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Evidence for the Incursion of Intermediates in the Hydrolysis of Tertiary, Secondary, and Primary Substrates

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Abstract: The temperature dependences related to a series of solvolytic displacement reactions of primary, secondary, and tertiary carbon centers are examined using a new equation. The equation is derived by integrating the van't Hoff isochore in a form related to the absolute rate theory on the assumption that the heat capacity of activation ($\Delta C_p^{\ddagger}$) is constant. Unexpectedly, the new equation is capable of correctly sensing changes in $\Delta C_p^{\ddagger}$ with temperature. The new equation is used to show that in some instances $\Delta C_p^{\ddagger}$ is partly abnormal and derives from the nonunitary nature of the displacements in a way outlined previously by Albery and Robinson. The significance of this new mechanistic tool is considered in relation to the displacement reaction of 2-bromopropane in heavy water and the reactions of adamantyl nitrate, *tert*-butyl chloride, *S*-propyl methanesulfonate, *m*-trifluoromethylbenzyl nitrate, and ethyl bromide with ordinary water.

Introduction

The temperature dependence of many ionogenic displacement reactions in water and mixed aqueous solvents is inadequately represented by the Arrhenius equation. The possible origins of such behavior have been the subject of a general review by Hulett[2a] and the displacement reactions have been specifically reviewed by Robertson[2] and Kohnstam[3] and form part of a more recent summary by Blandamer.[4] If the absolute rate theory formalism is adopted, then departures from the Arrhenius equation may be interpreted in terms of heat capacities of activation ($\Delta C_p^{\ddagger}$). For hydrolytic displacements of organic esters (RX)

$$RX + 2H_2O \rightarrow ROH + H_3O^+ + X^- \qquad (1)$$

the measured values of $\Delta C_p^{\ddagger}$ are invariably negative. Odd exceptions to this rule have their own particular explanation.[5]

The negative values of $\Delta C_p^{\ddagger}$ can be rationalized qualitatively in terms of various model processes. For example, the ionization reactions of amines and carboxylic acids are all characterized by negative ΔC_p° values. Likewise, the heat-capacity change for the hypothetical process

$$Ar(aq) \rightarrow Cl^-(aq) \qquad (2)$$

has been estimated to be negative.[6] These analogies draw attention to the solvation changes which characterize the activation of a neutral molecule (RX) to an ionic transition state which is postulated to show varying degrees of charge separation as the structures of R and X are changed.

The range of ΔC_p for many solvolytic substrates reacting in water is ca. -50 ± 30 cal mol^{-1} K^{-1} and this is consistent with the thermodynamic models mentioned above. Individual differences arising from structural alterations in the substrates (RX) have led to a variety of mechanistic speculations.[2b,3] Broadly speaking, such speculations have been related to the Ingold S_N1–S_N2 classification[7] together with the basic idea that S_N1 displacements demonstrate a greater sensitivity to solvation and are consequently characterized by more negative $\Delta C_p^{\ddagger}$ values. Many aspects of this picture are satisfactory; nevertheless, some nagging doubts remain.

For instance, a recent report[8] concerning the solvolysis of *t*-BuCl in *t*-BuOH gives a value of -627 cal mol^{-1} K^{-1} for $\Delta C_p^{\ddagger}$. The wholesale destruction of entropy which must be associated with such a large negative $\Delta C_p^{\ddagger}$ value is physically unreasonable. Similarly the hydrolyses of adamantyl nitrate[9] and *m*-trifluoromethylbenzyl nitrate[10] have respectively provided values of $\Delta C_p^{\ddagger}$ in the region of -150 cal mol^{-1} K^{-1} and these values are also outside the range of what might be anticipated reasonably on thermodynamic grounds.

One might argue that 1-adamantyl nitrate reacts only by a limiting (S_N1) mechanism and hence the large negative $\Delta C_p^{\ddagger}$ is that characteristic of a truly limiting displacement with the nitrate as a leaving group. However, the same mechanistic description for the substituted benzyl nitrate is not plausible. In the present paper we propose to seek alternative

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Table I. Rate and Thermodynamic Data Related to the Solvolysis of 2-Bromopropane in Deuterium Oxide[17]

	T_0, °C	10^5k,[a] s^{-1}	−slope[b]	10^3 × intercept[b]	$\Delta H^\ddagger$, kcal mol^{-1}	$-\Delta C_{p,n}^\ddagger$,[c] cal mol^{-1} K^{-1}
1	80.01	212.9 ± 0.2	35.32 ± 0.69	11.372 ± 0.010	22.596 ± 0.020	70.18 ± 1.37
2	74.83	129.6 ± 0.2	34.63 ± 1.02	11.576 ± 0.013	23.002 ± 0.026	68.83 ± 2.03
3	69.99	79.54 ± 0.03	33.01 ± 0.65	11.753 ± 0.007	23.353 ± 0.014	65.59 ± 1.29
4	64.81	46.19 ± 0.04	33.21 ± 0.93	11.929 ± 0.008	23.703 ± 0.016	65.99 ± 1.85
5	59.89	26.85 ± 0.03	30.31 ± 1.04	12.090 ± 0.008	24.023 ± 0.016	60.23 ± 2.07
6	54.97	15.30 ± 0.014	30.29 ± 1.32	12.231 ± 0.010	24.303 ± 0.020	60.19 ± 2.62
7	49.97	8.473 ± 0.002	35.62 ± 1.59	12.406 ± 0.013	24.651 ± 0.026	70.78 ± 3.16
8	44.87	4.475 ± 0.002	34.54 ± 0.76	12.591 ± 0.007	25.018 ± 0.014	68.63 ± 1.51
9	40.00	2.370 ± 0.002	34.12 ± 0.52	12.756 ± 0.006	25.346 ± 0.012	67.80 ± 1.03
10	35.04	1.206 ± 0.001	33.96 ± 0.39	12.921 ± 0.005	25.674 ± 0.010	70.78 ± 0.77

[a] Mean of three to five separate kinetic measurements. [b] From the least-squares regression according to eq 7; errors are probable errors, i.e., 0.6745 × standard error. [c] The mean $\Delta C_{pn}^\ddagger = -66.90 \pm 3.95$ cal mol^{-1} K^{-1}, which compares favorably with the least-squares value obtained from a regression using eq 5 which yielded $\Delta C_p^\ddagger = -65.3$ cal mol^{-1} K^{-1}.

explanations for these large negative $\Delta C_p^\ddagger$ values and in doing so generate some interesting mechanistic alternatives for the reactions mentioned above.

The Albery-Robinson Treatment of Non-Arrhenius Behavior

Over a decade ago Albery and Robinson[11] pointed out that, if solvolytic displacement reactions take place via a nonunitary mechanism such as

$$\text{substrate} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{ion pair} \xrightarrow{k_3} \text{product} \quad (3)$$

this would provide an explanation for both the non-Arrhenius dependence and the negative $\Delta C_p^\ddagger$ values. This idea was applied by these workers to the aqueous hydrolysis of *t*-BuCl and the solvation considerations mentioned earlier in this paper were ignored completely. Briefly, Albery and Robinson assumed that the activation parameters $\Delta H_n^\ddagger$ and $\Delta S_n^\ddagger$ (n = 1, 2, and 3) associated with the individual rate constants k_1, k_2, and k_3 of eq 3 were all true temperature-independent quantities. Using this premise they were able to show that the steady-state rate law appropriate to eq 3

$$k_{\text{obsd}} = k_1k_3/(k_2 + k_3) \quad (4)$$

would give rise to a spurious negative $\Delta C_p^\ddagger$. This conclusion is formally correct but the assumption that the individual processes contributing to the overall process are devoid of real $\Delta C_p^\ddagger$ terms remains contentious. The Albery-Robinson hypothesis was scrutinized critically by two of the present authors[12] and it was emphasized that the abnormal $\Delta C_p^\ddagger$ term[22] would be temperature dependent and manifest itself as a large "peak" superimposed on real terms. Hence it follows that, if the Albery-Robinson hypothesis is to be confirmed, $\Delta C_p^\ddagger$ must be shown unequivocally to be temperature dependent. The temperature dependence of the very large body of solvolytic rate data produced by Robertson and co-workers[2] has usually been represented by the Valentiner equation

$$\ln k_r = AT^{-1} + B \ln T + C \quad (5)$$

This equation is now recognized to be inherently unsuitable for the detection of variations of $\Delta C_p^\ddagger$ with temperature since the constancy of $\Delta C_p^\ddagger$ is implicit. If $\Delta C_p^\ddagger$ is temperature dependent, eq 5 is evidently a blunt tool since any variations in $\Delta C_p^\ddagger$ with temperature which do occur will be readily accommodated as errors in the derived parameters *A*, *B*, and *C*. The problem is, unfortunately, not alleviated by adding further polynomial terms in *T* to eq 3 since the latter has poor regression properties.[13] Furthermore, the additional coefficients in extended versions of eq 3 are determined with low precision and may not be unique.[14]

The problems inherent in the regression of eq 5 or appropriately extended versions have been examined by Glew and Clarke[15] but we are not convinced that their method offers any improvement inasmuch as it does not ensure the coefficients of (5) or any extended versions of (5) are independent.[16]

A New Equation for Examining the Temperature Dependence of Rate and Equilibrium Constants

The problems associated with the regression of eq 5 have forced us to reconsider the problem of calculating thermodynamic parameters from the temperature dependence of rate and equilibrium constants. As a result of these considerations we have derived the equation

$$\ln \frac{k_rT_0}{k_{0r}T} = \frac{\Delta H_0^\ddagger}{R}\left\{\frac{1}{T_0} - \frac{1}{T}\right\} + \frac{\Delta C_p^\ddagger}{R}\left\{\ln \frac{T}{T_0} + \frac{T_0}{T} - 1\right\} \quad (6)$$

$$k_r = \frac{k_BT}{h}k_T^\ddagger \text{ and } k_{0r} = \frac{k_BT_0}{h}K_0^\ddagger$$

and k_B is the Boltzmann constant.

The equation is simply obtained by the integration of the absolute rate version of the van't Hoff isochore between two temperatures T_0 and T with the condition that $\Delta C_p^\ddagger$ is temperature independent. The quantities k_{0r} and k_r are respectively the rate constants measured at temperatures T_0 and T, and $\Delta H_0^\ddagger$ is the enthalpy of activation at T_0. In deriving eq 6 the boundary conditions related to the integration are carefully considered, whereas in eq 5 they are completely ignored. The full details of these considerations will appear elsewhere.[13]

Equation 6 may be regressed linearly in the form

$$\frac{TT_0}{T - T_0} \ln \frac{k_rT_0}{k_{0,r}T} = \frac{\Delta H_0^\ddagger}{R} + \frac{\Delta C_p^\ddagger}{R}\left\{\ln \frac{T}{T_0} + \frac{T_0}{T} - 1\right\}\frac{TT_0}{T - T_0} \quad (7)$$

giving $\Delta H_0^\ddagger/R$ as the intercept and $\Delta C_p^\ddagger/R$ as the slope. For a given k_r,T data set, containing *n* data point pairs, any particular pair can be selected as $k_{0,r}$ and T_0 and thus allows the calculation of $\Delta H_0^\ddagger$ for each value of *T*. Hence a set of *a* data point pairs gives rise to *an* unique regressions, each regression providing an estimate of $\Delta H_{0,n}^\ddagger$ at $T_{0,n}$ and a value of $\Delta C_{p,n}^\ddagger$. Any particular set of data is characterized by three possibilities with respect to $\Delta H_{0,n}^\ddagger$ and $\Delta C_{p,n}^\ddagger$. These are (a) $\Delta H_0^\ddagger$ temperature independent, i.e., $\Delta C_p^\ddagger = 0$; (b) $\Delta H_0^\ddagger$ temperature dependent, $\Delta C_p^\ddagger$ temperature independent; finally, (c) $\Delta H_0^\ddagger$ temperature dependent, $\Delta C_p^\ddagger$ temperature dependent. The original assumptions in the derivation of eq 6 accommodate both items (a) and (b) above and when these assumptions are appropriate the data should provide, following regression, a series of $\Delta H_{0,n}^\ddagger$ values linearly related to T_0 and a constant $\Delta C_p^\ddagger$ (i.e., ΔC_{pn} = constant; $n = 1, 2, 3, \ldots, n$). More realistically for the latter parameter the spread of $\Delta C_{p,n}^\ddagger$ values

Table II. Results from the Regression of Synthetic Rate Data Related to the Albery-Robinson Ion-Pair Mechanism

T_0, °C	−slope[a]	10^{-3} × intercept[b]	$-\Delta C_p^\ddagger/R^c$
90.00	79.88 ± 0.29	11.898 ± 0.005	−68.13
85.00	80.15 ± 0.39	12.288 ± 0.005	−72.92
80.00	80.72 ± 0.32	12.681 ± 0.004	−77.31
75.00	81.31 ± 0.25	13.081 ± 0.003	−80.92
70.00	81.75 ± 0.23	13.488 ± 0.002	−83.37
65.00	81.90 ± 0.24	13.898 ± 0.002	−84.31
60.00	81.70 ± 0.25	14.309 ± 0.002	−83.53
55.00	81.19 ± 0.29	14.715 ± 0.003	−80.98
50.00	80.45 ± 0.38	15.114 ± 0.004	−76.80
45.00	79.72 ± 0.48	15.504 ± 0.006	−71.32
40.00	79.40 ± 0.36	15.890 ± 0.005	−64.97

[a] Slope = $\Delta C_{p,n}^\ddagger/R$. [b] Intercept = $\Delta H_0^\ddagger/R$. [c] Values calculated from eq 12. [d] The Valentiner equation gives −79.33.

should remain within the largest error limit observed and the values of $\Delta C_{p,n}^\ddagger$ should show no marked trend with temperature. Since the dependent variable on the left-hand side of eq 7 contains *four* measured quantities and also involves the difference $T - T_0$, we anticipated that this equation would represent a serious test of the quality of the data (ca. 140 systems). The errors in $\Delta C_p^\ddagger$ are, as anticipated, generally larger than those determined by the Valentiner equation. This is a consequence of the factor mentioned above and also a consequence of the fact that the errors must now be weighted between two coefficients ($\Delta H_0^\ddagger$ and $\Delta C_p^\ddagger$) rather than three (A, B, and C of eq 5).

In Table I we report the results obtained subsequently by treating the rate data for the solvolysis of 2-bromopropane in deuterium oxide[17] in the way described above. The derived values of $\Delta H^\ddagger$ and $\Delta C_p^\ddagger$ are in agreement with those reported using eq 5 but this is not invariably so with other substrates. The $\Delta C_{p,n}^\ddagger$ values are not constant but show no large or systematic variations with temperature and the $\Delta H_{0,n}^\ddagger$ values demonstrate an excellent linear relationship with the latter quantity. These results are also illustrated in Figure 1. In the present case there are two reasons which make it impossible to decide whether or not $\Delta C_p^\ddagger$ is partly or completely abnormal. Firstly, $\Delta C_p^\ddagger$ is in the "thermodynamic" region; secondly, there is no marked variation of $\Delta C_p^\ddagger$ with temperature.

The way eq 7 would behave when the conditions appropriate to item (c) prevailed were not considered at the commencement of the present study. The observation that eq 5 would remain useful (rather than stictly valid) when $\Delta C_p^\ddagger$ was also a function of temperature was revealed when this expression was used to regress synthetic data calculated to mimic the Albery-Robinson mechanism. It is to this part of the present contribution that we now turn.

Synthetic Data Related to the Albery-Robinson Mechanism

The steady-state rate law appropriate to the Albery-Robinson mechanism can be expressed as

$$k_{\text{obsd}} = k_1/(1 + \alpha) \qquad (8)$$

where

$$\alpha = k_2/k_3 \qquad (9)$$

For the purpose of generating synthetic data, k_1 was calculated via the expression

$$\ln k_1 = AT^{-1} + B_1 \ln T + C_1 \qquad (10)$$

and α via the expression

$$\ln \alpha = A_2T^{-1} + B_2 \ln T + C_2 \qquad (11)$$

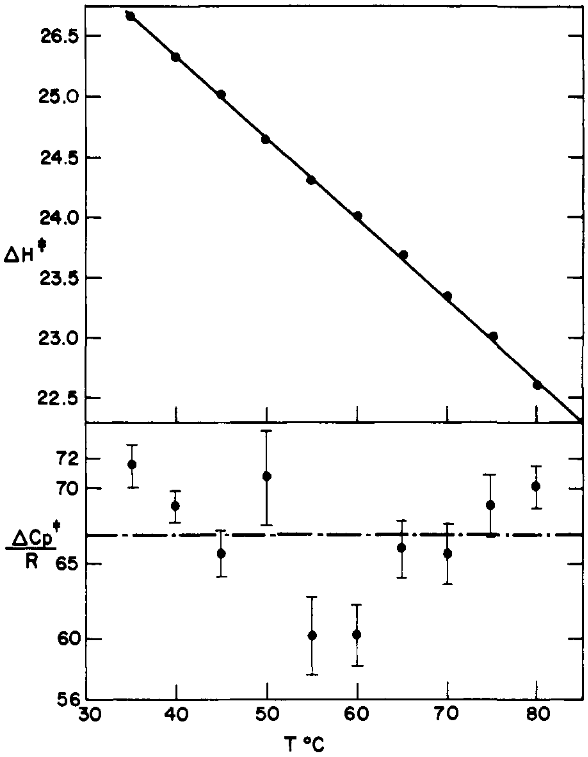

Figure 1. Variation of $\Delta C_{p,n}^\ddagger$ and $\Delta H_0^\ddagger$ with temperature for 2-bromopropane in D_2O; see Table I.

Table III. Results from the Regression of Synthetic Rate Data Related to the Albery-Robinson Ion-Pair Mechanism ($A_2 = 2 \times 10^4$)

T_0, °C	−slope[a]	10^{-3} × intercept[b]	$-\Delta C_p^\ddagger/R^c$
90.00	348.4 ± 10.6	10.09 ± 0.17	82.19
85.00	357.4 ± 13.9	11.52 ± 0.19	125.4
80.00	376.7 ± 12.1	13.05 ± 0.14	197.1
75.00	399.0 ± 9.7	14.78 ± 0.10	304.2
70.00	418.6 ± 8.7	16.76 ± 0.09	432.8
65.00	427.3 ± 9.0	18.92 ± 0.07	529.6
60.00	419.9 ± 8.9	21.10 ± 0.08	527.6
55.00	399.6 ± 9.9	23.11 ± 0.09	422.4
50.00	375.2 ± 12.4	24.86 ± 0.13	281.9
45.00	355.5 ± 13.8	26.39 ± 0.18	167.0
40.00	347.1 ± 10.5	27.83 ± 0.16	94.2

[a] Slope = $\Delta C_{p,n}^\ddagger/R$. [b] Intercept = $\Delta H^\ddagger/R$. [c] Values calculated from eq. 12. [d] The Valentiner equation gives −389.2.

By keeping B_1 and B_2 finite in eq 10 and 11 we relax the constraint originally imposed by Albery and Robinson whereby the $\Delta C_p^\ddagger$ related to the temperature dependence of k_{obsd} would be entirely spurious. The expression for $\Delta C_p^\ddagger$ as a function of temperature can be derived from considerations elaborated elsewhere[12]

$$\frac{\Delta C_p^\ddagger}{R} = B_1 - \frac{\alpha}{(1+\alpha)^2}\left\{\frac{A_2 + B_2T}{T}\right\}^2 + \frac{B_2\alpha}{1+\alpha} \qquad (12)$$

providing the true value of $\Delta C_p^\ddagger$ at any temperature. Since α is also a function of temperature, the variation of $\Delta C_p^\ddagger$ with temperature is evidently complex.

Ten synthetic data sets (k_{obsd}, T) were generated with $A_1 = -1.2 \times 10^4$, $B_1 = -25$, and $C_1 = 197$, with these three quantities remaining fixed for every set. The quantity B_2 was also held fixed for each set, the value adopted being $B_2 = -10$. The individual sets were calculated by varying A_2 from 0.2×10^4 to 2×10^4 in increments of 0.2×10^3. For each value of A_2

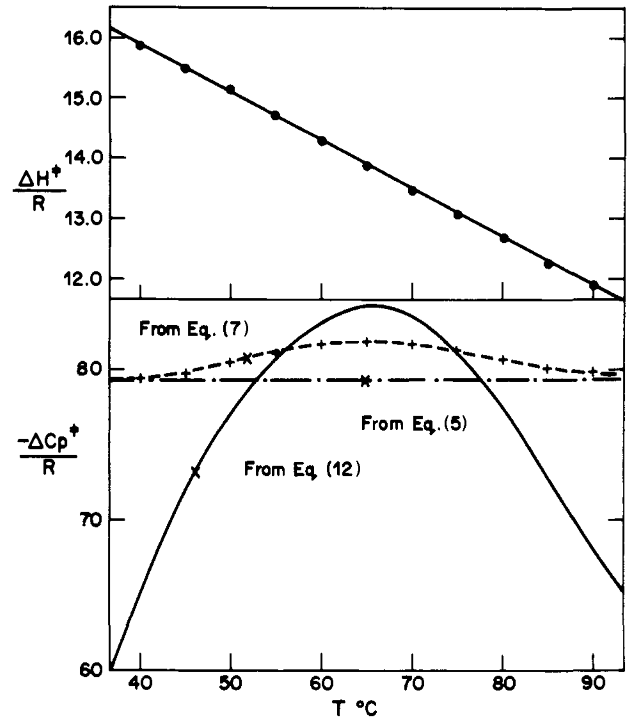

Figure 2. Variation of $\Delta C_{p,n}{}^{\ddagger}$ and $\Delta H_0{}^{\ddagger}$ with temperature for synthetic data; A_2 = 2.0 × 10³; see Table II.

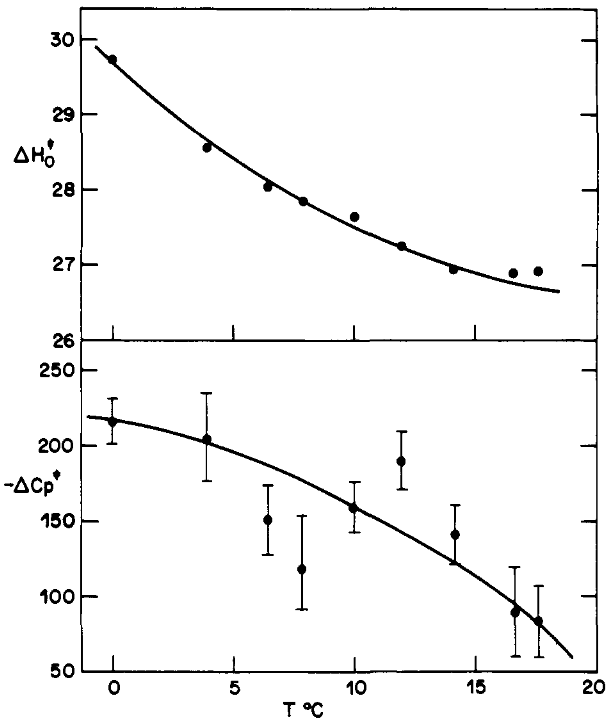

Figure 4. Variation of $\Delta C_{p,n}{}^{\ddagger}$ and $\Delta H_0{}^{\ddagger}$ with temperature for the solvolysis of 1-adamantyl nitrate; see Table IV.

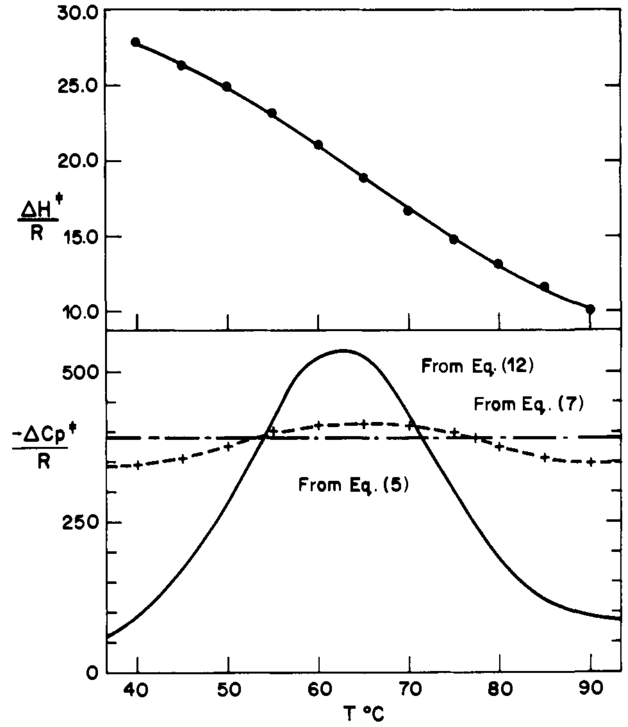

Figure 3. Variation of $\Delta C_{p,n}{}^{\ddagger}$ and $\Delta H_0{}^{\ddagger}$ with temperature for synthetic data; A_2 = 1.2 × 10⁴; see Table III.

the quantity C_2 was adjusted so that $\alpha = 1$ at $T = 65$ °C. The reasons for this tactic are as follows. Although k_{obsd} was calculated at 5 °C intervals between 0 and 100 °C, only the data between 40 and 90 °C were regressed (11 data point pairs). If the quantity α is unity at 65 °C, this ensures that the "abnormal" component of $\Delta C_p{}^{\ddagger}$ will have a maximum value at the midpoint of the temperature range of the regressed data. The ten sets of data produced in this way were realistic in the sense that k_{obsd} remained in a range accessible to experiment; i.e., the values A_n, B_n, and C_n (n = 1 or 2) did not give rise to values of k_{obsd} "inaccessible to measurement" as a consequence of excessively short or inordinately long half-lives.

The synthetic data so calculated were first regressed via the Valentiner equation giving an "average $\Delta C_p{}^{\ddagger}$ appropriate to the range 40 → 90 °C. The data were then regressed using eq 7 as described above, providing 11 values of $\Delta H_0{}^{\ddagger}$ and 11 values of $\Delta C_p{}^{\ddagger}$ at 5 °C intervals between 40 and 90 °C. The response of eq 7 to a situation where both $\Delta H_0{}^{\ddagger}$ and $\Delta C_p{}^{\ddagger}$ are functions of temperature was now evident; i.e., *eq 7 is capable of sensing correctly the way $\Delta C_p{}^{\ddagger}$ varies with temperature, although the regression underestimates the true value of this quantity.* Thus, if a similar situation is revealed by regressing experimental data, the true magnitude of *the abnormal component of $\Delta C_p{}^{\ddagger}$ will always be greater than that revealed by eq 7.* This provides the cornerstone to the mechanistic proposals offered later in this paper.

The observations with respect to the variation of $\Delta C_p{}^{\ddagger}$ with temperature elaborated above are illustrated in Figures 2 and 3 and the related data are assembled in Tables II and III for A_2 = 0.2 × 10³ and A = 1.2 × 10³, respectively. The horizontal lines in Figures 2 and 3 represent the constant $\Delta C_p{}^{\ddagger}$ obtained from the regression of the data via eq 7. The more strongly "spiked" bell-shaped curve corresponds to a combination of temperature-independent real terms and abnormal terms calculated via eq 12. The relative constancy of the $\Delta C_p{}^{\ddagger}$ values from eq 7 in Figure 2 suggests that, even when the $\Delta C_p{}^{\ddagger}$ parameter from real experimental data is apparently constant, the Albery-Robinson mechanism may be operative. Furthermore, if the condition that $\alpha = 1$ does not prevail in the middle of the experimental data, or alternatively the "peak" in $\Delta C_p{}^{\ddagger}$ occurs outside the experimental temperature range, the detection of the variation of $\Delta C_p{}^{\ddagger}$ with temperature will be less likely. With this in mind we observe that these phenomena are most likely to be associated with the larger negative $\Delta C_p{}^{\ddagger}$ values previously obtained via the Valentiner equation; otherwise, detection is likely to be a rather random event.

The "errors" in $\Delta C_p{}^{\ddagger}$ obtained when the synthetic data are

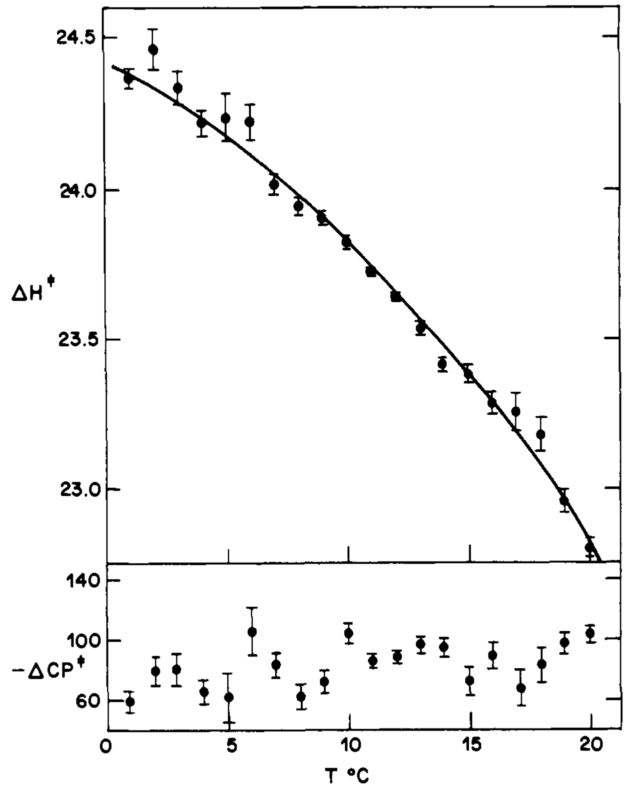

Figure 5. Variation of $\Delta C_{p,n}^{\ddagger}$ and $\Delta H_0^{\ddagger}$ with temperature for the solvolysis of *tert*-butyl chloride.

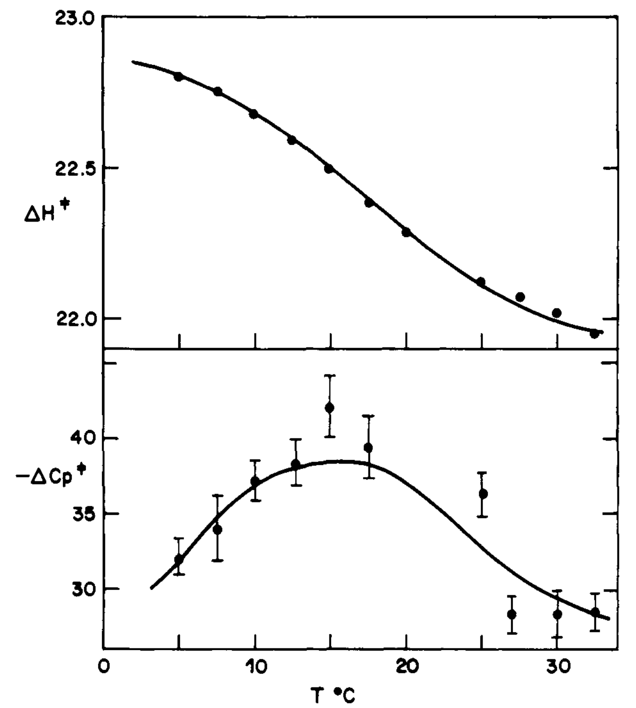

Figure 6. Variation of $\Delta C_{p,n}^{\ddagger}$ and $\Delta H_0^{\ddagger}$ with temperature for the solvolysis of *S*-propyl methanesulfonate; see Table VI.

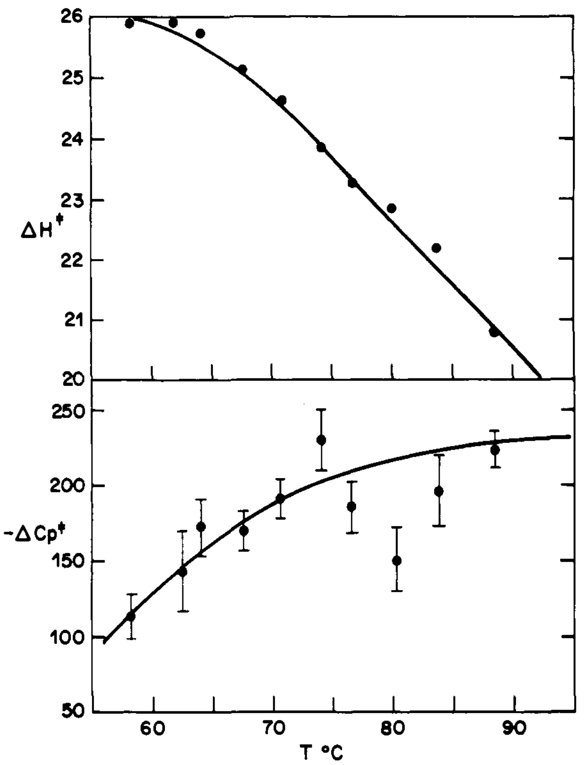

Figure 7. Variation of $\Delta C_{p,n}^{\ddagger}$ and $\Delta H_0^{\ddagger}$ with temperature for the solvolysis of *m*-trifluoromethylbenzyl nitrate; see Table VII.

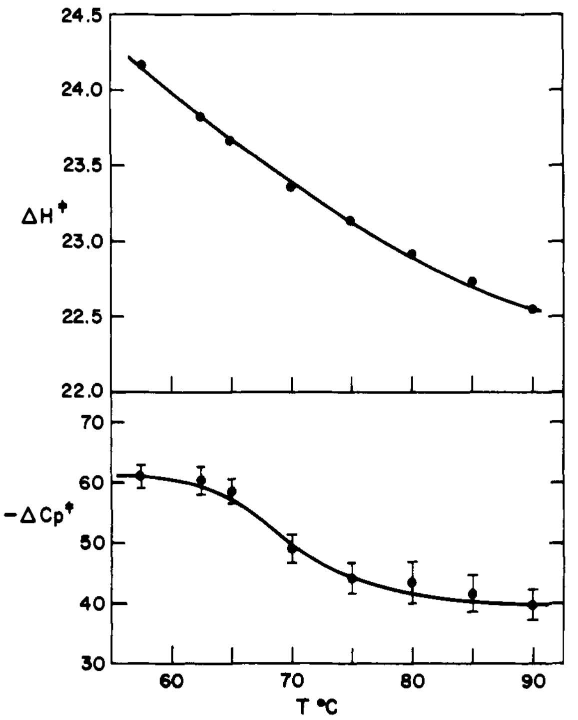

Figure 8. Variation of $\Delta C_{p,n}^{\ddagger}$ and $\Delta H_0^{\ddagger}$ with temperature for the solvolysis of ethyl bromide; see Table VIII.

processed via eq 7 deserve comment. These arise *entirely* from the fact that the "wrong" equation is being used to regress the data. Thus when real experimental data containing random experimental errors are used the latter will be superimposed on the limitations of eq 7 and this may give rise to the situation observed in the results obtained for 2-bromopropane solvolyzing in D_2O (see Figure 1). Clearly one approach to this problem is to fit the data to the Albery-Robinson equation (see ref 11, eq 7). However, to do this, the $\Delta C_p^{\ddagger}$ must be considered to be entirely abnormal. As yet, we are not convinced that such a proposal would be correct and we leave such a possibility and the technicalities associated with it to a future communication.

An alternative tactic might be envisaged, namely, to integrate the van't Hoff isochore in the way used to derive eq 7 assuming $\Delta C_p^{\ddagger}$ to be temperature dependent. But this ap-

Table IV. Rate and Thermodynamic Data Related to the Solvolysis of Adamantyl Nitrate in Water[9]

T_0, °C	10^4k,[a] s^{-1}	−slope[b]	10^{-3} × intercept[b]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$-\Delta C_{pn}^{\ddagger}$,[c] cal mol^{-1} K^{-1}
0.068	2.094	108.85 ± 7.58	14.946 ± 0.045	29.733 ± 0.089	216.28 ± 15.60
4.154	4.733	103.43 ± 15.00	14.381 ± 0.063	28.575 ± 0.125	205.51 ± 29.80
6.464	7.254	76.49 ± 11.62	14.120 ± 0.040	28.056 ± 0.079	151.99 ± 23.12
8.103	9.738	58.93 ± 12.99	14.022 ± 0.040	27.862 ± 0.079	117.09 ± 25.81
9.984	13.69	80.25 ± 8.09	13.920 ± 0.024	27.659 ± 0.048	159.46 ± 16.07
12.090	19.83	95.83 ± 9.37	13.711 ± 0.030	27.244 ± 0.060	190.41 ± 18.61
14.182	28.14	70.94 ± 9.70	13.565 ± 0.036	26.954 ± 0.072	140.95 ± 19.27
16.657	42.39	45.08 ± 14.30	13.544 ± 0.066	26.912 ± 0.131	89.57 ± 28.41
17.682	50.31	41.76 ± 11.77	13.553 ± 0.060	26.930 ± 0.119	82.98 ± 23.39

[a] Mean of three to five replicate runs. [b] See footnote *b*, Table I. [c] The Valentiner equation gives −155.9 cal mol^{-1} K^{-1}.[9,20]

Table V. Rate Constants and Thermodynamic Data Related to the Solvolysis of *tert*-Butyl Chloride in Water[19]

n	T_0, °C	10^2k,[a] s^{-1}	−slope[b]	intercept	$\Delta H_0^{\ddagger}$, kcal mol^{-1}	$-\Delta C_{pn}^{\ddagger}$,[c] cal mol^{-1} K^{-1}
1	1.008	0.8418	30.01 ± 3.11	12.263 ± 0.017	24.367 ± 0.034	59.63 ± 6.18
2	2.014	0.9925	39.83 ± 5.16	12.314 ± 0.027	24.468 ± 0.068	79.14 ± 10.25
3	3.010	1.174	41.23 ± 5.18	12.249 ± 0.025	24.339 ± 0.050	81.92 ± 10.29
4	4.009	1.379	32.76 ± 4.47	12.187 ± 0.019	24.216 ± 0.038	65.09 ± 8.88
5	5.015	1.618	33.86 ± 9.00	12.198 ± 0.039	24.237 ± 0.078	62.23 ± 17.88
6	5.961	1.896	58.22 ± 8.22	12.191 ± 0.031	24.224 ± 0.062	115.68 ± 16.33
7	7.029	2.241	42.28 ± 4.44	12.087 ± 0.015	24.017 ± 0.030	84.01 ± 8.82
8	8.016	2.609	31.56 ± 4.32	12.047 ± 0.014	23.937 ± 0.028	62.71 ± 8.58
9	9.019	3.051	36.70 ± 3.43	12.031 ± 0.010	23.906 ± 0.020	72.92 ± 6.81
10	10.023	3.569	47.76 ± 3.28	11.990 ± 0.010	23.824 ± 0.020	94.90 ± 6.51
11	11.012	4.145	43.34 ± 1.99	11.940 ± 0.006	23.725 ± 0.012	86.12 ± 3.95
12	12.025	4.829	44.18 ± 1.86	11.896 ± 0.006	23.637 ± 0.012	87.79 ± 3.70
13	13.015	5.602	48.83 ± 2.46	11.842 ± 0.008	23.530 ± 0.016	97.03 ± 4.89
14	14.020	6.491	47.84 ± 2.85	11.786 ± 0.010	23.419 ± 0.020	95.06 ± 5.66
15	15.016	7.488	36.19 ± 4.58	11.769 ± 0.017	23.385 ± 0.034	71.91 ± 9.10
16	16.010	8.667	45.05 ± 4.44	11.720 ± 0.018	23.289 ± 0.036	89.51 ± 8.82
17	17.006	9.964	34.07 ± 6.10	11.704 ± 0.028	23.256 ± 0.056	67.70 ± 12.12
18	18.012	11.54	42.07 ± 6.06	11.667 ± 0.030	23.182 ± 0.060	83.59 ± 12.04
19	19.008	13.24	49.59 ± 3.27	11.555 ± 0.018	22.960 ± 0.036	98.54 ± 6.50
20	20.013	15.19	51.95 ± 2.39	11.478 ± 0.014	22.807 ± 0.028	103.22 ± 4.75

[a] Mean of three to five replicate runs. [b] See Table I, footnote *b*. [c] The Valentiner equation gave −83 cal mol^{-1} K^{-1}.

Table VI. Rate and Thermodynamic Data Related to the Solvolysis of *S*-Propyl Methanesulfonate in Water[20]

n	T_0, °C	10^5k,[a] s^{-1}	−slope[b]	10^3 × intercept[c]	$\Delta H_0^{\ddagger}$, kcal mol^{-1}	$-\Delta C_{p,n}^{\ddagger}$,[c] cal mol^{-1} K^{-1}
1	32.520	50.28	14.35 ± 0.59	11.045 ± 0.005	21.946 ± 0.010	28.51 ± 1.17
2	30.004	36.92	14.21 ± 0.76	11.081 ± 0.006	22.018 ± 0.012	28.24 ± 1.51
3	27.508	27.00	14.31 ± 1.27	11.108 ± 0.009	22.072 ± 0.018	28.43 ± 2.52
4	25.000	19.64	17.42 ± 0.79	11.133 ± 0.005	22.121 ± 0.010	36.61 ± 1.57
5	20.005	10.19	16.48 ± 1.10	11.216 ± 0.005	22.286 ± 0.010	32.76 ± 2.19
6	17.496	7.268	19.85 ± 1.07	11.263 ± 0.005	22.380 ± 0.010	39.44 ± 2.13
7	14.997	5.147	21.19 ± 1.05	11.321 ± 0.005	22.495 ± 0.010	42.10 ± 2.09
8	12.495	3.610	19.26 ± 0.78	11.370 ± 0.004	22.592 ± 0.008	38.27 ± 1.55
9	10.003	2.519	18.79 ± 0.66	11.414 ± 0.004	22.680 ± 0.008	37.34 ± 1.31
10	7.501	1.741	17.14 ± 1.09	11.450 ± 0.008	22.751 ± 0.016	34.06 ± 2.17
11	4.997	1.196	16.18 ± 0.73	11.475 ± 0.006	22.801 ± 0.012	32.15 ± 1.45

[a] Mean of three to five replicate runs. [b] See Table I, footnote *b*. [c] Valentiner equation gave −35 cal mol^{-1} K^{-1}.[20]

proach would introduce the problem of regressing an equation containing at least four unknowns.[18] Nothing is therefore to be gained at the present time by adding further terms to eq 7.

It must be emphasized that the thrust of the present paper is not to provide "true" thermodynamic parameters characterizing the reactions considered. This is a difficult problem if either the Albery-Robinson mechanism is operative or a more elaborate scheme involving real $\Delta C_p^{\ddagger}$ terms is appropriate.[12] Rather, we are concerned here with seeking clues concerning the temperature dependence of $\Delta C_p^{\ddagger}$ and whether the temperature dependence conforms in any way to the proposals of Albery and Robinson. In this enterprise eq 7 is clearly an imperfect but nevertheless useful tool since it allows the kinetic data to be probed in a way which has been hitherto neglected.

Some Experimental Results

In Figures 4-8 we illustrate data obtained from regressions using eq 7 for adamantyl nitrate,[9] *tert*-butyl chloride,[19] *s*-propyl methanesulfonate,[20] *m*-trifluoromethylbenzyl nitrate,[10] and ethyl bromide.[20] The chloride, methanesulfonate, and bromide all provide examples where the Valentiner equation gives $\Delta C_p^{\ddagger}$ values in the "thermodynamic" regions. This latter

Table VII. Rate and Thermodynamic Data Related to the Solvolysis of *m*-Trifluoromethylbenzyl Nitrate in Water[10]

n	T_0, °C	10^4k [a]	−slope [b]	10^{-3} × intercept [b]	$\Delta H_0^{\ddagger}$, kcal mol^{-1}	$-\Delta C_p^{\ddagger}$, [c] cal mol^{-1} K^{-1}
1	58.302	0.1357	57.26 ± 7.45	13.018 ± 0.065	25.867 ± 0.129	113.78 ± 14.88
2	62.315	0.2168	72.10 ± 13.63	13.028 ± 0.098	25.887 ± 0.195	143.26 ± 27.08
3	64.144	0.2705	86.83 ± 9.20	12.944 ± 0.060	25.720 ± 0.119	172.53 ± 18.28
4	67.578	0.4001	84.76 ± 6.57	12.647 ± 0.036	25.130 ± 0.072	168.42 ± 13.41
5	70.704	0.5661	95.81 ± 6.71	12.391 ± 0.034	24.621 ± 0.068	190.37 ± 13.33
6	74.025	0.8087	116.12 ± 10.56	12.005 ± 0.052	23.854 ± 0.103	230.73 ± 20.98
7	76.781	1.057	93.39 ± 8.69	11.717 ± 0.047	23.282 ± 0.093	185.57 ± 17.27
8	80.296	1.478	76.43 ± 10.68	11.504 ± 0.069	22.858 ± 0.137	151.87 ± 21.22
9	83.811	2.075	98.98 ± 12.32	11.156 ± 0.096	22.167 ± 0.191	196.67 ± 24.48
10	88.704	3.132	107.73 ± 6.05	10.456 ± 0.060	20.776 ± 0.119	214.06 ± 12.02

[a] Mean of three to five replicate runs. [b] See footnote *b*, Table **I**. [c] The Valentiner equation gave −157 ± 10 cal mol^{-1} K^{-1}.

Table VIII. Rate and Thermodynamic Data Related to the Solvolysis of Ethyl Bromide in Water[20]

n	T, °C	10^4k, [a] s^{-1}	−slope [b]	10^{-3} × intercept	$\Delta H_0^{\ddagger}$, kcal mol^{-1}	$-\Delta C_{p,n}^{\ddagger}$, [a] cal mol^{-1} K^{-1}
1	90.000	6.831	20.05 ± 0.94	11.347 ± 0.010	22.546 ± 0.020	39.83 ± 1.88
2	85.016	4.350	20.21 ± 1.19	11.437 ± 0.010	22.725 ± 0.020	40.16 ± 2.37
3	80.008	2.724	22.02 ± 0.92	11.531 ± 0.006	22.912 ± 0.012	43.75 ± 1.83
4	74.840	1.649	22.32 ± 1.16	11.642 ± 0.007	23.133 ± 0.014	44.35 ± 2.30
5	69.986	1.012	25.10 ± 1.32	11.756 ± 0.008	23.359 ± 0.016	49.87 ± 2.62
6	65.067	0.6052	29.47 ± 1.80	11.910 ± 0.012	23.665 ± 0.024	58.56 ± 3.58
7	62.583	0.4625	30.36 ± 1.67	11.995 ± 0.013	23.834 ± 0.026	60.33 ± 3.32
8	57.600	0.2646	30.75 ± 1.28	12.164 ± 0.012	24.170 ± 0.024	61.10 ± 2.54

[a] Mean of three to six determinations. [b] See Table **I**, footnote *b*. [c] Valentiner equation gave −49.31 ± 3.82 cal mol^{-1} K^{-1}.

observation suggests, but does not demand, that all $\Delta C_p^{\ddagger}$ values are spurious in the Albery-Robinson sense. As stated previously, we are not as yet prepared to accept such a drastic hypothesis, although we recognize it to be a possibility which must be considered. The error limits related to $\Delta C_p^{\ddagger}$ for the nitrates are rather large and the errors are also large in the case of *t*-BuCl but for different reasons. The data for the latter compound involve 19 data points determined at 1 °C intervals. With this in mind the data are impressive and consistent with the original proposals of Albery and Robinson[11] that α for this compound is unity in the vicinity of 33 °C. Summaries of the data related to these displacements are reported in Tables IV-VIII.

Some Mechanistic Considerations

While the notion that the tertiary displacements represented by 1-adamantyl nitrate and *t*-BuCl proceed via a nonunitary mechanism is probably acceptable, the idea that the primary centers represented by ethyl bromide and the substituted benzyl nitrate proceed by such a mechanism is surprising. The above evidence is quite compelling and, if the S_N2 description for ethyl bromide were to be maintained,[21] it would be difficult to explain the results for this compound illustrated in Figure 8. Furthermore, any mixed kinetics description involving a combination of the classical S_N1-S_N2 paths must yield an activation energy which increases with temperature.[5,12] This is not borne out by the experimental results. The k_1, k_2, and k_3 steps for the five substrates demonstrating temperature-dependent $\Delta C_p^{\ddagger}$ values are probably similar in the case of adamantyl nitrate and *t*-BuCl and also similar in the case of the two primary centers, but differ between the primary and tertiary substrates. Definitive mechanistic conclusions must await a comprehensive reexamination of the large body of data available.[2b]

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Semiconductor Electrodes. 26. Spectral Sensitization of Semiconductors with Phthalocyanine

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Abstract: Spectral sensitization by metal-free phthalocyanine (H_2Pc) films was observed on various semiconductor electrodes (single-crystal n-TiO_2, n-$SrTiO_3$, n-WO_3, n-ZnO, n-CdS, n-CdSe, n-Si, and n-GaP; SnO_2 conducting glass). The spectral response of the sensitized photocurrent was generally the same as the absorption spectrum of the phthalocyanine. The rather thick (400 Å to 1 μm) H_2Pc films showed both anodic and cathodic photocurrents depending upon the applied potential. The anodic photocurrents represented the usual sensitization of the n-type semiconductor, while the cathodic photocurrents were attributed to p-type behavior of the phthalocyanine itself. The current-potential curves of the semiconductor electrodes depended on the nature of the H_2Pc film, the presence of a redox couple (i.e., *p*-hydroquinone/*p*-benzoquinone) in solution, and the wavelength of the irradiating light. The magnitude of the steady state sensitized photocurrent was linear with light intensity and was strongly affected by the addition of a supersensitizer.

Introduction

Many studies have been conducted utilizing dyes to sensitize reactions at semiconductor and metal electrodes.[1-5] Such sensitization is of interest, because it provides information about the nature of charge transfer between excited states and electrodes and, from a more practical standpoint, because it allows the utilization of longer wavelength light to promote photoprocesses at semiconductors. The problem with utilizing dye sensitization to increase the efficiency of semiconductor processes arises primarily from the relatively low absorbance of the monolayer films of dyes adsorbed on the surface. This results in a very low overall quantum efficiency in terms of incident (rather than absorbed) light. The use of concentrated solutions of dyes ($>10^{-4}$ M) to maintain adsorbed monolayers can reduce the sensitized photocurrents, because the dye solution itself acts as a filter and thereby decreases the light intensity at the electrode surface. The use of thick, insoluble dye films[6] has generally not proven successful because of the high ohmic resistance of these films. Gerischer has, in fact, suggested that not much can be gained by using dye multilayers because of the ohmic resistance to electron transfer and an increased quenching probability.[1] With the exception of sensitization by adsorbed dyes on sintered zinc oxide electrodes,[7] the overall quantum efficiency for these processes is usually quite small. We report here spectral sensitization on semiconductor electrodes by thicker metal-free phthalocyanine (H_2Pc) films (400 Å to 1 μm thick).

Sensitization by phthalocyanines is of interest for a number of reasons. Research on these materials has been very active recently,[8] and much is known about the redox behavior of these species in solution,[9,10] the catalytic activity of phthalocyanine electrodes (e.g., in fuel cells),[11-13] and their photoproperties.[14-17] These compounds have many characteristics which suggest that they might be useful sensitizers for semiconductor electrodes: (1) they absorb light strongly in the visible region of the solar spectrum; (2) a wide variety of small phthalocyanines have been prepared which allow a range of different compounds with different energy levels (i.e., redox potentials); (3) many phthalocyanines are readily available, very stable, and insoluble in water; (4) the redox behavior of these compounds has been studied extensively; (5) the phthalocyanines often exhibit semiconducting behavior.

The initial studies reported in this paper concern the utilization of films of H_2Pc primarily on single-crystal n-type semiconductors. The results are discussed according to a proposed mechanism of reactions of excited dye molecules on semiconductors[1] and the relative positions of the energy levels of the semiconductors, H_2Pc and the redox couples in solution. The action spectra of the sensitized photocurrent and the current-potential (*i*-*V*) behavior are presented. The dependence of the sensitized photocurrent on light intensity and the concentration of a supersensitizer in solution is discussed. The stability of these systems both in the dark and under illumination and the p-type semiconductor properties of the H_2Pc films are also described.

Experimental Section

Materials. The metal-free phthalocyanine was purchased from Eastman (Rochester, N.Y.) and purified by repeated sublimation. The single-crystal semiconductors were obtained from several sources (CdSe and CdS, Cleveland Crystals; GaAs, GaP, and Si, Monsanto; ZnO and $SrTiO_3$, Atomergic; TiO_2, Fuji Titanium; WO_3, Sandia). All of the semiconductors were n-type. Unless stated otherwise all other chemicals were reagent grade and the water had been triply distilled from an alkaline potassium permanganate solution. Ohmic contacts were made to the back of the semiconductors. An electrical contact was made to this ohmic contact using silver conducting paint (Acme Chemicals, New Haven, Conn.). On the back and sides, 5-min epoxy cement (Devcon Corp., Danvers, Mass.) was used to cover the electrode and mount the crystal to a glass tube.

The films were prepared by sublimation in a vacuum deposition apparatus (Vacuum Engineering Co., North Billerica, Mass.). The H_2Pc was placed in a porcelain crucible. The H_2Pc was heated under vacuum (10^{-5}–10^{-6} Torr) by means of a tungsten wire (0.060 in. in diameter). A current of 20 A, which corresponds to a crucible temperature of 400–450 °C, was passed through the wire. The electrode substrate was about 25 cm above the crucible. The film thicknesses of the sublimed H_2Pc were determined by spectrophotometric

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