micropower level to reach the point of saturation. In exchange narrowed lines, one does not have the usual effect of saturation broadening but rather a narrowing of the central part of the line.

Alternatively the strong line can be due to the defects in the bulk of the silica gel as has also been suggested by Kazansky, et al.,[2] who interpret the defects as trapped electrons in oxygen vacancies. If the defects are far below the surface, admission of O_2 and NO could not relax these centers by dipolar interaction. Since the dipolar interaction varies inversely as the cube of the distance between defect and paramagnetic molecule, only small effects, if any, can be expected.

The results obtained in the present study indicate that the effect of O_2 and NO is due to magnetic dipolar interaction of the paramagnetic molecules and the trapped electrons on the surface. The molecules can either be physically adsorbed or just be present in the vicinity of the surface defect without being adsorbed. By change in temperature of the system it is possible to differentiate between the two possibilities.

The present observation indicates the care that must be taken in obtaining meaningful e.s.r. measurement of surface defects and their interaction with gaseous molecules.

Heat Capacity of Activation in Hydrolytic Displacement from a Tertiary Carbon[1]

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Values of the heat capacity of activation (ΔC_p^*) for the hydrolysis of 2-chloro-2-methylbutane, 2-chloro-2-methylpropyl methyl ether, and t-butyldimethylsulfonium ion were determined for hydrolysis in water. These values were shown to support a working hypothesis based on the recognition that part of the energy requirement in the activation process is the work required to break down the initial state solvation shell. Differences in ΔC_p^* values can be understood in terms of modification of the initial state solvation shell through the presence of a lyophilic group or of a charge, and by modification of the degree of solvent disorganization in the transition state through a change of mechanism.

The experimental fact that ionogenic reactions such as the hydrolysis of alkyl halides in water[3] or the ionization of weak acids[4] are characterized by large negative heat capacity changes has long been recognized.[5,6] It is accepted that these large negative temperature coefficients reflect mainly the summation of heat capacity changes associated with the reorganization of a number of adjacent water molecules as a consequence of developing electrostatic interaction. Since interaction between the neutral solute and the water molecules in the solvent sheath is small compared to ion-water interaction, the simplest explanation would seem to be that the water is frozen down about the formed (or forming) ions, reference being made to the well-known heat capacity change of -9 cal./mole deg. for the freezing of water to ice. This argument is undoubtedly an oversimplification in the case of weak acid ionization[6] and as normally applied[5,7,8] is probably incorrect for the activation process accompanying solvolysis.[9]

Glew and Moelwyn-Hughes[10] were among the first to recognize that the hydrogen-bonded solvation shell about alkyl halides in aqueous solutions is an important factor in hydrolysis.[11,12] While subsequent research does not appear to support their detailed mechanism, all pertinent work has tended to reinforce the basic idea that for ionogenic reactions in water the free energy change (ΔF_s^*) associated with the breakdown of the solvent shell about neutral solutes is a significant factor in the activation process, particularly with respect to the associated ΔC_p^* values. The kinetic solvent isotope effect (k_{D_2O}/k_{H_2O})[13] and the phenomena associated with the curious term "hydrophobic bond"[14] are further examples in which the importance of this solvent shell is made evident.

(1) Issued as N. R. C. No. 8461.
(2) National Research Council of Canada Postdoctorate Fellow, 1959–1961.
(3) E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A164**, 295 (1938).
(4) D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).
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We have explored the significance of ΔF_s^* with reference to kinetic results for the hydrolysis of several alkyl halides and sulfonates which react by an SN2 mechanism[15,16] and have extended our working hypothesis to account for the more negative value of ΔC_p^* which characterizes the hydrolysis of t-butyl chloride in water[17] where the mechanism is presumably SN1. Here we review the arguments and assumptions used to account for the differences in ΔC_p^* observed between alkyl halides hydrolyzing by SN1 or SN2 mechanisms and report rate data and derived parameters for the hydrolysis of (1) 2-chloro-2-methylbutane (t-pentyl chloride), (2) 2-chloro-2-methylpropyl methyl ether (methoxy-t-butyl chloride), and (3) t-butyldimethyl-sulfonium ion, all of which, like t-butyl chloride, involve displacement from a tertiary carbon.

The study of t-pentyl chloride provides a check on the single remarkable value of ΔC_p^* found for t-butyl chloride.[17] The other series illustrate the effect on ΔC_p^* of modifying the initial state solvation shell by the introduction of a lyophilic group or of a charge.

Rate Data and Derived Parameters

Average rate data for a series of temperatures for the solvolysis of the above three compounds in water are given in Tables I–III. The temperature dependence of these, in common with previous rate data, can be fitted to an empirical three-constant equation of the form

$$\log k = A/T_K + B \log T_K + C \tag{1}$$

with random errors of the same order as those found experimentally. The corresponding constants determined by the method of least squares from individual rather than average rates are given in Table IV.

Table I. Rate Data for the Hydrolysis of t-Pentyl Chloride in Water

Temp., °C.	$k \times 10^3$ sec.$^{-1}$ Obsd.[a]	Calcd.
12.032	14.38 ± 0.05	14.40
10.019	10.87 ± 0.01	10.87
8.024	8.192 ± 0.025	8.167
6.046	6.113 ± 0.018	6.116
4.007	4.496 ± 0.004	4.509
3.013	3.879 ± 0.012	3.876
2.032	3.330 ± 0.004	3.334
0.294	2.535 ± 0.003	2.542

[a] Data consisted of 24 rates, 3 at each temperature. This table includes every determined rate.

Corresponding rates calculated from these constants are given in column 3, Tables I–III.

If one accepts the assumptions of the transition state theory and the further restriction that ΔC_p^* is temperature independent within the experimental range, the corresponding values[18] of ΔH^*, ΔS^*, and ΔC_p^* may be calculated (Table V). The direct determination of $d\Delta C_p^*/dT$ is difficult but we have found no indication

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(18) $A = -\Delta H_0^*/2.3026R$; $\Delta H_T^* = \Delta H_0^* + \Delta C_p^* T$; $B = \Delta C_p^*/R + 1$; $C = (\Delta S_0^* - \Delta C_p^*)/2.3026R + \log k/h$; $\Delta S_T^* = \Delta S_0^* + C_p^* \log T \times 2.3026$.

Table II. Rate Data for the Hydrolysis of 2-Chloro-2-methylpropyl Methyl Ether in Water[a]

Temp., °C.	$k_1 \times 10^5$ sec.$^{-1}$ Obsd.	Calcd.
40.560	76.74 ± 0.11	76.79
37.504	55.33 ± 0.07	55.38
35.002	39.68 ± 0.04	39.68
32.501	28.29 ± 0.01	28.22
30.007	19.96 ± 0.04	19.94
27.502	13.92 ± 0.01	13.96
25.00	9.714 ± 0.004	9.694
22.500	6.675 ± 0.009	6.680
17.510	3.101 ± 0.001	3.096
15.009	2.070 ± 0.010	2.077
8.004	0.6473 ± 0.001	0.6465

[a] Three rates determined at 0° were omitted from the least-squares determination.

Table III. Rate Data for the Hydrolysis of t-Butyldimethylsulfonium Ion in Water

Temp., °C.	$k_1 \times 10^5$ sec.$^{-1}$ Obsd.	Calcd.
90.007	156.8 ± 0.3	156.5
85.004	84.05 ± 0.08	84.10
82.505	61.24 ± 0.06	61.17
80.007	44.26 ± 0.05	44.32
77.501	31.95 ± 0.01	31.9$_2$
75.00$_1$	22.91 ± 0.02	22.89
70.00$_3$	11.59 ± 0.01	11.60
62.50$_5$	4.02$_8$ ± 0.001	4.024
60.00$_1$	2.79$_2$ ± 0.004	2.79$_6$
57.50$_1$	1.93$_3$ ± 0.001	1.93$_2$
52.49$_9$	0.90$_7$ ± 0.014	0.906$_6$
45.00$_9$	0.278$_9$ ± 0.001	0.278$_9$

that this coefficient is comparable to that known to characterize the solvation of ions over the 0–30° temperature range.[19] The corresponding coefficient for the solvation of neutral molecules is only $^1/_5$–$^1/_{10}$ as large,[20] and it is the latter which would be significant for the proposed hypothesis.

The range of temperature covered for the t-pentyl chloride was smaller than normally desirable for the determination of ΔC_p^* but was dictated by experimental limitations. The derived parameters for that compound accordingly have greater probable errors than for the other two examples. There can be no doubt, however, that the value for ΔC_p^* for the hydrolysis of t-pentyl chloride is more negative than the average value of this coefficient for the primary and secondary halides.[21] While we regard this value as supporting the general conclusions concerning solvent reorganization about t-butyl chloride, more detailed conclusions from this more negative value of ΔC_p^* are not warranted.

Discussion of Results

Water is an unusual solvent because of the unique property of forming three-dimensional hydrogen bonded structures in dynamic equilibrium of varying and largely

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Table IV. Empirical Constants for Rate Eq. 1

Halide	A	B	C	n^a	Δ^b
t-Pentyl chloride	−10,467.6	−45.051	145.468	24	0.0015
2-Chloro-2-methylpropyl methyl ether	−9,572.7	−30.007	102.344	43	0.0010
t-Butyldimethylsulfonium ion	−7,468.8	−2.760	24.826	47	0.0006

^{a} n = the number of individual rates. ^{b} $\Delta = \sqrt{\Sigma (\log k_{\text{calcd}} - \log k_{\text{obsd}})^2/n}$. Δ was calculated by computer using 18-digit accuracy. The 12-digit output was arbitrarily rounded to be consistent with experimental error.

Table V. Summary of Derived Parameters for the Hydrolysis of Certain Halides

Halide	ΔH^*, kcal.		ΔS^*, 25°	ΔS^*, 10°	ΔC_p^*	Ref.
	25°	10°				
Methyl chloride	26,600	...	−4.31	...	−52	a
Benzyl chloride	21,400	...	−9.09	...	−40	b
t-Butyl chloride	22,550	23,800	+10.10	+14.4	−83	c
t-Pentyl chloride	20,610	21,983	+5.48	+10.2	−92	d
2-Chloro-2-methylpropyl methyl ether	25,430	26,350	+8.38	+11.6	−62	d
t-Butyldimethylsulfonium ion	31,560	...	+15.74	...	−8	d

^{a} Reference 21a. ^{b} Reference 21b. ^{c} Reference 17. ^{d} This work.

unknown complexity.[14,20,22] Without attempting to define the exact nature of these structures, there is ample evidence that this dynamic equilibrium[22] is altered in different ways by the presence of weakly polar solutes such as the alkyl halides and by ions. Modification of the structured nature of water by whatever means has an energy requirement and will show a temperature dependence corresponding to the imposed changes on hydrogen bonding. It is not surprising therefore to find that ionogenic reactions occurring in water not only give indications of the structured nature of water but that these indications change with temperature. The application of these generalizations to the solvent reorganization associated with the activation process in hydrolysis leads to a reasonable understanding of the source of the large negative heat capacity changes which are known to characterize such reactions.[15]

Initial State Solvation Shell. The present state of our knowledge of aqueous solutions of weakly polar molecules has been summarized recently by Glew[20] and by Némethy and Scheraga.[14] The former tends to emphasize the close analogy between the condition of the solute in aqueous solution and in the gas hydrate, a comparison made in an earlier paper in connection with a study of the solvolysis of methyl halides[10] and further supported by a study of the solution of methane in water.[20] In order to extend this concept to larger molecules it is necessary to accept the assumption that the hydrogen bond permits large angular distortions, as first proposed by Pople.[23,24] The alternative would appear to be some variation of the "fluttering cluster" hypothesis of Frank and Wen,[22] and it is in this direction that Némethy and Scheraga develop a detailed model.

For the purpose of this discussion it is sufficient to recognize that either description leads to the common conclusions that water–water interaction >> water–

solute interaction; that the solvent shell has inherent stability; that this stability appears to vary with temperature; and that this stability is subject to modification by the introduction of lyophilic groups in the solute.

As we have stressed in many papers[9,15,16] it is a logical corollary of the above conclusions that part of the free energy of activation (ΔF_s^*), will be required to break down this solvent shell in the activation process for hydrolysis. This hypothesis is supported not only by the existence of large negative heat capacity changes which characterize ionogenic reactions in water but also by the existence and the differences in the kinetic solvent isotope effect (k_{D_2O}/k_{H_2O}). The latter, though less sensitive than ΔC_p^*, has the apparent advantage of being calculated directly from rates. Further support is given by the sensitivity of this ratio to the addition of a cosolvent such as dioxane.[25]

In this connection the recent extensive calorimetric work of Arnett and co-workers on the heat of solution of solutes in ethanol–water mixtures provides supplementary evidence that the initial solvation differences parallel and appear to be the source of many puzzling changes in ΔH^* and ΔS^* which have been observed[26−29] in systematic studies of the effect of solvent change on these derived parameters.

The above considerations relating to the initial state solvation of alkyl halides will apply as well to the unionized state of weak acids though a greater degree of interaction between the carboxylic oxygens and the water will be anticipated with a corresponding modification of the adjacent solvent shell.

The Activation Process and Ionization. It is important to recognize that this similarity of initial-state

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solvation shells and the common requirement in an ionogenic reaction that this solvent shell be disrupted does not imply a similarity between the organization of the solvent molecules about the ions and about the transition state or that the $\Delta C_p{}^*$ for the ionization of acetic acid (e.g.) provides a point of reference for discussing the corresponding $\Delta C_p{}^*$ value from the "ionization" of t-butyl chloride. Since, in both cases, a similar initial-state solvation shell is disrupted by charge development and we know that the final state for the acid involves solvated ions, the following evidence suggests that the transition state for t-butyl chloride does not involve the same strong solvent–ion interaction.

Thus the ionization of a weak acid is characterized by a large negative entropy ($\Delta S \cong -20$ cal./mole deg. at 25°) while the activation process for t-butyl chloride gives $\Delta S^* = +10$ cal./mole deg. at 25°. Even more striking in the present context is the observation[4] that, whereas ΔC_p for the ionization of acetic acid becomes 5–10 cal./mole deg. more *negative* on the addition of methanol or dioxane to aqueous solutions,[4] $\Delta C_p{}^*$ for the solvolysis of t-butyl chloride becomes more *positive* by many times this amount ($\Delta C_p{}^*$ = -83 cal./mole deg. in water[17] but -30 cal./mole deg. in 50:50 ethanol–water).[30] Kohnstam found a similar value for solvolysis of this compound in acetone–water mixtures.[31]

These differences can be understood if it is recognized that the solvent order which characterized the initial state about the alkyl halide is not re-established at the transition state, and that the latter is characterized by some measure of solvent disorganization about the "seat of reaction." This is just the opposite to the conventional view of solvent molecules being "frozen" about the forming ions.

Mechanism, Charge Development, and $\Delta C_p{}^*$. Undoubtedly the most important step toward an understanding of the detailed mechanism of solvolysis was the recognition of the basic difference between the SN1–SN2 mechanism and the resulting differences in solvation requirements.[32] To find, at this later date, that such solvation differences are accompanied by large differences in $\Delta C_p{}^*$ is not too surprising. To postulate that this difference is the result of a greater degree of solvent disorganization in the transition state of the SN1 mechanism would seem a logical consequence of the available evidence though it may seem less evident to some. The key problem remains, as it always has, in deciding on the degree of charge development at the transition state, and this decision must be based on kinetic data.

For the SN2 mechanism, we chose that degree of charge development where

anion–water interaction = nearest-neighbor water–water

interaction   (A)

for the following reasons. Presuming nucleophilic interaction and thermal activation are sufficient to reach that level, then up to this point on the reaction coordinate work will have to be done against water–

water interaction; hence anion–water interaction will not contribute to a lowering of ΔF^*. Charge development beyond the equilibrium condition specified in eq. A will lead to compensatory making and breaking of bonds as normally assumed, but without the requirement for an *increase* in ΔF^*. Thus while the nucleophile may be described as "pushing" the reaction, the assumption that solvation forces on the anion lower ΔF^* through "pulling" is not consistent with the above hypothesis for the SN2 mechanism.

Since the stability of the initial-state solvation shell is known to be temperature dependent, a process involving the disorganization of this shell will be characterized by a corresponding decrease in free energy with temperature and less directly by $\Delta C_p{}^*$.

We do not imply by eq. A that nucleophilic interaction can occur without some degree of solvent disorganization, but all evidence supports the conclusion that either this is small or, as seems more likely, the nucleophile and incipient proton act as an initiator of a new and equivalent water cluster.[22] The relatively small values of the kinetic solvent isotope values (k_{H_2O}/k_{D_2O} = 1.2–1.3 for halides) suggest that the proton cannot be bonded very differently in the transition state and initial state.

$\Delta C_p{}^*$ for the SN1 Mechanism. The more negative $\Delta C_p{}^*$ values found for t-butyl chloride[17] and for t-pentyl chloride (Table V) point to a more extensive solvent disorganization in the SN1 mechanism compared to the SN2 mechanism. This difference does more than confirm the solvation difference already well established in that it provides a clue to detailed mechanism not previously appreciated (but see ref. 33a).

In the SN1 mechanism, the initial-state solvation shell must be broken down by the development of charge resulting from thermal activation and favorable structural features, nucleophilic "catalysis" being sterically unfavorable. Since the forming t-butyl cation is larger than the Cl anion,[33b] the transition state will not be reached when charge development corresponds to eq. A but at some higher value. It is a logical extension of the argument given above that any increase in charge above condition A will lead to electrophilic "catalysis" through anion–water interaction. We have arbitrarily assumed that the transition state will be reached when

cation–water interaction = nearest neighbor water–water

interaction   (B)

The reasoning here resembles that given previously. Having achieved this point of equilibrium, further charge development will add to a stabilization of the ions without the requirement of any further increase in ΔF^*, the energy derived from the latter process being adequate to balance the energy of this carbon–halogen bond.[34] The above mechanism provides a framework for understanding the more negative $\Delta C_p{}^*$ values since the initial-state solvation shell will have to be broken down about the forming cation *in addition* to that about the forming anion. The effect of the latter contribution may be reduced in some degree by anion–

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water interaction beyond the level corresponding to eq. A.

Examples of S$_N$1 Hydrolysis. While the value of ΔC_p^* (-93 cal./mole deg.) found for t-pentyl chloride is less certain than the corresponding value for t-butyl chloride, we regard this ΔC_p^* value as both confirming the more negative value of ΔC_p^* for these compounds compared to primary and secondary halides[9] and lending further support to the hypothesis advanced to account for them.

It would seem a corollary of the above hypothesis that, if a group were included in the t-butyl group which (by contrast with the methyl group of t-pentyl chloride) interacts with the initial-state water shell, then less work will have to be done in disorganizing this shell in the activation process and ΔC_p^* will be reduced accordingly. The less negative value of ΔC_p^* (-62 cal./mole deg.) reported here for the hydrolysis of 2-chloro-2-methylpropyl methyl ether confirms this premise.

The reasoning here with regard to the effect of substituting the lyophillic MeO group on ΔC_p^* is the same as we previously used to account for the difference in ΔC_p^* between primary and secondary halides (average value of $\Delta C_p^* = -50$ cal./mole deg.) and the corresponding value of this coefficient for the sulfonates ($\Delta C_p^* = -35$ cal./mole deg.). The same argument also provides a satisfactory explanation for the reduced solvent isotope effect for the same reactions ($k_{H_2O}/k_{D_2O} = 1.25$ for the halides but 1.10 for the sulfonates).

The possibility that the less negative ΔC_p^* for the methoxy-substituted solute is the consequence of the latter group acting as an internal nucleophile (neighboring group effect) is discounted both by the large rate decrease (by a factor of $^1/_{350}$) largely due to an increase in activation energy and by agreement with Streitwieser's correlation.[35]

While the hydrolysis of t-butyldimethylsulfonium ion involves displacement from a t-butyl group, there must necessarily be a considerable difference between the solvation of this ion and that of the neutral t-butyl chloride. Accordingly, the condition for the transition state specified for the latter need not apply. However, at this exploratory stage it is sufficient that the corresponding C_p^* is far less negative by comparison (-8 cal./mole deg.) and there is a corresponding reduction in k_{D_2O}/k_{H_2O},[36] a ratio as we have noted above which also depends on the relative work required to break down the initial-state solvation shell.

Thus, the three ΔC_p^* values resulting from the rate studies presented here provide further support for the hypothesis that the more negative values of ΔC_p^* for the hydrolysis of t-butyl chloride compared to the values of this coefficient for the hydrolysis of primary and secondary halides is a consequence of the added requirement that the initial-state water structure be broken down about the developing cation as well as about the forming anion. In the S$_N$2 mechanism, either the former requirement was absent or, more probably, as a consequence of nucleophilic interaction

a new structure was formed which is equivalent to that in the initial state, with a consequent cancellation of changes in ΔC_p^*.

These data do not provide any obvious basis for a quantitative estimation of either the fractional charge on the halide at the transition state or even of the number of water molecules affected save in very approximate terms. Equation B is presented as a working hypotheses only, based on the assumption that the transition state for the S$_N$1 mechanism in water is not one in which strong cation–water interaction has been established but rather a state where such interaction is just beginning to balance carbon–halogen bond breaking.

Experimental

t-Pentyl chloride was a commercial product which was redistilled (b.p. 86° at 766 mm.), then passed through a column of alumina for adsorption—the latter treatment having been found of particular advantage in the preparation of halides for kinetic studies by the conductance method. The reactant was kept refrigerated and in the dark during the study. Strict first-order plots were considered the best test of kinetic purity.

2-Chloro-2-methylpropyl Methyl Ether. The corresponding alcohol was synthesized by the method of Palomaa,[37] b.p. 115–116° (761 mm.), n^{24}D 1.4016. The alcohol was converted to the chloride, b.p. 95–96° (757 mm.), n^{23}D 1.4058, by treatment with concentrated HCl and CaCl$_2$. It was believed that this sample contained some unchanged alcohol. This did not interfere with the kinetic studies.

t-Butyldimethylsulfonium iodide was synthesized by the method of Hughes and Ingold[38] and recrystallized from absolute methanol. The crystals were washed with ether, dried under vacuum, and protected from light and heat during the course of the work, m.p. $\sim$160°. The melting point provides a poor test of purity here[39] and we regarded the strict adherence to first-order kinetics over the whole temperature range studied as a better indication of kinetic purity.

Kinetic Rates. Rate data were determined by a conductance method either as described in previous papers[40] or in a special cell used in our study of the hydrolysis of t-butyl chloride.[17] The main feature of the latter was provision for rapid mixing of the t-pentyl chloride from the gas phase after temperature equilibrium had been achieved in the cell.

Changes in resistance and time were recorded on a 365-A Hewlett-Packard 11-line Digital printer coupled to the five-dial Leeds and Northrup resistance box through an L and N No. 31/3/0/1 switch coupled to the end of the axis of each decade and a five-figure digital clock designed by Mr. Brian Weston of these laboratories. With the assistance of these adjuncts to our normal bridge, rate data down to $t_{1/2} = 45$ sec. could be determined conveniently. Rates were then calculated as previously described.

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