H bond weakening is different for primary, secondary, and

tertiary hydrogen atoms and parallels the increase of stability of the corresponding olefin formed from the methyl, methylene, and methyne groups. According to Shiner, this would not be expected if hyperconjugation alone were responsible for the isotope effect and the solvation to β-hydrogen atoms is important.

Lewis and Boozer[19] have studied the rates of solvolysis of 2-pentylbromide and toluenesulfonate and their 1-and 3-deuterated compounds in formic acid, acetic acid and 80%ethanol and the rates of decomposition of 2-pentyl chlorosulfite and its 1-and 3-deuterated compounds in dioxane and isooctane.

$$CH_3CH_2CH_2\underset{\displaystyle X}{\underset{|}{C}}HCH_3 \qquad CH_3CH_2CH_2\underset{\displaystyle X}{\underset{|}{C}}HCD_2 \qquad CH_3\text{-}CH_2CD_2\underset{\displaystyle X}{\underset{|}{C}}HCH_3$$

(X = Br, $OSO_2C_7H_7$ OSOCl)

The rates were retarded in all deuterated compounds compared with undeuterated compounds. According to the authors the isotope effect is due to weakening of the hydrogen in the transition state and the process leads to the carbonium ion intermediate, or if there is no change of the bond to hydrogen in the final product, the bond weakening is attributed to hyperconjugation which results in the withdrawal of the bonding electrons from a β-carbon atom to satisfy the electron deficiency of an α-carbon atom. The authors proposed that the solvents and the leaving group are believed to modify the electron deficiency, thus a strongly nucleophilic leaving group, or a highly nucleophilic solvent, would both be able to supply electrons readily in the transition state, i.e., reduce the amount of hyperconjugation, and its action on the α-carbon atom must be more important than on the β-carbon hydrogen bond.

Recently, Shiner and Verbanic[20] have studied the rates of solvolysis of a number of *p*-alkylbenzhydryl chlorides, by a conductimetric method, in aqueous ethanol and aqueous acetone solutions at O°C. Two sequences of results were obtained, namely, *p*-Me>*p*-Et>-*p*-i-Pr>*p*-t-Bu and *p*-Et>*p*-n-Pr>*p*-i-Bu>*p*-neo-Pe. The former sequence is explained by hyperconjugation. The latter sequence, combined with the fact that the solvolysis rates of the *m*-Me and *m*-t-Bu compounds is inverted from a hypeconjugative sequence to an inductive sequence in 90% ethanol, is explained in terms of solvent effects. The authors pointed out that "in general the compounds with the larger alkyl substituents or with the substituent closer to the reaction center show rates which are less sensitive to solvent composition. These results may be most readily rationalized in terms of solvation as-

sistance to hyperconjugation and/or of steirc hindrance to solvation."[20]

A mild Baker-Nathan effect is found in the rate constants for the solvolysis of *m*-alkylbenzhydrylchlorides in 80% acetone[21] and for the solvolysis of *m*-alkylphenylcarbinyl chlorides in 90% acetone.[22] Brown, Brady, Grayson and Bonner, and Berliner and Chen have attributed these results to a slight predominance of C-H hyperconjugative over inductive release from m-position. Schubert and Sweeney have pointed out these results are equally consistent with mild steric hindrance to ring solvation, acting to invert an inherent inductive order of stabilization of the polar transition state relative to the ground state. It is presumed that a bulky substituent will be less efficient in shielding ring solvation when it is meta than when it is para.

Shiner and Verbanic[23] have determined the influence of solvents on the rate constants at O°C for the solvolysis of a large number of *p*-alkylbenzhydryl chlorides and concluded that the results could be most readily rationalized in terms of solvent assistance to hyperconjugation and/or steric hindrance to solvation."

Schubert and Minton[24],[25] have measured the rate of solvolysis of 3,5-dimethyl- and 3,5-di-t-butylbenzhydryl chloride in a number of solvents at least three temperatures. The Baker-Nathan effect on the rate constants has been found to be both temperature and solvent dependent. The changes in Kinetic parameters brought about by the introduction of the second m-methyl and the second m-t-butyl groups follow the predictions of the hypothesis that the Baker-Nathan effect is due to steric hindrance to solvation in the vicinity of bulky alkyl substituents.

Alkyl groups may affect the reaction rates of certain reactions by combination of hyperconjugation effect and steric effect, which are to some extent conflicting. For RCO_2R' with α-hydrogens in R, hyperconjugation will stabilize the unsaturated reaction state relative to the saturated transition state and, therefore, will increase the activation energy and decrease the rate constant. However, the replacement in the reference CH_3CO_2R' of α-hydrogens by alkyl groups increases the steric effect which decreases the rate constant and decrease the hyperconjugation effect which increases the rate constant. Quantitative separation of hyperconjugation effects from steric substituent constants has been attempted by Hancock, Meyer and Yager[26] by L.C A.O.—M.O. Calculations.

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