We propose that the rho values for the ionization of substituted benzoic acids *increase* as the solvation of the carboxylate ion decreases.[23] With regard to the solvation of the ion, two variables may be considered: the water content of the solvent and the effect of ortho methyl groups. It seems evident that the solvation will decrease with decreased water content and with increased ortho methyl substitution. In line with the first of these hypotheses it may be noted that as the weight per cent. of dioxane varies from 0 to 21.1 to 26.5 to 43.5 the rho values vary from 1 to 1.17 to 1.23 to 1.35 for the *p*-substituted benzoic acids. Also, the rho value increases from 1 to 1.46 in going from water to 50% alcohol.

In assessing the effect of ortho methyl groups on solvation it is seen that the rho value rises from 1.46 to 1.67 in going from non-ortho substituted acids to mono-ortho methyl substituted acids. This result may be explained by assuming that the change produced by one ortho methyl group is exerted more on the solvation effect than on the polar transmission effect and would lead one to believe that in the diortho methyl substituted series an even greater rho value would be obtained. However, for the latter series the rho value falls to 1.40. This must mean that although both polar transmission and solvation are affected by the increased steric factor, the former is affected to a much greater extent. In other words, the coplanarity of the carboxylate function is not greatly affected by one ortho methyl group but is greatly affected by two ortho methyl groups.

The above explanations are obviously only working hypotheses and must be tested by further experimental approaches.

In conclusion we would like to thank Professor J. D. Roberts for valuable discussions about this work and for his data on ionization in 50% alcohol prior to publication.

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[23] In connection with solvation we assume that the solvation is effected mainly by the water and that the solvation is more pronounced in the carboxylate ion than in the acid molecule.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

Isotope Effects in Carbonium Ion Reactions. I. Determination of Solvent and Leaving Group Participations

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The solvolysis of 2-pentyl bromide and toluenesulfonate is retarded by substitution of deuterium for hydrogen in the 1- and 3-positions. The retardation is attributed to a difference in the loss of zero point energy of vibration of the bonds to these hydrogens on going to the transition state for this ionization process. The loss of zero point energy arises from a reduction in the vibrational force constants, which is believed to arise from the withdrawal of the bonding electrons to satisfy the electron deficiency on carbon by a hyperconjugation process. It is proposed that the extent of rate retardation is a measure of the importance of the hyperconjugation, and therefore a measure of electron deficiency on carbon. The solvents and the leaving group are believed to modify the electron deficiency, and the nucleophilic characters of the solvent and of the leaving group are in complete agreement with those determined by other methods. The magnitudes of the retardation by extensive deuterations vary between factors of 1.3 and 1.7.

Introduction

The extensive study of solvolytic reactions has used a great variety of methods to get information about the nature of the intermediate. Recently, emphasis has been placed on the role of the solvent. The approach to this has been based on determining the order with respect to nucleophilic "solvents,"[2] the effect of solvent changes on the rate,[3] and also by the effect of solvents on the extent of racemization of optically active esters.[4] In all cases the solvent was shown to be a very important part of the carbonium ion and the transition state leading to it. The recently observed retardation in rate of ionization of 2-pentyl chlorosulfite with deuterium substitution[5,6] suggested that the same tool would be useful in studying solvolytic reactions, and the presence of the effect in solvolytic reactions would also confirm the ionic nature of the chlorosulfite decomposition. In this paper the effect has been found in the solvolytic reactions, the magnitude of the effect is related to solvent participation and leaving group nature, and the source of the effect is examined in some detail. In a recent paper by Shiner[7] a similar retardation in the rate of solvolysis of *t*-amyl chloride has been observed.

Experimental

Materials.—The anhydrous formic acid, m.p. 4.80°, was prepared by distillation and fractional crystallization of J. T. Baker 99–100% formic acid. The acetic acid, Baker best grade glacial acid, was used without further purification. The "80%" ethanol was prepared by mixing 100 g. of U.S.P. 100% ethanol and 31.75 g. of distilled water as described by Grunwald and Winstein.[8] The method described by Cason and Mills[9] was used to prepare 2-bromopentane, b.p. 117.0–117.8° (uncor.), and 1,1,1,3,3-pentadeutero-2-bromopentane, b.p. 116.5–117.0° (uncor.), in 80% yield from phosphorus tribromide and the corresponding alcohols. The alcohols were the same ones used in the ex-

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[1] From the 1953 Ph.D. Thesis of C. E. Boozer, Ethyl Corporation Fellow 1952–1953.

[2] C. G. Swain, THIS JOURNAL, **72**, 4578 (1950).

[3] S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

[4] W. v. E. Doering and A. Streitwieser, Jr., Abstracts, 119th Meeting of the American Chemical Society, 45 M (1951).

[5] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 6306 (1952).

[6] C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).

[7] V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

[8] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[9] J. Cason and R. H. Mills, *ibid.*, **73**, 354 (1951).

periments with the chlorosulfites.[6] The 2-pentyl-*p*-toluenesulfonates were prepared in 30% yield by the method used by Cram[10] with the modification that the toluenesulfonate was extracted with carbon tetrachloride from a solution acidified with hydrochloric acid. The yield was doubled in one case by permitting the pyridine solution of the pentanol-2 and *p*-toluenesulfonyl chloride to stand in the refrigerator for three weeks instead of one. These toluenesulfonates did not crystallize when the solvent was removed, but analysis by solvolysis indicated that they were 98–99% pure.

Kinetic Measurements.—The solvolysis reactions were followed by direct or indirect titration of the acid produced with 0.05 *N* reagents. About 0.1 *N* ester was used in all determinations. Two-milliliter samples were taken for titration and diluted with ten milliliters of glacial acetic acid except in the case of the "80%" ethanol where water was used to dilute the samples. Formic acid dehydrates in the presence of strong acid, so the runs were made in the presence of 0.11 *N* sodium formate in this solvent. The excess sodium formate was titrated potentiometrically with perchloric acid in acetic acid using a Beckman model H-2 *p*H meter modified according to Winstein.[11] The runs in acetic acid were followed by direct potentiometric titration of the acid produced with sodium acetate in acetic acid. When "80%" ethanol was the solvent, the acid was titrated with sodium hydroxide solution, using the *p*H meter. After the reaction was about one third complete, the formation of a weak acid was detectable from the titration curves for the samples, and the concentration of this acid increased toward the end of the reaction. This did not produce an error in titer since the two breaks in the titration curves were distinct and it was easy to correct for presence of the weak acid.

The first-order rate constants were calculated and the errors estimated for these runs by essentially the same procedure as that used on the chlorosulfite decomposition data,[6] using reagent volume instead of optical density. Final titers were taken as the value after at least ten half-lives.

Discussion

Table I shows the results of the kinetic runs on the various solvolytic reactions. The errors are estimated as before.[6]

TABLE I

RATES OF SOLVOLYSIS OF DEUTERATED AND UNDEUTERATED 2-PENTYL COMPOUNDS

Derivative	Temp., °C.	Solvent	$k_H \times 10^4$, sec.$^{-1}$	$k_D \times 10^4$, sec.$^{-1}$
Bromide	98	HCOOH	2.24 ± 0.02	1.61 ± 0.02
Toluenesulfonate	98.2	CH_3COOH	7.6 ± .1	4.90 ± .02
Toluenesulfonate	78.4	CH_3COOH	0.97 ± .01	0.62 ± .01
Toluenesulfonate	58.2	CH_3COOH	0.074 ± .002	0.045 ± .002
Toluenesulfonate	39.9	HCOOH	3.36 ± .02	1.99 ± .02
Toluenesulfonate	24.9	HCOOH	0.52 ± .02	0.30 ± .02
Toluenesulfonate	58.2	80% EtOH	1.33 ± .03	0.95 ± .03

On the assumption that the difference in rate between the protium and deuterium compounds is due to a difference in the heat of activation alone, one can calculate $\Delta H^{\ddagger}_D - \Delta H^{\ddagger}_H$ by the expression $\Delta H^{\ddagger}_D - \Delta H^{\ddagger}_H = 2.3\ RT \log k_H/k_D$, the result of this calculation is shown below for the data of Table I and also for the chlorosulfite decompositions.[6]

TABLE II

EFFECT OF DEUTERIUM ON $\Delta H^{\ddagger}$ FOR IONIZATION OF 2-PENTYL DERIVATIVES

Derivative	Solvent	Temp., °C.	k_H/k_D	$\Delta H^{\ddagger}_D - \Delta H^{\ddagger}_H$
OSOCl	Dioxane	61.5	1.47	0.26
OSOCl	Dioxane	77.5	1.41	.24
OSOCl	Isoöctane	95.5	3.34	.88
Br	HCOOH	98	1.39	.24
$OSO_2C_7H_7$	CH_3COOH	98.2	1.55	.324
$OSO_2C_7H_7$	CH_3COOH	78.4	1.57	.315
$OSO_2C_7H_7$	CH_3COOH	58.2	1.64	.326
$OSO_2C_7H_7$	HCOOH	39.9	1.69	.326
$OSO_2C_7H_7$	HCOOH	24.9	1.73	.325
$OSO_2C_7H_7$	80% EtOH	58.2	1.40	.22

The near constancy of the last column when only temperature changes supports the assumption that the effect is indeed virtually only in the exponential term of the Arrhenius equation.

Isotope effects have previously been explained on the basis that in the transition state of a reaction which breaks a bond to hydrogen, the force constant of the stretching vibration of this bond is much reduced. Thus the zero point energy of vibration is greatly reduced in the transition state and the isotope effect arises from the fact that the zero point energy of the C–D bond is less, thus less zero point energy is lost on going to the transition state and the activation energy of the deuterium compound is higher. The difference in zero point energies of the C–H and C–D bond is 1.140 kcal. For the oxidation of isopropyl alcohol and the 2-deutero compound, Cohen and Westheimer[12] found 1.140 kcal., for the rate of dehydrohalogenation of isopropyl bromide with ethoxide the value is 1.130 kcal.,[13] and for the rate of ionizations of deuterated and undeuterated nitroethane with hydroxide ions the figure is 1.150 kcal.,[14] all these values calculated from the observers data. While much smaller values have been reported in other types of reactions, these do not involve attack of a base and removal of the hydrogen as a proton. In the cases where the difference of heat of activation attains this maximum value, one can assume that the reaction can be well represented by the simple motion of the proton along a line between the base and the carbon atom. The transition state then represents a point on this line where the hydrogen is equally attracted to the base and the carbon. It is surprising that this very simple picture can even come close to representing a real situation, since many other changes in molecular configuration might be expected to accompany the proton transfer.

The weakening of the bonds to hydrogen is probably also the explanation of the isotope effect observed in the solvolysis. If the force constants for the stretching of the carbon–hydrogen bonds are less in the transition state than in the initial state then some of the zero point energy of this vibration will be lost and an isotope effect will result. Since both the immediate product of the reaction (the carbonium ion) and most of the final products have all of the bonds to hydrogen intact, the reason for the reduction in force constant may not be the same as in the previously mentioned cases. A different source of bond weakening is hyperconjugation in the carbonium ion, which results in the withdrawal of the bonding electrons on the β-carbon atom to lessen the electron deficiency of the α-carbon atom. The withdrawal of these electrons might well be expected to reduce the force constants in the carbonium ion and also in the transition state leading to

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(10) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5851 (1952).

(11) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

(12) M. Cohen and F. H. Westheimer, THIS JOURNAL, **74**, 4387 (1952).

(13) V. J. Shiner, *ibid.*, **74**, 5285 (1950).

(14) W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934).

this ion. Table III shows the values for one C–H bond being weakened in the transition state from an initial force constant of 5×10^5 dynes per cm. and in the last column $\Delta H^{\ddagger}_{\mathrm{D}} - \Delta H^{\ddagger}_{\mathrm{H}}$ for 4.3 C–H bonds being weakened by the amount shown in the transition state corresponding to the average number of deuterium atoms in the compounds studied. It can be seen that this average bond weakening changes from just under 10% for the solvolysis of the toluenesulfonate in 80% ethanol to more than 30% for the decomposition of the chlorosulfite in isoöctane. There is, of course, no reason to assume that all five bonds are equally weakened.

TABLE III

DIFFERENCES IN ZERO POINT ENERGY FOR WEAKENED C–H AND C–D BONDS IN TRANSITION STATES

Weakening	Force constant × 10^{-5}, dynes/cm.	$\Delta H^{\ddagger}_{\mathrm{D}} - \Delta H^{\ddagger}_{\mathrm{H}}$, cal.	$4.3(\Delta H^{\ddagger}_{\mathrm{D}} - \Delta H^{\ddagger}_{\mathrm{H}})$, cal.
0	5.0	0	0
10	4.50	58	250
20	4.00	119	510
30	3.50	186	800
100	0.00	1140	...

The values of $\Delta H^{\ddagger}_{\mathrm{D}} - \Delta H^{\ddagger}_{\mathrm{H}}$ in Table II, while apparently temperature independent, are very dependent on the nature of the reaction. We have related the isotope effect to the withdrawal of carbon–hydrogen bonding electrons to the electron deficient center. It seems reasonable that the magnitude of this withdrawal will depend on how readily the electron deficiency can be ameliorated by the leaving group or the solvent. Thus a strongly nucleophilic leaving group, or a highly nucleophilic solvent would both be able to supply electrons readily in the transition state, so the demand on the bonding electrons would be much reduced. From the last column of Table II we can on this basis arrange the solvents in increasing order of nucleophilic character. For the solvolysis of the 2-pentyl toluenesulfonate this order is $HCOOH < CH_3COOH << 80\%\ C_2H_5OH$, in exact agreement with the conclusions of Winstein with respect to the participation of these solvents,[15] although the difference between acetic and formic acids is very small. In 80% ethanol the average energy of activation change per deuterium is 51 cal., whereas Shiner[7] observed 56 for primary and 95 for secondary deuterium in his case. This agrees with the usual idea of more solvent participation for the secondary compound than the tertiary. For the solvolysis in formic acid we can classify the leaving group toluenesulfonate as less nucleophilic than bromide, in conformity with the very much greater rate of solvolysis of the former. For the ionization of chlorosulfites, we can say that isoöctane is very much less nucleophilic than dioxane, a statement that is eminently reasonable. We have no comparison at the present of the leaving chlorosulfite group with either of the groups which undergo solvolytic reactions, but it is reasonable that it is less nucleophilic than either of them since these esters ionize even in these very low dielectric constant solvents.

These conclusions, in agreement with those from other sources, lend support to the basic idea that the extent of electron deficiency on carbon determines the magnitude of this effect. Further support is given by the observations of Shiner[13] that the rate of the bimolecular displacement of bromide by ethoxide is retarded by only about 10% by substitution of deuterium for hydrogen in isopropyl bromide corresponding to $\Delta H^{\ddagger}_{\mathrm{D}} - \Delta H^{\ddagger}_{\mathrm{H}} = 66$ cal. This case is one where a powerful nucleophilic agent is attacking, hence the electron deficiency will be very small at all stages. We cannot say that the only effect of solvent is to contribute electrons to carbon. An alternative mode of action in addition to the pure dielectric effect would be to contribute electrons to the β-hydrogens by forming a hydrogen bond from β-carbon to solvent. This may in fact exist, but since the increase in nucleophilic character of the solvent reduces the isotope effect, it seems likely that it must reduce hyperconjugation, thus the action of solvent on the α-carbon must be more important than that on hydrogen. It is in this respect only that the explanation offered here differs from that of Shiner,[7] who emphasizes the effect of solvent on promoting elimination in the rate-determining step.

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(15) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).