[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

π-Complex and Carbonium Ion Intermediates in Olefin Hydration and E1 Elimination from *t*-Carbinols. II. Trimethylethylene, Methylenecyclobutane, Triptene and the Effect of Acidity on their Hydration Rate[1,2]

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The rates of hydration of gaseous olefin at unit pressure, k_p, have been determined in one to five molar nitric acid with aliphatic olefins of varying sizes and shapes. Log k_p values parallel precisely the acidity function, H_0, with slopes varying from 1.20 to 1.30. These results show the activity coefficient of the hydration transition state to be approximately but not precisely independent of structure. The rates of hydration at unit concentration of dissolved olefin, k_c, follow the acidity function, h_0, essentially with unit slopes. Accordingly, the hydration transition states must be free from firmly bound water molecules. Entropies of activation for olefin hydration and corresponding carbinol dehydration are reported which are in good accord with this conclusion. As pointed out earlier,[1] π-complex and carbonium ion intermediates are consistent with and apparently required by the nature of the transition state.

In paper I, the rates of hydration of gaseous isobutene at unit pressure, k_p, by one-tenth to five molar aqueous nitric acid solutions at 25° were reported. The rates of hydration of dissolved isobutene at unit concentration, k_c, were estimated using the Setschenow equation to obtain the olefin activity coefficients. The logarithm of k_c plotted against the acidity function, H_0, gives a linear relationship of near unit slope. On the basis of this result, and the theory of Zucker and Hammett as to its significance, a hydration mechanism was proposed in which the rate-determining step is the isomerization of a π-complex to a carbonium ion. In support of this mechanism it was further shown that entropies of activation for olefin hydration and carbinol dehydration involving both ordinary aliphatic olefins (leading to tertiary carbinols) and α,β-unsaturated aldehydes correlate with the type of dependence on acidity of the hydration rate.

We now report measurements similar to those given in paper I for gaseous aliphatic olefins of appreciably varying sizes and shapes, namely, trimethylethylene, methylenecyclobutane and triptene (*asym*-methyl-*t*-butylethylene). The results obtained are in accord with the ideas expressed in paper I.

Experimental

Apparatus and Procedure.—These have been described in detail in earlier papers.[1,4]

Materials.—Trimethylethylene[4c] and methylenecyclobutane[5] used in this work are described elsewhere. Triptene was refractionated from a sample of the olefin available at Pennsylvania State Univ., b.p. 77.7° (760 mm.), n^{20}_D 1.4030.

Results

In Table I are listed the rates of hydration of the three gaseous olefins at unit pressure obtained in one to five molar nitric acid solutions.

Table V lists entropies of activation at unit acid and substrate concentrations for olefin hydration and for the dehydration of corresponding carbinols. The values for the ordinary aliphatic olefins have been calculated from recently obtained data which are reported elsewhere.[4-6] Except in the cases noted these entropies of activation are accurate to within two or three e.u.

TABLE I

RATE CONSTANTS FOR THE HYDRATION OF GASEOUS TRIMETHYLETHYLENE, TRIPTENE AND METHYLENECYCLOBUTANE AT UNIT PRESSURE, k_p, BY NITRIC ACID SOLUTION IN UNITS OF 10^4 MOLE-L.$^{-1}$-ATM.$^{-1}$-MIN.$^{-1}$

HNO_3, M	Trimethylethylene at 30.00° k_p	Methylenecyclobutane at 25.17° k_p	Triptene at 25.12° k_p
0.973	2.58	3.97	1.22
1.500	5.42	....	...
2.011	10.04	16.14	...
2.995	25.7	45.0	15.08
4.000	56.5	109.2	...
4.941	99.0	209	74.2

Discussion

Structure and k_p Values.—Paul,[7] and Long and McIntyre[8] have found recently that in solutions of strong acids or acid and salt mixtures having total electrolyte concentrations in the region one to about six molar the activity coefficient, f_{BH^+}, of the conjugate acid of a base, B, is more nearly (but not exactly) independent of structure than is the activity coefficient ratio f_B/f_{HB^+}. The conjugate acid may be a reaction transition state if this consists of substrate plus a proton. The Hammett acidity function is based upon the term f_B/f_{HB^+}, being independent of structure.[9] Long and McIntyre point out that the distinction between the above two conditions is rarely seen in acid solutions alone, because of the relatively small "salting-in" or "salting-out" parameters of these electrolytes. Presumably for this and the reason given in the next section, the present results do not distinguish as to which is the better general approximation. However, the present results do provide a precise indication of whether the activity coefficients of the hydration transition states in the moderately con-

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[1] Paper I, R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952).

[2] The work reported herein was carried out on Project NR055-295 between the Office of Naval Research and The Pennsylvania State University.

[3] Allied Chemical and Dye Corp. Fellow for 1953–1954; taken in part from the Ph.D. Thesis of E. Lee Purlee, The Pennsylvania State University, June, 1954.

[4] (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951); **75**, 3955 (1953); (b) R. W. Taft, Jr., J. B. Levy, D. Aaron, and L. P. Hammett, *ibid.*, **74**, 4735 (1952); (c) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *ibid.*, **77**, 837 (1955).

[5] P. Riesz and R. W. Taft, Jr., *ibid.*, **77**, unpublished (1955).

[6] R. W. Taft, Jr., and P. Riesz, *ibid.*, **77**, 902 (1955).

[7] M. A. Paul, *ibid.*, **76**, 3236 (1954).

[8] (a) D. McIntyre and F. A. Long, *ibid.*, **76**, 3240 (1954); (b) F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954).

[9] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 264.

TABLE II

DEMONSTRATION OF FIT OF HYDRATION RATES OF GASEOUS OLEFINS TO EQUATION 2

		Trimethylethylene, $\rho = 1.20$		Methylenecyclobutane, $\rho = 1.29$		Triptene, $\rho = 1.30$				Isobutene, $\rho = 1.20$	
HNO_3, M	$-H_0$	$\log k_p + \rho H_0$	d	$\log k_p + \rho H_0$	d	$\log k_p + \rho H_0$	d	HNO_3, M	$-H_0$	$\log k_p + \rho H_0$	d
0.973	0.08	−3.69	0.00	−3.50	0.02	−4.01	0.01	0.506	−0.26	−3.77	0.02
1.498	.34	−3.68	.01					0.973	+ .08	−3.76	.01
2.011	.57	−3.67	.02	−3.53	.01			1.515	.34	−3.73	.02
2.995	.90	−3.69	.00	−3.51	.01	−3.99	.00	2.525	.76	−3.75	.00
4.00	1.19	−3.69	.00	−3.50	.02			4.03	1.20	−3.76	.01
4.94	1.44	−3.74	.05	−3.54	.02	−4.00	.00	5.04	1.48	−3.74	.01
Average		−3.69	0.01	−3.53	0.02	−4.00	0.00			−3.75	0.01

centrated nitric acid solutions are structure independent.[10] This may be seen from the basic equation[1]

$$k_p = k_p^0 a_{H^+} \frac{1}{f_\ddagger} \qquad (1)$$

in which a_{H^+} is the proton activity, $a_{H_3O^+}/a_{H_2O}$, and $f_\ddagger$ is the activity coefficient of the hydration transition state. It is apparent that the hydration rate constant for gaseous olefin, k_p, is affected by only one variable at a given acid concentration, namely, the activity coefficient, $f_\ddagger$. Thus if the latter is structure independent, the hydration rate constants, k_p, should show exactly the same dependence on acidity for any olefin. In as much as the four olefins studied (isobutene, paper I, plus the three olefins reported here) vary in content from four to seven carbon atoms and have widely varying carbon chain skeletons we are in a position to put this requirement to severe test.

A convenient manner of examining the results in this regard makes use of a precise linearity existing between the logarithm of k_p and H_0.[11] Thus the median deviation in these plots is within the estimated average accuracy of k_p values (2–3%). Table II summarizes the data on the basis of the relationship

$$\log k_p = -\rho H_0 + \text{constant} \qquad (2)$$

Since the slopes, ρ, of the plots of $\log k_p$ *vs.* H_0 are not the same for each olefin, $f_\ddagger$ is not precisely independent of structure. On the other hand, it is a reasonably good (and may sometimes be a useful) approximation to make this assumption. Thus the average deviation of ρ from the mean value of 1.25 for Table II is only 3.6%.

Log k_c *vs.* H_0.—The rate of hydration of dissolved olefin at unit concentration, k_c, may be calculated by the equation[1]

$$\log k_c = \log (k_p/h^0) + \log f_0 \qquad (3)$$

where h^0 is the distribution constant of olefin between the gas phase and its saturated aqueous solution in mole-l.$^{-1}$-atm.$^{-1}$ and f_0 is the activity coefficient of olefin in a given acid solution (the standard state is the water solution of olefin). At temperatures sufficiently low (~0°) so that the hydration rate is small, direct solubility measurements in acid solutions up to 3 M have shown the familiar Setschenow equation to be precisely followed[12]

$$\log f_0 = KC \qquad (4)$$

where C is the molar acid concentration, and K is a parameter characteristic of olefin, acid and temperature. At higher temperatures (25 or 30°) and acidities greater than one molar the speed of the hydration reaction prevents direct measurements. The Setschenow parameter, K, may be obtained, however, on the basis of direct measurements in acid solutions up to one molar. It therefore appears that eq. 4 may be used together with eq. 3 to calculate reasonably accurate $\log k_c$ values for the higher acidities at 25 and 30°.

Table III summarizes the Setschenow parameters, K, which have been obtained.

TABLE III

SETSCHENOW PARAMETERS, K, FOR OLEFIN IN NITRIC ACID SOLUTIONS

Olefin	Temp., °C.	K
Isobutene	25.00	−0.052 ± 0.004[a]
Trimethylethylene	30.00	− .074 ± .003[a]
Methylenecyclobutene	25.17	− .056 ± .013[b]
Triptene	25.12	− .111 ± .003[a]

[a] Obtained from direct solubility measurements in solutions up to 1 M, *cf.* ref. 12. [b] Obtained indirectly, *cf.* ref. 5.

The calculated $\log k_c$ values follow the equation

$$\log k_c = -\rho' H_0 + \text{constant} \qquad (5)$$

as illustrated by the summary given in Table IV. The average value of ρ' in Table IV is 1.04. The deviations from this value or unity are not reliably outside the uncertainties in the calculated rate constants (the value for methylenecyclobutane is

TABLE IV

DEMONSTRATION OF THE FIT OF CALCULATED LOG k_c VALUES TO EQUATION 5

HNO_3, M	$-H_0$	Trimethylethylene, $\rho' = 0.98$ $\log k_c + \rho' H_0$	Methylenecyclobutane, $\rho' = 1.11$ $\log k_c + \rho' H_0$	Triptene, $\rho' = 0.99$ $\log k_c + \rho' H_0$	HNO_3, M	$-H_0$	Isobutene, $\rho' = 1.07$ $\log k_c + \rho' H_0$
0.973	0.08	−1.43	−1.73	−1.4[illegible]	0.506	−0.26	−1.54
1.498	.34	−1.40	....	....	0.973	+ .08	−1.51
2.011	.57	−1.40	−1.72	....	1.515	.34	−1.47
2.995	.90	−1.39	−1.70	−1.43	2.525	.76	−1.50
4.00	1.19	−1.41	−1.69	....	4.03	1.20	−1.52
4.94	1.44	−1.47	−1.74	−1.50	5.04	1.48	−1.51
Average		−1.42	−1.72	−1.47			−1.51

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(10) We are considering here only those olefins which give a hydration transition state of the fixed composition, olefin plus proton *cf.* ref. 1.

(11) Figures 1 and 2 of ref. 1 contain considerable errors in H_0 values at the higher acidities. The necessary corrections have been made in the present manuscript. Above 0.5 M acid the relationship between $\log k_p$ and H_0 is precisely linear (*cf.* Table II), contrary to the earlier quotation.

(12) R. W. Taft, Jr., E. L. Purlee and P. Riesz, THIS JOURNAL, **77**, 899 (1955).

particularly uncertain because of the relatively large uncertainty in the parameter K). In the present case, however, the fact that eq. 5 is followed with an average deviation of ρ' from unity of 5% indicates that the approximation that f_B/f_{BH^+} is independent of structure is probably at least as accurate as the same approximation for f_{HB^+} alone. This is not inconsistent with the conclusions of Long and McIntyre, for the present work has been confined to aqueous nitric acid solutions.[8]

Acidity Dependence and Mechanism.—Zucker and Hammett, noting that acid-catalyzed reactions in general fall into two categories—those having rates paralleling H_0 and others paralleling the stoichiometric acid concentration—proposed that the reactions of the former type involve transition states in which no added water molecule is firmly bound (*i.e.*, are effectively substrate plus proton).[13] In the olefin hydration reaction the condition that rates, k_c, follow h_0 is[1]

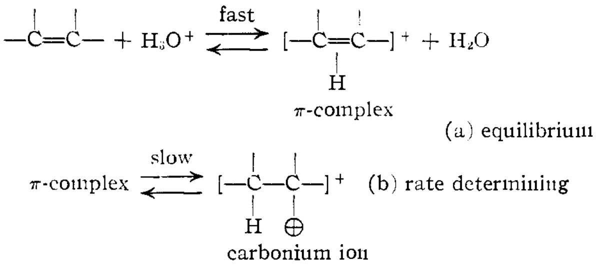
$$f_B f_{\ddagger}/f_0 f_{BH^+} = \text{constant} \qquad (6)$$

where f's are activity coefficients, and subscripts denote: o, olefin; $\ddagger$, hydration transition state; B, base indicator (aniline type) used to set up the H_0 function; BH$^+$, conjugate acid of B.

The argument then is to the effect that since $f_0/f_{\ddagger}$ changes with the acidity of the media in the same way as f_B/f_{BH^+}, and the latter involves an anilinium type ion which cannot firmly bind (by covalent interaction) a water molecule, the hydration transition state too must be free of a firmly bound water molecule. The utility of this argument depends upon there being appreciably different behavior shown by the activity coefficients of two species differing only by the presence in one of a firmly bound water molecule. That the activity coefficients of two such species are completely different functions of changing acid media (in the approximate region 1 to 6 M[14]) is now well established.

Long, Dunkle and McDevit have found that the term f_B/f_{BOH_2}—where B is γ-butyrolactone and BOH$_2$ is γ-hydroxybutyric acid—far from being constant decreases by about two powers of ten between one and six molar acid.[15] More recently Deno, Jaruzelski and Schriesheim[14b] have found the term $f_{R^+}/f_{ROH_2^+}$—where R$^+$ is a substituted di- or triphenylcarbonium ion and ROH$_2^+$ is the conjugate acid of the corresponding carbinol—decreases by about the same amount for this change in sulfuric acid molarity. In striking accord with Zucker and Hammett's theory, the logarithms of these activity coefficient ratios change by an amount about equal to the change in the acidity function, H_0.[16]

Accordingly, the transition state in the olefin hydration reaction must be effectively a conjugate acid of the olefin which is not firmly bound to any water molecule. Since the reactants are olefin and hydronium ion, such a transition state apparently can only be formed by a step involving a unimolecular isomerization from one unstable intermediate to another—neither of which are firmly bonded to a solvent water molecule. The π-complex and the carbonium ion fit the needs of the two required intermediates, and thus the hydration mechanism has been formulated as[1]



$$-\overset{|}{C}=\overset{|}{C}- + H_3O^+ \underset{}{\overset{\text{fast}}{\rightleftarrows}} [-\overset{|}{C}=\overset{|}{C}-]^+ + H_2O$$

π-complex (with H below the double bond)

(a) equilibrium

$$\pi\text{-complex} \overset{\text{slow}}{\rightleftarrows} [-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{\oplus}{\overset{|}{\underset{|}{C}}}-]^+ \quad \text{(b) rate determining}$$

carbonium ion

$$\text{carbonium ion} + H_2O \overset{\text{fast}}{\rightleftarrows} ROH_2^+ \quad \text{(c) equilibrium}$$

$$ROH_2^+ + H_2O \overset{\text{fast}}{\rightleftarrows} ROH + H_3O^+ \quad \text{(d) equilibrium}$$

It is important to observe that the reverse of the hydration mechanism gives the detailed mechanism of E1 elimination in the dehydration of *t*-carbinols (the ones studied here at least) in moderately concentrated aqueous acids. It seems likely that this detailed process (reverse of steps b and a) may apply to other reactions classified as E1. Thus, for example, this reaction sequence is not inconsistent with the Hughes and Ingold[17] formulation and the recent observations of Shiner[18] in support of it, namely, that the loss of proton from carbonium ion is fast in the solvolysis of tertiary alkyl halides. Nor is it inconsistent with the observations and conclusions of Otvos, Stevenson, Wagner and Beeck[19] regarding deuterium exchange in hydrocarbons in concentrated sulfuric acid. This is because the equilibrium of combined steps c and d is certainly of such magnitude that under the conditions of the dehydration experiments the steady state carbonium ion concentration is vanishingly small (much less than that in the above reactions). Thus even though the specific rate constant, k_{-H}, for the reverse of step b is very large, the rate of this step, $k_{-H}[R^+]$, may yet be the slowest step of the dehydration sequence.

Entropies of Activation and Mechanism.—Table V shows that the entropies of activation for the hydration of the ordinary aliphatic olefins are small numerical values while those for the dehydration of the resulting carbinols are large and positive. The entropy changes for the hydration reactions in acidified aqueous solution are on the order of a negative 20 cal./deg. This is only slightly larger than the standard entropy change at 25° of the reaction

$$\text{olefin(l)} + H_2O(l) = \text{carbinol(l)}$$

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[13] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2791 (1939).

[14] (a) This appears *not* to be the case in concentrated sulfuric acid (83–100 wt. %) where activity coefficients of most species approach constancy; *cf.* N. C. Deno and R. W. Taft, Jr., THIS JOURNAL, **76**, 244 (1954), and (b) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *ibid.*, in press.

[15] F. A. Long, F. B. Dunkel and W. F. McDevit, *J. Phys. Colloid Chem.*, **55**, 829 (1951).

[16] This follows from the fact that the difference in H_0 and $-\log(H_3O^+)$—which is approximately equal to H_0—according to Zucker and Hammett's theory (*cf.* ref. 9, pp. 275, 276) is essentially equal to $\log(f_{R^+}/f_{ROH_2^+})$.

[17] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1271 (1937).

[18] J. V. Shiner, THIS JOURNAL, **75**, 2925 (1953).

[19] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck *ibid.*, **73**, 5741 (1951).

The entropy change for this reaction for isobutene–*t*-butyl alcohol is −24 cal./deg. and for trimethylethylene–*t*-amyl alcohol is −22 cal./deg.[20] Numerically these entropy changes are on the same order as the absolute entropy of water at 25°, *i.e.*, $S^0_{298} = 16.7$ cal./deg.

TABLE V

ENTROPY RELATIONSHIPS IN OLEFIN–ALCOHOL INTERCONVERSIONS

Olefin–carbinol	Rate hydration $\Delta S_f^{\ddagger}$	Rate dehydration $\Delta S_r^{\ddagger}$	Equilibrium hydration reaction ΔS^a
Isobutene–*t*-butyl alc.	−3	+19	−22
Trimethylethylene–*t*-amyl alc.	0	+15 (±4)	−15 (±4)
Methylenecylcobutane-1-methylcyclobutanol-1	+1	....	....
1-Methylcyclopentene-1–*t*-methylcyclopentanol	−5	+14	−19
asym-Methylethylethylene–*t*-amyl alcohol	−4	+15 (±4)	−19 (±4)
Triptene–triptanol	−8	....	....
α,β-Unsaturated aldehydes[b]			
Crotonaldehyde–aldol	−23	−2	−21
β,β-Dimethylacrolein-β-hydroxyisovaleraldehyde	−23	−9	−14

[a] $\Delta S_f^{\ddagger} - \Delta S_r^{\ddagger}$. [b] From data of H. J. Lucas, *et al.*, *cf.* ref. 1.

The entropies of activation are in accord with the proposed mechanism, for there is pictured no loss of translational or rotational motions of a water molecule and its solvation shell on the formation of the transition state from olefin, but the gain of these motions in the formation of this state from the carbinol.[1]

In the case of the hydration of α,β-unsaturated aldehydes the entropy change for the reaction is virtually the same as for the ordinary aliphatic olefins, but exactly the reverse of the above situation applies for the entropies of activation. The large negative entropies of activation for these hydrations indicate that a water molecule is tightly bound in the transition states for these reactions. The Zucker–Hammett theory is in striking accord with this conclusion,[1] for the rates of these hydrations follow the stoichiometric acid concentration.[21]

Conclusion.—The dependence of the hydration rate on acidity shows according to the evidence cited that no water molecule is firmly bonded in the transition state for the hydration of the ordinary aliphatic olefins. Thus the molecularity of the reaction with respect to the solvent water is zeroth. Critical evidence from three additional independent sources supports this conclusion. These are the entropies of activation (as presented above), rate and equilibrium studies in the hydration of small ring olefins,[5] and the effect of isotopic (deuterium) solvent composition on hydration and dehydration rates.[22] It is apparent therefore that means have been found for determining the reaction molecularity with respect to solvent—a task which classical kinetics is incapable of accomplishing.

In setting a criterion for the molecularity of solvent in the hydration reactions, we have chosen to consider only solvent which is kinetically strongly bound in the transition state. That so many independent phenomena may be correlated by this criterion is to us very striking and conclusive.

It is of course recognized that weaker interactions of the ion–dipole type must be involved between the positively charged hydration transition state and solvent. Particularly pertinent evidence indicating that interactions of this type lead to kinetically feebly bound water molecules is that of Hunt and Taube who found the aquo complexes of Al^{III}, Ga^{III} and Fe^{III} to exchange with solvent H_2O^{18} within the time required for the first experimental observation.[23] These trivalent ions bind water molecules by ion–dipole interaction much more firmly than does a univalent carbonium ion.[24] The case of Fe^{III} is particularly interesting because it involves an element which has available a stable orbital (d's), just as does the central carbon atom (p) in the carbonium ion.

The extent to which this type of solvent participation may influence other phenomena associated with the olefin hydration reaction, *e.g.*, stereochemistry, is uncertain and is beyond the scope of present considerations. The strength of ion-dipole interaction is sufficiently large,[25] however, to make it probable that its influence on certain aspects of the reaction mechanism cannot be overlooked. Studies directed along these lines are in progress.

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[20] Calculated from data of the following references: (a) "Selected Values of Properties of Hydrocarbons," Circular of the National Bureau of Standards C461; (b) D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 2767 (1949); G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," (The Chemical Catalog Co.) Reinhold Publ. Corp., New York, N. Y., 1932, p. 109.

[21] S. Winstein and H. J. Lucas, THIS JOURNAL, **59**, 1461 (1937).

[22] R. W. Taft, Jr., Abstract of Papers, Joint Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions, March, 1954, Kansas City, Missouri, p. 33; *cf.* Ph.D. Thesis of E. L. Purlee, The Pennsylvania State University, June, 1954; work to be reported soon by E. L. Purlee and R. W. Taft, Jr.

[23] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

[24] By the Born equation (*Z. Physik*, **1**, 45 (1920), solvation energy $= \frac{e^2}{2r}\left(1 - \frac{1}{D}\right)$ where e = change of spherical ion, r = ion radius and D = dielectric constant.

[25] A. G. Evans ("Reactions of Organic Halides in Solution," Manchester University Press, 1946, p. 14) has estimated the solvation energy (by ion–dipole interaction) of *t*-butyl cation to be 69 kcal./mole.