

gests proton transfer in the critical step but which, on good testimony,⁶¹ is probably an S_N2 displacement on methyl carbon. If so, w^* should be about -3 .

Yet another is presented by hydrolyses of three pyridine-carboxamides (38-40) which have w -values (about $+4.9$) indicating a mechanism different from hydrolyses of benzamide or acetamide. It is difficult to see why changing from a

(61) C. A. Bunton, D. R. Llewellyn, K. G. Oldham and C. A. Vernon, *J. Chem. Soc.*, 3574 (1958).

benzene to a pyridine ring should cause a change in mechanism.

Some understanding of these difficulties is provided by a theory of w -values developed in the following paper.

Acknowledgment.—I wish to express my gratitude for the hospitality of the Institut für Organische Chemie der Universität München (Professor Rolf Huisgen), where the preparation of this manuscript was completed.

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY, PROVIDENCE, R. I.]

Kinetics of Reactions in Moderately Concentrated Aqueous Acids. III. Theory of w - and w^* -Values¹

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RECEIVED FEBRUARY 3, 1961

An extreme interpretation of w^* -values would be that they represent the number of water molecules of change of hydration between reactants and transition states, and that w represents the same quantity on an adjusted scale. The extent to which this extreme view may be valid is examined. Expressions are developed showing how w , w^* and the divergence of $-H_0$ from $\log[HX]$ are related to the extent of hydration change and to the activity coefficients for hydrated species. These expressions are shown to be consistent with the more conventional treatment of these problems. Evidence is presented that this extreme interpretation cannot be wholly correct. However, correlation of w with ΔS^\ddagger values indicates that hydration change is a major influence. Advantages of interpretation in terms of hydration change are discussed and demonstrated.

In paper I,² it was shown that plots of $(\log k_\psi + H_0)$ and of $(\log k_\psi - \log [HX])$, or appropriate other functions for more basic substrates, against $\log a_{H_2O}$ are often linear or approximately so, and that their slopes define parameters (w and w^* , respectively) useful for the classification of reactions. In paper II,³ an empirical criterion of mechanism was developed by associating w - or w^* -values for reactions of established mechanism with the manner of involvement of water in rate-determining steps.

All of this was empirical in the sense that the activity of water entered the treatment only in a mechanical way. No theoretical significance was attached to the fact that the quantities mentioned are more or less linear with $\log a_{H_2O}$.

These linear relationships suggest that the activity of water may be a fundamental variable in these systems. The objective of this paper is to examine this question.

The straight line plots do not prove that the activity of water is a fundamental variable. It is possible that, for example, both $(\log k_\psi + H_0)$ and $\log a_{H_2O}$ depend on some more fundamental factor, and that the correlations noted merely reflect mutual dependence on that factor. Or the linear plots may be wholly fortuitous. Indeed, leading authors⁴⁻⁶ have dismissed the activity of water as

a significant variable in these systems. Only a few publications⁷⁻⁹ have regarded the activity of water as an important influence.

When the activity of water is taken as a fundamental variable, it is admitted into the rate or equilibrium law to a power greater than the minimum number of water molecules called for by the ordinary chemical equation for the reaction concerned. This admission may be partial or total. In the extreme, w becomes virtually the kinetic order in water of the transformation of protonated substrate, SH^+ , to transition state.

The conventional treatment^{4,5,10} of these phenomena does not admit the activity of water to be a major influence. For reactions not requiring water for transformation of SH^+ to transition state, eq. 1 was developed.^{4,11}

$$k_\psi = \frac{k}{K_{SH^+}} \cdot h_0 \cdot \frac{f_{BH^+} f_S}{f_B f_{\ddagger^+}} \quad (1)$$

(7) V. K. Kriehle and K. A. Holst, *ibid.*, **60**, 2976 (1938); M. Duboux and A. de Sousa, *Helv. Chim. Acta*, **23**, 1381 (1940); J. A. Leisten, *Chemistry & Industry*, 397 (1959); C. A. Bunton and S. G. Perry, *J. Chem. Soc.*, 3070 (1960).

(8) K. N. Bascombe and R. P. Bell, *Faraday Soc. Disc.*, **24**, 158 (1957).

(9) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 267-277.

(11) Definition of symbols:

k_ψ measured pseudo-first order rate coefficient
 K equilibrium constant for protonation of substrate, S
 k rate coefficient for conversion of protonated substrate to products
 a no. of waters of hydration of indicator conjugate acid, BH^+
 b no. of waters of hydration of indicator base, B
 f activity coefficient
 n no. of waters of hydration of proton, H^+
 p no. of waters of hydration of protonated substrate, SH^+
 s no. of waters of hydration of substrate, S
 t no. of waters of hydration of transition state, \ddagger
 $[S]_{st} = [S] + [SH^+]$

(1) Described tersely in a preliminary Communication: J. F. Bunnett, *J. Am. Chem. Soc.*, **82**, 499 (1960). Presented in part to the Eighth Conference on Reaction Mechanisms, Princeton, N. J., Sept., 1960.

(2) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961).

(3) J. F. Bunnett, *ibid.*, **83**, 4968 (1961).

(4) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

(5) R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 303 (1958).

(6) C. G. Swain and A. S. Rosenberg, *J. Am. Chem. Soc.*, **83**, 2154 (1961).

And for reactions in which a molecule of water was required, eq. 2⁴ was used

$$k_{\psi} = \frac{k}{K_{\text{SH}^+}} [\text{H}^+] \frac{f_{\text{S}} f_{\text{H}^+} a_{\text{H}_2\text{O}}}{f_{\ddagger}} \quad (2)$$

With use of the definition,¹⁰ $h_0 = a_{\text{H}^+} f_{\text{B}} / f_{\text{BH}^+}$, eq. 2 is readily transformed into

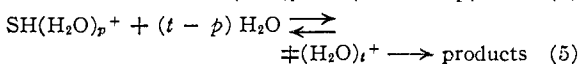
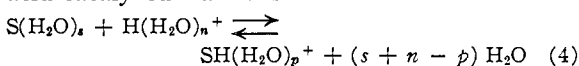
$$k_{\psi} = \frac{k}{K_{\text{SH}^+}} \cdot h_0 \cdot a_{\text{H}_2\text{O}} \frac{f_{\text{BH}^+} f_{\text{S}}}{f_{\text{B}} f_{\ddagger}} \quad (3)$$

which differs from eq. 1 only in the $a_{\text{H}_2\text{O}}$ factor. Since $a_{\text{H}_2\text{O}}$ to the first power does not change much within the acid concentration range of greatest interest (ca. 0.5–6 M), eq. 1 and 3 are nearly the same in their apparent call for kinetic dependence on acidity.

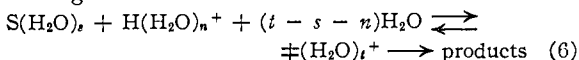
In view of evidence that many reactions in the first class show a nearly linear dependence of rate on h_0 while some reactions in the second class deviate sharply from such behavior (rates approximately linear with $[\text{H}_3\text{O}^+]$), it has in effect been postulated that the activity coefficient ratio in eq. 1 is nearly independent of acid concentration while the corresponding ratio in eq. 3 (which relates to a transition state somewhat different because of the water molecule it contains) is strongly depressed at higher acid concentrations.

A System of Hydration Changes.—In this alternative approach, it is allowed that each molecule, ion or transition state in aqueous solution may be hydrated. Since many kinds of hydration are possible, ranging from incorporation of water *via* covalent bonding to the weakest van der Waals associations, a definition of hydration is required. An operational definition seems best. Let water molecules of hydration be defined as all those bound with sufficient energy measurably to affect reaction rates or positions of equilibria. Obviously such a definition relates to the *average* degree of hydration of the species concerned.

The following generalized mechanism⁴ represents acid-catalyzed reactions



adding



It is understood that transformation of protonated substrate to transition state (eq. 5) may comprise one step, as written, or a series of rapid equilibria followed by one rate-determining step.

w^* -Values.—The rate law stemming from eq. 6 is rate = $k_{\psi} [\text{S}]_{st} =$

$$\frac{k}{K_{\text{SH}^+}} [\text{S}(\text{H}_2\text{O})_s] [\text{H}(\text{H}_2\text{O})_n^+] a_{\text{H}_2\text{O}}^{(t-s-n)} \frac{f_{\text{S}(\text{H}_2\text{O})_s} f_{\text{H}(\text{H}_2\text{O})_n^+}}{f_{\ddagger(\text{H}_2\text{O})_t^+}} \quad (7)$$

For the common case where very little of the substrate is protonated, $[\text{S}]_{st}$ is virtually equal to $[\text{S}(\text{H}_2\text{O})_s]$, and therefore

$$k_{\psi} = \frac{k}{K_{\text{SH}^+}} [\text{H}(\text{H}_2\text{O})_n^+] a_{\text{H}_2\text{O}}^{(t-s-n)} \frac{f_{\text{S}(\text{H}_2\text{O})_s} f_{\text{H}(\text{H}_2\text{O})_n^+}}{f_{\ddagger(\text{H}_2\text{O})_t^+}} \quad (8)$$

Taking logarithms

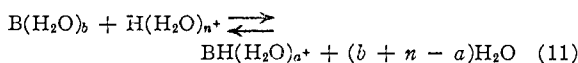
$$\log k_{\psi} - \log [\text{H}(\text{H}_2\text{O})_n^+] = (t - s - n) \log a_{\text{H}_2\text{O}} + \log \frac{f_{\text{S}(\text{H}_2\text{O})_s}}{f_{\text{B}(\text{H}_2\text{O})_b}} + \log \frac{f_{\text{H}(\text{H}_2\text{O})_n^+}}{f_{\ddagger(\text{H}_2\text{O})_t^+}} + \log (k/K_{\text{SH}^+}) \quad (9)$$

If the plot from which w^* is determined² is truly straight

$$\log k_{\psi} - \log [\text{H}_3\text{O}^+] = w^* \log a_{\text{H}_2\text{O}} + \text{constant} \quad (10)$$

Let us make an extreme assumption: that activity coefficient ratios for species of like charge are medium-independent. In the ensuing discussion, this will be referred to as The Assumption. With respect to it, and in view of evidence that activity coefficients of neutral species are relatively insensitive to changes in acid concentration in the media of interest,¹² it follows from eq. 9 and 10 that w^* should approximately equal $(t - s - n)$, hydration of transition state less total hydration of substrate plus proton.

Relation of H_0 to $\log [\text{HX}]$.—For protonation of an indicator base



$$K_{\text{BH}^+} = \frac{[\text{B}(\text{H}_2\text{O})_b] [\text{H}(\text{H}_2\text{O})_n^+]}{[\text{BH}(\text{H}_2\text{O})_a^+] a_{\text{H}_2\text{O}}^{(b+n-a)}} \frac{f_{\text{B}(\text{H}_2\text{O})_b} f_{\text{H}(\text{H}_2\text{O})_n^+}}{f_{\text{BH}(\text{H}_2\text{O})_a^+}} \quad (12)$$

By the Hammett definition¹⁰

$$K_{\text{BH}^+} = ([\text{B}]/[\text{BH}^+]) \times h_0 \quad (13)$$

Since the Hammett notations, B and BH^+ , refer to the actual species in solution, equations 12 and 13 may be combined to give

$$h_0 = \frac{[\text{H}(\text{H}_2\text{O})_n^+]}{a_{\text{H}_2\text{O}}^{(b+n-a)}} \frac{f_{\text{B}(\text{H}_2\text{O})_b} f_{\text{H}(\text{H}_2\text{O})_n^+}}{f_{\text{BH}(\text{H}_2\text{O})_a^+}} \quad (14)$$

Taking logarithms and rearranging

$$\log [\text{H}(\text{H}_2\text{O})_n^+] + H_0 = (b + n - a) \log a_{\text{H}_2\text{O}} - \log \frac{f_{\text{B}(\text{H}_2\text{O})_b}}{f_{\text{BH}(\text{H}_2\text{O})_a^+}} + \log \frac{f_{\text{H}(\text{H}_2\text{O})_n^+}}{f_{\text{BH}(\text{H}_2\text{O})_a^+}} \quad (15)$$

On The Assumption, and again recognizing the small medium-dependence of activity coefficients for neutral organic molecules,¹² this calls for a plot of $(\log [\text{HX}] + H_0)$ against $\log a_{\text{H}_2\text{O}}$ to be linear providing the change in hydration, $(b + n - a)$, is medium-independent. The actual plots (Fig. 7, paper I²) are fairly straight through a middle range of about 4–7 M acid concentration, though curved at both ends.

Equation 14 implies that $-H_0$ diverges from $\log [\text{HX}]$ because of the difference of hydration of reactants and products in eq. 11. It says that the equilibrium for protonation of an indicator base is shifted strongly to the right in more concentrated acids, apart from the effect of increased oxonium ion concentration, because of the decreased activity of water.¹³

w -Values.—In eq. 8, we may insert a value for $[\text{H}(\text{H}_2\text{O})_n^+]$ taken from eq. 14.

$$k_{\psi} = \frac{k}{K_{\text{SH}^+}} \cdot h_0 \cdot a_{\text{H}_2\text{O}}^{(t-s-n)} \frac{f_{\text{S}(\text{H}_2\text{O})_s} f_{\text{BH}(\text{H}_2\text{O})_a^+}}{f_{\text{B}(\text{H}_2\text{O})_b} f_{\ddagger(\text{H}_2\text{O})_t^+}} \quad (16)$$

Taking logarithms and rearranging

$$\log k_{\psi} + H_0 = (t - s + b - a) \log a_{\text{H}_2\text{O}} + \log \frac{f_{\text{S}(\text{H}_2\text{O})_s} f_{\text{BH}(\text{H}_2\text{O})_a^+}}{f_{\text{B}(\text{H}_2\text{O})_b} f_{\ddagger(\text{H}_2\text{O})_t^+}} + \log (k/K_{\text{SH}^+}) \quad (17)$$

If the plot from which w is determined is truly straight

$$\log k_{\psi} + H_0 = w \log a_{\text{H}_2\text{O}} + \text{constant} \quad (18)$$

(12) F. A. Long and W. F. McDevitt, *Chem. Revs.*, **51**, 119 (1952); N. C. Deno and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 1345 (1957).

(13) Resemblances to discussions of Bascombe and Bell³ and of Taft⁹ are to be noted.

From eq. 17 and 18, and on The Assumption

$$w = (t - s) - (a - b) \quad (19)$$

In words, the hydration hypothesis in its extreme form says that w equals hydration of transition state less substrate on a scale set by the "water balance" in protonation of an indicator base.

Strongly Basic Substrates.—The expression corresponding to eq. 16 is

$$k_{\psi} = ka_{\text{H}_2\text{O}}^{(t-p)} \frac{f_{\text{BH}(\text{H}_2\text{O})p^*}}{f_{\neq(\text{H}_2\text{O})t^*}} \quad (20)$$

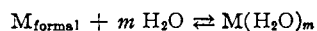
On The Assumption, $w = (t - p)$, hydration of transition state less substrate conjugate acid.

The expression corresponding to eq. 8 is

$$k_{\psi} \frac{h_0}{[\text{H}_2\text{O}^+]} = ka_{\text{H}_2\text{O}}^{(t-p-b-n+a)} \frac{f_{\text{B}(\text{H}_2\text{O})b} f_{\text{H}(\text{H}_2\text{O})n^*} f_{\text{BH}(\text{H}_2\text{O})p^*}}{f_{\text{BH}(\text{H}_2\text{O})n^*} f_{\neq(\text{H}_2\text{O})t^*}} \quad (21)$$

w^* for weakly and for strongly basic substrates can be considered comparable if $f_{\text{B}(\text{H}_2\text{O})b}$ is approximately $f_{\text{S}(\text{H}_2\text{O})s}$, $b \approx s$, and $p \approx a$.

Interrelationship of the Two Approaches.—The conventional approach treats *formal* species while the hydration change approach deals with *hydrated* species. Consider an equilibrium between the two types, in the case of some substance M



With attention to conditions at infinite dilution, and setting $[M_{\text{formal}}] = [M(\text{H}_2\text{O})_m]$ because both refer to the same molecule or ion, one can show¹⁴ that

$$f_{\text{M}} = f_{\text{M}(\text{H}_2\text{O})_m} a_{\text{H}_2\text{O}}^{-m} \quad (22)$$

With use of a series of such relationships, eq. 1 is transformed into eq. 16. Similarly eq. 3 may be transformed into eq. 16; the latter is a general equation, allowing for any number of water molecules to be involved in the activation process and not distinguishing the one water molecule required as a minimum in certain reactions from others that may also be incorporated into the transition state.

The two systems are consistent. This means that insofar as hydration changes take place during conversion of reactants to transition state, they both call for quantitatively the same dependence of rate on h_0 and the activity of water.¹⁵ This consistency does not depend on the validity of The Assumption; insofar as it is not valid, both approaches attribute divergence of rate or equilibrium behavior from linear dependence on $[\text{HX}]$ to medium-dependence of activity coefficients or activity coefficient ratios for hydrated species.

The consistency of the two approaches does not extend to the associated mechanistic interpre-

(14) I am indebted to Dr. E. Grunwald who called my attention to this relationship and its importance.

(15) In this connection, a recent statement by Melander and Myhre¹⁶ is misleading. In discussing aspects of this general problem, they said, "Pure solvation of the proton, however, does not affect the kinetics." The inference was that hydration in general cannot affect the form of dependence of rate on acid concentration. This statement was supported by deriving an equation much like the present eq. 7, and then getting rid of the $a_{\text{H}_2\text{O}}$ factor with use of an expression such as the present eq. 22. This had the incidental effect of converting *hydration* activity coefficients to *formal* ones. While this apparently removed kinetic dependence on hydration, it did so only by incorporating the $a_{\text{H}_2\text{O}}$ factor into a formal activity coefficient.

(16) L. Melander and P. C. Myhre, *Arkiv. Kemi*, **13**, 507 (1959).

tations, *viz.*, the Zucker-Hammett hypothesis^{4,10} versus the new empirical criterion.⁸ Indeed, neither follows directly from the theory. Even the comparatively non-controversial deduction that w of zero (that is, slope 1.00 in a plot of $\log k_{\psi}$ versus $-H_0$) indicates water not to be involved in the rate-determining step fails to find theoretical support. In hydration language, $(t - s)$ may have its usual value for such a mechanism, namely, about equal to $(a - b)$, either because $(t - p)$ were zero or because $(t - p)$ were positive while $(p - s)$ were unusually small. As discussed below, proton transfer from the conjugate acids of hydrocarbon-like bases may be such a case.

Since the two theoretical approaches are compatible, what is to be gained from interpretation according to the system of hydration changes when a conservative thermodynamic approach is available? Let us first note two difficulties with the conventional treatment. One is that a major advantage in dealing with equilibrium systems, namely, the possibility of directly measuring activity coefficients for reactants and products, is largely lost in kinetic problems because transition state activity coefficients cannot be measured. The second is that, though mathematically correct, formal activity coefficients are chemically uninformative: they give no description of the chemical factors responsible for their deviation from unity.

The system of hydration changes singles out one presumably major factor affecting reactivity and handles it in a characteristically chemical way, letting all other factors be represented by a new kind of activity coefficient which is wholly inaccessible to direct measurement. Its advantage is that it allows the chemist to think, even quantitatively, about this major factor in familiar terms. The system of hydration changes has somewhat the same advantage as, in another area, the qualitative theory of mesomerism or resonance has with respect to more mathematical quantum-mechanical methods.

There remains the question of whether hydration changes really are a major influence. Can hydration changes reasonably account for the magnitudes of w - and w^* -values, and for the divergence of $-H_0$ from $\log [\text{HX}]$? Is there any compulsive evidence for this system?

Noting strong evidence that the proton in aqueous solution is tetrahydrated¹⁷ (H_9O_4^+ has been detected even in the gas phase¹⁸), and indications that a further six water molecules are, in dilute solution, more loosely attached in a second hydration sheath,¹⁹ we may judge it not unrealistic to encounter hydration changes as high as six or eight units as suggested by w -values. Close examination of the equilibrium reaction of protonation of an indicator base shows, however, that hydration change is unable to account for all the deviation of $-H_0$ from $\log [\text{HX}]$.

With reference to eq. 15, if two extreme assumptions are made, to wit, that both $f_{\text{B}(\text{H}_2\text{O})b}$ and

(17) E. Wicke, M. Eigen and T. Ackermann, *Z. physik. Chem.*, **1**, 340 (1954).

(18) H. D. Beckey, *Z. Naturforsch.*, **14a**, 712 (1959).

(19) J. B. Hasted, D. M. Ritson and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948); T. Ackermann, *Faraday Soc. Disc.*, **24**, 180 (1957).

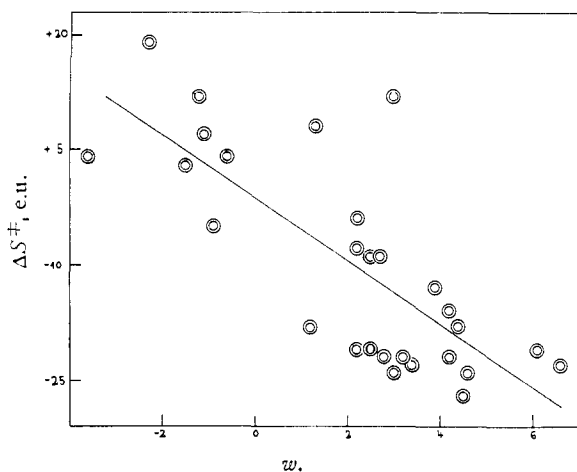


Fig. 1.—Correlation of w with ΔS^\ddagger -values.

$(f_{\text{B}(\text{H}_2\text{O})a^+}/f_{\text{H}(\text{H}_2\text{O})n^+})$ are medium-independent, $(\log [\text{HX}] + H_0)/\log a_{\text{H}_2\text{O}}$ should equal $(b + n - a)$, the hydration change accompanying reaction 11. Selected data for perchloric acid (Table I) are pertinent.

TABLE I
INDICATOR ACID-BASE REACTIONS IN HClO_4

$[\text{HClO}_4], M$	$\frac{\log [\text{HClO}_4] + H_0}{\log a_{\text{H}_2\text{O}}}$	$\frac{[\text{H}_2\text{O}]}{[\text{HClO}_4]}$
2.0	11.2	25.8
4.0	8.3	11.5
6.0	6.2	6.9
8.0	4.8	4.6
9.0	4.2	3.8

At 8.0 and 9.0 M , the value of $(\log [\text{HClO}_4] + H_0)/\log a_{\text{H}_2\text{O}}$ exceeds the total number of water molecules present in the medium per acidic proton. Though one does not know how much hydration to grant the indicator base (b) and conjugate acid (a), he is sure that a would exceed b . Thus even when no allowance is made for anion hydration or for free water in the medium, hydration change falls short of accounting for the magnitude of deviation of $-H_0$ from $\log [\text{HX}]$.²⁰ This shows that at least part of the deviation must be attributed to medium-dependence of $f_{\text{B}(\text{H}_2\text{O})b}$ or $(f_{\text{B}(\text{H}_2\text{O})a^+}/f_{\text{H}(\text{H}_2\text{O})n^+})$. In view of evidence that the former is not greatly medium-dependent,¹² variation in the latter must bear a share of the responsibility. The Assumption is clearly not 100% correct.

This simple calculation does not exclude that hydration change may nevertheless be a major factor. Bascombe and Bell⁸ have shown that with the assignments $n = 4$, $a = b = 0$, and with a conservative allowance for medium-dependence of $f_{\text{B}(\text{H}_2\text{O})b}$, a good account of the deviation of $-H_0$ from $\log [\text{HX}]$ in the region of 1–8 M mineral acid may be given.

For the kinetic problem, important support for the hypothesis of hydration change comes from the correlation of w with ΔS^\ddagger values. A major de-

(20) It is even worse when one attempts to account for the deviation of $-H_R$ ²¹ from $\log [\text{HX}]$ entirely by hydration change. In 50% (7.1 M) sulfuric acid, $(\log [\text{H}_2\text{SO}_4] + H_R)/\log a_{\text{H}_2\text{O}}$ is 12.6 but $[\text{H}_2\text{O}]/[\text{H}_2\text{SO}_4]$ is only 5.45.

(21) N. C. Deno, P. T. Groves and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959), and earlier papers.

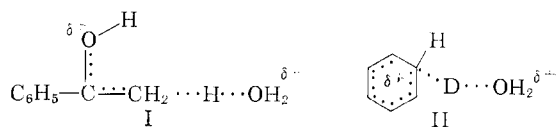
terminant of ΔS^\ddagger for reactions in solution is solvation change between reactants and transition state. The incorporation of solvent into the transition state entails a loss of entropy. Therefore the hypothesis of hydration change calls for correlation of w with ΔS^\ddagger in the sense of decreasing ΔS^\ddagger with increasing w . A precise correlation is not predicted, however, because a number of factors not related to solvation change also affect the entropy of activation.

Figure 1 is a plot of ΔS^\ddagger against w for all the reactions for which data are available.²² The expected correlation is demonstrated, both as to the general trend and as to its lack of precision.²³ The slope is -4.09 e.u. per w unit, with standard deviation 0.68 and correlation coefficient 0.763. The inference is that binding of one water molecule into the transition state causes a loss of entropy of 4.1 cal. deg.⁻¹ per mole. This may be compared with the entropy of fusion of ice, 5.26 cal. deg.⁻¹ per mole. The correlation is satisfying, both qualitatively and quantitatively.

We tentatively conclude that hydration change is a major influence, and that real advantages therefore attach to interpretation with respect to this factor.

Auxiliary support for the system of hydration changes is the circumstance that it provides a consistent qualitative understanding of certain relationships among w - and w^* -values. Particularly satisfying are the explanations it gives for certain deviations of w and w^* from the values ordinarily associated with the reaction mechanism involved. Some of these will now be considered; others are discussed in the following paper.

The Hydration of Certain Transition States.—In the transition state for proton transfer, positive charge is shared between an atom or atoms of the receiving base and the oxygen atom of the donating oxonium species or, for the reverse process, between one or more cationic centers in the conjugate acid and the water oxygen atom. For example, in acetophenone enolization both the erstwhile carbonyl oxygen and an oxygen atom of water are cationic, as shown in structure I. The positive charge is more diffused than in the oxonium ion,



and total hydration should be somewhat lower. On the hydration change hypothesis, w^* should approximately equal $(t - s - n)$; since s is probably near zero, a small negative w^* is predicted. In fact, w^* for typical ketone enolizations are about -1.6 .²

(22) Because a special chemical complication is suspected for acetal hydrolyses in concentrated hydrochloric acid,⁹ w -values in this acid were not used in constructing the plot. For methylal hydrolysis, the average w from sulfuric and perchloric acids was used together with the entropy of activation from *dilute* hydrochloric acid, in which the complication is probably negligible.

(23) Scatter is caused not only by the many other factors that influence ΔS^\ddagger , but also by the use of w -values based on various ranges of acid concentration (whatever range was covered by the published data) for construction of the plot. Perhaps a better correlation would result if some sort of standardized w -value were used.

Equation 19 calls for w to be exceptionally high for a given mechanism if transition state hydration (t) is exceptionally high or substrate hydration (s) exceptionally low. Conversely, w should be unusually low if t is abnormally low or s unusually high.

Structure II represents the transition state for protodeuteration of benzene- d .²⁴ Because deuterium removal from the tetrahedral intermediate, $C_6H_5D^+$, is probably strongly exothermic, the transition state probably lies quite close to said intermediate.²⁵ That is, most of the positive charge is on ring carbon atoms and relatively little on the water oxygen. Because the positive charge is both highly diffused and mainly located on atoms which are not good sites for hydrogen bonding, an exceptionally low degree of hydration is predicted. The actual w -value is -0.6 , some four units lower than for most ketone enolizations.²⁶⁻²⁸

When water acts as a nucleophile in the rate-determining step, there is some development of positive charge on its oxygen, some sharing of this charge with its hydrogens, and consequently some opportunity for hydrogen bonding. The associated w -values suggest that clusters of three water molecules may be most effective as nucleophiles²⁹

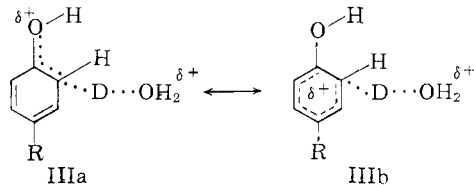
(24) Rate determination in aromatic hydrogen isotope exchange is shared between attachment of one isotope to carbon and detachment of the other from it. When a heavy isotope is displaced by a light, bond breaking bears the brunt of rate determination. Since the two steps are the opposite of one another (the principle of microscopic reversibility) and since the water requirement is probably the same for all hydrogen isotopes, only the slower step is considered.

(25) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(26) This interpretation is influenced by stimulating conversations with Dr. A. J. Kresge. Ideas of Taft⁹ are also incorporated.

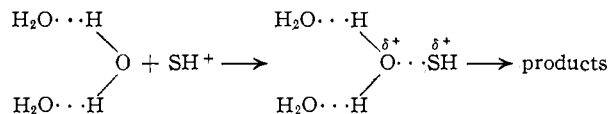
(27) It is not meant to assert that all the change in w represents directly a change in $(t - s)$. Altered transition state hydration may affect also the activity coefficient ratio in eq. 16.

(28) For the transition state for hydrogen isotope exchange in the α -position of phenols, two prominent mesomeric structures are IIIa and IIIb. These resemble I and II, respectively. From the fact that w -values are similar to those for protodeuteration in aromatic hydro-



carbons and ethers (compare reactions 26-28 with 24, 25 and 29-31, Table I, ref. 2), one gathers that IIIb is the dominant mesomeric structure. Hydration of transition state III appears to exceed that of II by little more than hydration of the phenols exceeds that of benzene.

(29) In some cases nucleophilic attack by water may be general base catalyzed (by water), as in the mechanism of eq. 1, paper II.³ Actual removal of one of the nucleophile's protons may be concerted with nucleophilic attack. In such a case the aspect of proton transfer presumably predominates in determining the over-all w -value.



Hydrated species are expected gradually to lose their hydration as water becomes more scarce, the loss being greater for the more heavily hydrated species. For example, $(b + n - a)$ is expected to decrease as acid concentration increases because n is larger than a ; part of the decrease in $(\log [HClO_4] + H_0)/\log a_{H_2O}$ shown in Table I may stem from this source. Likewise w , of which $(t - s) - (a - b)$ is judged to be an important component, should wane as acid concentration waxes if t is much larger than s or a ; that is, if w has a high value. A general tendency for high w 's to so diminish was noted in paper I.² However, in such cases w^* , which reflects $(t - s - n)$, should not change much because t and n are both large and should decrease in parallel. In fact, w^* near zero are usually medium-independent.²

The hydration theory provides a ready explanation for negative w -values, which are observed for many reactions which do not require water for progression from SH^+ to transition state. From eq. 19, if $(a - b)$ exceeded $(t - s)$, w should be negative. If hydration of SH^+ or BH^+ is a significant factor, it is not unreasonable that a should exceed p (which is the same as t for such reactions), while b perhaps equalled s . After all, the substrates of principal interest are quite different in chemical type from the indicators used to determine H_0 -values.

This type of reasoning leads to the view that the H_0 scale is not altogether a fundamental quality of acid solutions, but in part a function of the indicator systems (mostly aromatic amines) used for its measurement.³⁰ Nor do the w or w^* ranges associated with certain types of reaction mechanism³ appear to be fundamental. Almost certainly they reflect the hydration characteristics of the relatively small number of substrates and transition states involved in developing the empirical criterion of mechanism.

Acknowledgments.—Financial support from the Office of Ordnance Research, U. S. Army, the National Science Foundation (Grant No. G-6210), the John Simon Guggenheim Memorial Foundation and the U. S. State Department (Fulbright program) is greatly appreciated. The manuscript was written in the Institut für Organische Chemie der Universität München by virtue of the hospitality of Professor Rolf Huisgen.

(30) Cf. refs. 6 and 9, and E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).