

## The Dependence on Temperature of Rate Constants for Solvolysis of Alkyl Halides and Related Compounds in Water

By Michael J. Blandamer,\* John Burgess, and Phillip P. Duce, Department of Chemistry, The University, Leicester LE1 7RH

Ross E. Robertson, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada

John W. M. Scott, Department of Chemistry, Memorial University, St. John's, Newfoundland, Canada

Various explanations are considered for the observation that plots of  $\ln[k(\text{obs})]$  against  $T^{-1}$  for solvolysis of alkyl halides in water are generally curved. It is suggested that the two stage reaction scheme proposed by Albery and Robinson accounts for the patterns of behaviour in derived parameters previously reported which were calculated assuming that the mechanism involves a single activation barrier.

It is observed that, for the solvolysis of alkyl halides in water, a plot of  $\ln[k(\text{obs})]$  against  $T^{-1}$  is not a straight line.<sup>1</sup> Indeed with increase in temperature, the rate constant falls below that required by a linear dependence based on values of  $k(\text{obs})$  at low temperatures. The purpose of this paper is to consider how this trend can be accounted for. Three avenues of approach are available. First, we can assume that the chemical reaction is elementary, only one important activation barrier being involved. Therefore, the curvature is attributed to the complexity in the dependence of, for example, the related enthalpy of activation on temperature. Secondly, we can assume that the reaction scheme is complicated, the observed rate being a function of two or more rate constants,  $k_i$ , describing individual steps. The latter assumption is combined with the assumption that in each case  $\ln(k_i)$  is a linear function of  $T^{-1}$  with the result that  $\ln[k(\text{obs})]$  is not a linear function of  $T^{-1}$ . The third approach combines complexity in the reaction mechanism with complexity in the dependence of individual rate constants on temperature.

The curvature in plots of  $\ln[k(\text{obs})]$  against  $T^{-1}$  has been explained for the most part using the first approach<sup>1</sup> (model I). Thus Robertson accounted for this observation in terms of a non-zero heat capacity of activation.<sup>1</sup> The derived activation parameters were obtained by fitting the data to the Valentiner equation<sup>2</sup> using a conventional linear least squares technique. This equation<sup>2</sup> assumes that the heat capacity of activation is independent of temperature. However, there are indications that the Valentiner equation has a number of unsatisfactory features.<sup>3,4</sup> For example, the structure of the equation is such that the correlation coefficients (calculated from the variance-covariance matrix) between estimates of the derived parameters are close to unity. However, our major interest in this paper concerns the second avenue of approach. In particular we concentrate our attention on the proposal made by Albery and Robinson<sup>5</sup> in which the solvolysis of t-butyl chloride was described in terms of a two-stage mechanism (model II), see below. A feature<sup>6</sup> of this mechanism is that, if correct, the heat capacity of activation based on model I should be dependent on temperature. At the very least, an analysis of the data in terms of model II should show some measure of consistency with those previously reported, e.g. the derived parameters using

model II should be consistent with the negative values for  $\Delta C_p^\ddagger(\text{I})$  previously reported for model I. Indeed in a more recent study,<sup>7</sup> an attempt was made to estimate the dependence of  $\Delta C_p^\ddagger(\text{I})$  on temperature by calculating this parameter at a varying reference temperature  $\theta$  from the dependence of  $k(\text{obs})$  on temperature about a rate constant  $k(\theta)$  at  $\theta$ . The result was  $n$  values of  $\Delta C_p^\ddagger(\text{I})$  as a function of temperature from  $n$  rate constants. Although some evidence was obtained that  $\Delta C_p^\ddagger(\text{I})$  depends on temperature, the statistical basis of this analytical method is open to criticism. In the work described here we have examined the dependence of  $\ln(k)$  on temperature in terms of a polynomial<sup>4</sup> in  $(T - \theta)$ . It turns out that for the solvolysis of t-butyl chloride in water,  $\Delta C_p^\ddagger(\text{I})$  is dependent on temperature. This leads to the development of an analysis of kinetic data in terms of the mechanism proposed by Albery and Robinson.<sup>5</sup> The various problems which emerge from either the first or second approaches to the analytical task make it clear that adoption of the third approach is not justified at this stage.

### ANALYSIS

*A Elementary Reaction Scheme (Model I).*—As noted above, the dependence of  $\ln[k(\text{obs})]$  on temperature was previously analysed by the Valentiner equation to yield estimates of  $\Delta C_p^\ddagger(\text{I})$ . In all reported cases,<sup>1</sup>  $\Delta C_p^\ddagger(\text{I})$  is negative although the magnitude depends on the substrate. The same data can be analysed using other equations but retaining the underlying model I. In the present analysis, we have used the polynomial expression shown in equation (1). In the limit that  $T \rightarrow \theta$ ,  $\ln[k(\text{obs})]$  tends to  $b_1$ .

$$\ln[k(\text{obs})] = \sum_{i=1}^{i=m} b_i (T - \theta)^{i-1} \quad (1)$$

Application of transition theory<sup>8</sup> and the van't Hoff equation leads to a set of equations for the thermodynamic activation parameters as a function of temperature and at the reference temperature  $\theta$  [e.g. equations (2)—(4)].

$$\Delta H^\ddagger(\text{I}, \theta)/R = -\theta + b_2 \theta^2 \quad (2)$$

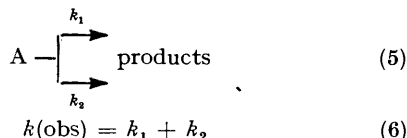
$$\begin{aligned} \Delta C_p^\ddagger/R = & -1 + 2b_2 T + 4b_3 T(T - \theta) + 2b_3 T^2 + \\ & 6b_4 T(T - \theta)^2 + 6b_4 T^2(T - \theta) + \\ & 8b_5 T(T - \theta)^3 + 12b_5 T^2(T - \theta)^2 + \\ & 10b_6 T(T - \theta)^4 + 20b_6 T^2(T - \theta)^3 \quad (3) \end{aligned}$$

$$\Delta C_p^\ddagger(\theta)/R = -1 + 2b_2 \theta + 2b_3 \theta^2 \quad (4)$$

Here we have considered the series, equation (1), up to the

sixth term. In a particular application,  $F$  tests of the variance and student  $t$  tests were applied to determine where the series should be terminated.

*B Complicated Reaction Schemes.*—A number of mechanistic schemes can be considered under this heading. Some, however, can be ruled out on the same grounds that they predict the wrong dependence of  $\ln[k(\text{obs})]$  on  $T^{-1}$ . Suppose, for example, that the scheme shown in equation (5) was adopted whereby  $k(\text{obs})$  is given by equation (6).



Differentiation of equation (6) with respect to temperature yields an equation (7) relating the apparent enthalpy of activation  $\Delta H^\ddagger(\text{app})$  to the activation enthalpies associated with  $k_1$  and  $k_2$ .

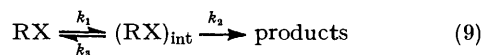
$$\Delta H^\ddagger(\text{obs}) = \frac{k_1}{(k_1 + k_2)} \Delta H_1^\ddagger + \frac{k_2}{(k_1 + k_2)} \Delta H_2^\ddagger \quad (7)$$

Consistent with the second approach discussed above (*i.e.* simplicity in the thermodynamic parameters) we assume that  $\Delta H_1^\ddagger$  and  $\Delta H_2^\ddagger$  are independent of temperature. However,  $\Delta C_p^\ddagger(\text{obs})$  is not zero as shown by differentiation of equation (7) with respect to temperature. Thus

$$\Delta C_p^\ddagger(\text{app}) = k_1 k_2 (\Delta H_1^\ddagger - \Delta H_2^\ddagger)^2 / RT^2 (k_1 + k_2)^2 \quad (8)$$

$\Delta C_p^\ddagger(\text{app})$  is always positive (or zero) requiring that the curvature of the plot of  $\ln[k(\text{obs})]$  against  $T^{-1}$  is opposite to that observed. Hence this mechanism [equation (5)] is unsatisfactory.

The solvolytic reaction will follow first order kinetics if the mechanism proposed by Albery and Robinson<sup>5</sup> is in operation [equation (9)].



$$k(\text{obs}) = k_1 / (1 + \alpha) \quad (10)$$

$$\alpha = k_2 / k_3 \quad (11)$$

Consequently, the observed first-order rate constant is a function of three rate constants. The quantity  $\alpha$  describes the ratio of two rate constants determining the kinetic fate of the intermediate. In the limit,  $\alpha \ll 1$ ,  $k(\text{obs}) = k_1$ , when  $\alpha \gg 1$ ,  $k(\text{obs}) = k_1 k_3 / k_2$ . The dependence of  $k(\text{obs})$  is determined by the dependence of both  $k_1$  and  $\alpha$  on temperature. Thus  $\Delta H^\ddagger(\text{app})$  is given by equation (12). If,

$$\Delta H^\ddagger(\text{app}) = \Delta H_1 - [RT^2 / (1 + \alpha)] d\alpha / dT \quad (12)$$

by definition, equation (13) applies, then (14) is obtained.

$$\Delta \Delta H^\ddagger = \Delta H_3^\ddagger - \Delta H_2^\ddagger \quad (13)$$

$$\Delta H^\ddagger(\text{app}) = \Delta H_1^\ddagger + [\alpha / (1 + \alpha)] \Delta \Delta H^\ddagger \quad (14)$$

Thus  $\Delta H^\ddagger(\text{app})$  will only equal  $\Delta H_1^\ddagger$  if  $\Delta \Delta H^\ddagger$  is zero. In keeping with the second approach, we assume that both  $\Delta H_1^\ddagger$  and  $\Delta \Delta H^\ddagger$  are zero. Differentiation of equation (14) with respect to temperature yields<sup>6</sup> an equation for  $\Delta C_p^\ddagger(\text{app})$  [equation (15)]. Because  $\alpha$  is dependent on

$$\Delta C_p^\ddagger(\text{app}) = -\alpha (\Delta \Delta H^\ddagger)^2 / (1 + \alpha)^2 RT^2 \quad (15)$$

temperature,  $\Delta C_p^\ddagger(\text{app})$  has a dependence on temperature which is not immediately apparent from equation (15).

Nevertheless, irrespective of the sign of  $\Delta H^\ddagger$ ,  $\Delta C_p^\ddagger(\text{app})$  is negative. Because this is consistent with the observed dependence of  $\ln[k(\text{obs})]$  on temperature, we have examined how the kinetic data can be fitted to equation (9). Consistent with the assumption discussed above, we set  $\ln k$ , and  $\ln \alpha$  as linear functions of  $T^{-1}$ . The dependence of  $k(\text{obs})$  on temperature is therefore given by equation (16).

$$k(\text{obs}) = \frac{a_1 \exp(a_2/T)}{1 + a_3 \exp(a_4/T)} \quad (16)$$

$$\Delta H_1^\ddagger = -R(a_2 + T) \quad (17)$$

$$\Delta \Delta H^\ddagger = a_4 R \quad (18)$$

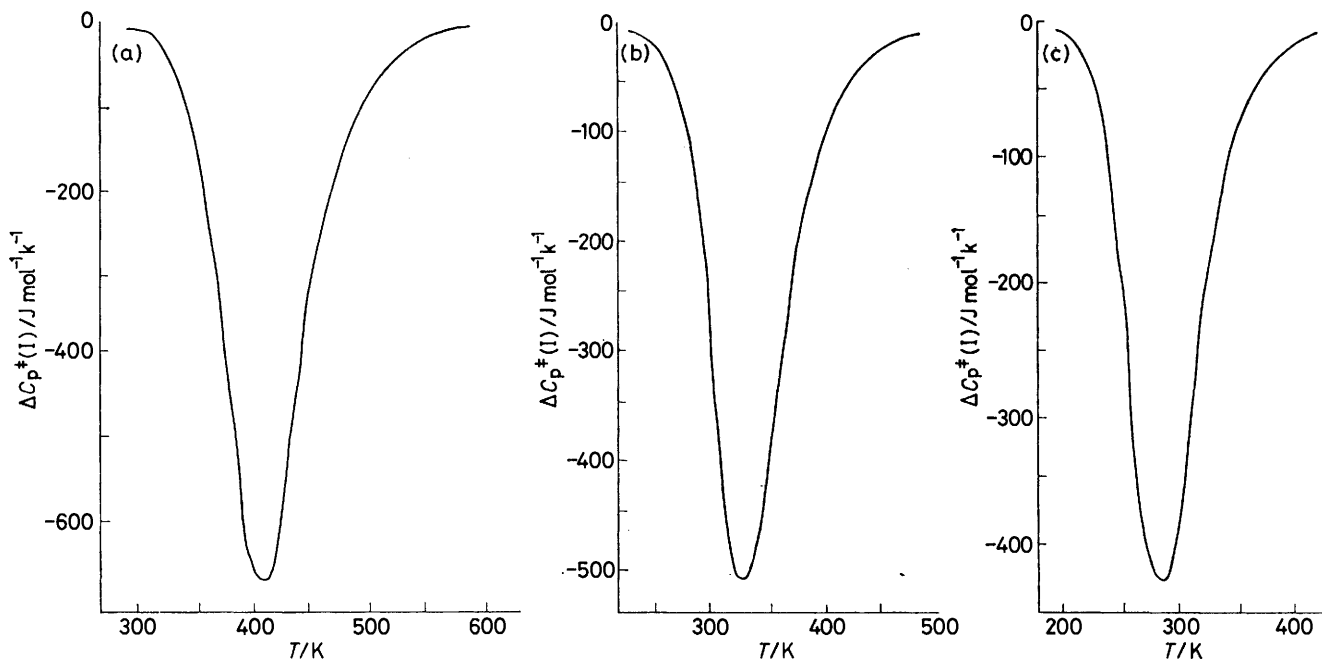
The dependence of  $k(\text{obs})$  on temperature cannot be fitted to equation (16) using a conventional linear least squares technique. A program (FORTRAN for the CDC Cyber 73 computer at the University of Leicester) incorporated a modified Gauss-Newton technique for fitting the data to equation (16), subroutines calculating the necessary Jacobian and Hessian matrices. The derived parameters were used to calculate the activation parameters, the dependence of  $k_1$ ,  $\alpha$ ,  $\Delta H^\ddagger(\text{app})$ , and  $\Delta C_p^\ddagger(\text{app})$  on temperature. The analysis also yielded the temperature at which  $\alpha = 1$ . The criterion for the fit was to minimise the residual sum of squares, *i.e.*  $\sum [k(\text{obs}) - k(\text{calc})]^2$  over  $n$  data points.

## RESULTS

The data for *t*-butyl chloride in water<sup>8</sup> were fitted to equation (1), only three terms in the series being statistically significant. When  $\theta = 283.17$  K,  $\Delta H^\ddagger(\theta) = 99.717$  kJ mol<sup>-1</sup> with a standard error (s.e.) of  $5 \times 10^{-5}$  kJ mol<sup>-1</sup>;  $\Delta C_p^\ddagger(\theta) = -342.3$  J mol<sup>-1</sup> K<sup>-1</sup> (s.e. 18.9);  $d\Delta C_p^\ddagger(\theta)/dT = 12.1$  J mol<sup>-1</sup> K<sup>-2</sup> (s.e. 0.25) and  $d^2\Delta C_p^\ddagger/dT^2 = 7.95 \times 10^{-2}$  J mol<sup>-1</sup> K<sup>-3</sup> (s.e.  $1.4 \times 10^{-3}$ ). Thus, across the experimental range of temperature the heat capacity of activation,  $\Delta C_p^\ddagger(\text{I})$  becomes more negative. The data for other solvolytic reactions also show that the calculated heat capacity of activation is dependent on temperature. It is observed that  $\Delta C_p^\ddagger(\text{I})$  at a reference temperature  $\theta$  near the middle of the experimental range is close to that previously reported.<sup>1</sup>

The complete set of data<sup>1</sup> has also been fitted to equation (16). For example, the data for ethyl bromide were satisfactorily fitted, the residuals showing satisfactory scatter about zero. In percentage terms, the largest derivation was 0.38%. The derived parameters are summarised in the Table. Thus  $k_1$  increases but  $\alpha$  decreases with increase in temperature;  $\alpha$  is less than 1.0 over the experimental range of temperatures, being equal to 1.0 at 412 K. The dependence of  $\Delta C_p^\ddagger(\text{app})$  on temperature [equation (15)] forms an inverted bell-shaped curve (Figure) with a minimum near 405 K where  $\Delta C_p^\ddagger(\text{app})$  equals  $-674$  J mol<sup>-1</sup> K<sup>-1</sup>. At 347.99 K  $\Delta C_p^\ddagger(\text{app})$  equals  $-125$  J mol<sup>-1</sup> K<sup>-1</sup>, which is close to the value of  $-107$  J mol<sup>-1</sup> K<sup>-1</sup> for  $\Delta C_p^\ddagger(\text{I})$  calculated from the polynomial equation. A similar pattern emerges for *t*-butyl chloride although the magnitude of the minimum in  $\Delta C_p^\ddagger(\text{app})$  is larger,  $-817$  J mol<sup>-1</sup> K<sup>-1</sup> at 315 K,  $\alpha$  being 1.0 at 317.7 K. The resulting value of  $\Delta C_p^\ddagger(\text{app})$  at 283.17 K is  $-309$  J mol<sup>-1</sup> K<sup>-1</sup> which is close to that obtained above for  $\Delta C_p^\ddagger(\text{I})$ . The minimum for  $\Delta C_p^\ddagger(\text{app})$  is still above the experimental range. However, for *n*-propyl bromide,  $\alpha = 1$  at a temperature within this range, while for isopropyl iodide this temperature falls below the range (Figure). Details for other solvolytic reactions are summarised in the Table, which includes the measured rate

Substrate	Ref.	No. of data points	T/K	T <sub>m</sub> /K	10 <sup>4</sup> k (T <sub>m</sub> )/s <sup>-1</sup>	10 <sup>4</sup> k <sub>1</sub> /s <sup>-1</sup>	α(T <sub>m</sub> )	ΔH <sub>1</sub> <sup>‡</sup> /kcal mol <sup>-1</sup>	ΔΔH <sub>1</sub> <sup>‡</sup> /kcal mol <sup>-1</sup>	T(α = 1)/K	ΔC <sub>p</sub> <sup>‡</sup> (I) max./cal mol <sup>-1</sup> K <sup>-1</sup> at T/K	ΔC <sub>p</sub> <sup>‡</sup> (I) /cal mol <sup>-1</sup> K <sup>-1</sup> at T <sub>m</sub>	ΔΔH <sub>1</sub> <sup>‡</sup> (I)/kcal mol <sup>-1</sup> at T <sub>m</sub>	
R = Methyl														
Iodide	11	12	323—373	348.17	0.4783	0.4895	0.0265	25.38	-15.09	418	164	415	23.6	25.0
Benzenesulphonate	12	37	278—343	302.55	0.1993	0.8383	3.23	28.39	-8.12	278	109	275	65.5	22.18
<i>p</i> -Methylbenzenesulphonate	12	42	288—353	323.16	1.381	9.505	5.90	28.50	-8.29	284	109	280	41.1	21.41
<i>p</i> -Methoxybenzenesulphonate	15	36	308—343	328.16	1.780	1.900	0.0696	22.33	-12.27	382	131	375	42.7	21.53
<i>p</i> -Nitrobenzenesulphonate	15	37	298—328	315.66	4.599	5.319	0.159	22.36	-8.30	367	66	355	41.2	21.22
<i>m</i> -Nitrobenzenesulphonate	15	33	288—328	315.66	4.023	131.4	31.69	29.70	-8.549	252	146	250	10.94	21.41
<i>p</i> -Bromobenzenesulphonate	15	40	288—338	313.17	1.132	1.167	0.034	22.09	-12.61	376	143	370	25.93	21.67
3,4-Dimethylbenzenesulphonate	16	9	303—353	338.17	5.051	51.52	9.22	29.19	-9.26	291	128	285	33.22	20.83
2,4,6-Trimethylbenzenesulphonate	16	9	303—353	338.17	2.240	17.45	6.73	27.62	-7.84	291	93	285	30.49	20.79
Methanesulphonate	13	37	273—333	298.06	0.05011	0.0547	0.0949	22.59	-7.42	367	53	355	24.76	21.95
R = Ethyl														
Bromide	10	33	331—363	347.99	1.647	1.706	0.036	24.36	-14.71	413	161	410	30.04	23.85
Benzenesulphonate	12	39	283—348	313.0	0.605	0.657	0.086	22.87	-8.27	384	60.4	370	25.6	22.22
<i>p</i> -Methylbenzenesulphonate	10	35	283—348	333.13	3.538	3.796	0.079	22.66	-13.37	381	155	380	54.73	21.68
Methanesulphonate	13	33	283—353	312.99	0.2366	0.2842	0.213	23.32	-6.45	368	-170	350	31.07	22.19
R = n-Propyl														
Bromide	17	40	343—373	358.22	2.582	9.959	2.847	30.56	-10.36	334	-122	330	81.02	22.89
Methanesulphonate	13	43	293—363	343.15	3.469	3.817	0.0970	21.65	-8.75	419	-184	405	26.37	20.88
R = Isopropyl														
Chloride	10	45	327—373	353.16	1.741	1.795	0.0282	24.88	-14.77	425	-154	420	23.45	24.47
Bromide	10	45	298—348	328.16	1.984	7.023	2.539	31.49	-9.28	308	-115	305	81.5	24.83
Iodide	10	48	298—348	335.66	4.172	36.07	7.647	32.65	-8.13	288	-102	280	30.11	25.46
<i>p</i> -Methylbenzenesulphonate	10	41	276—313	293.15	2.123	2.272	0.0732	23.68	-10.02	346	-107	340	37.3	23.00
Methanesulphonate	10	52	278—306	293.16	1.021	1.206	10.83	37.98	-9.902	257	-188	255	44.45	22.92
R = t-Butyl														
Chloride	9	20	274—293	283.17	35.69	38.87	0.091	25.43	-12.42	318	-194	315	73.86	24.39
R = Allyl														
Bromide	14	13	288—338	323.15	3.239	3.745	0.154	23.27	-10.30	366	-101	360	59.10	21.90
R = Benzyl														
Chloride	14	51	288—338	323.14	2.190	2.459	0.121	22.11	-8.82	382	-69	370	36.20	21.16



Dependence of  $\Delta C_p^\ddagger(\text{app})$  on temperature for (a) ethyl bromide, (b) n-propyl bromide, and (c) isopropyl iodide

constant,  $k(\text{obs})$ , derived parameters [e.g.  $\Delta H^\ddagger(\text{app})$ ] at a temperature  $T_m$  which is an experimental temperature near the middle of the experimental range. For t-butyl chloride,  $\Delta C_p^\ddagger(\text{app})$  becomes more negative over the experimental range, in agreement with the trend in  $\Delta C_p^\ddagger(\text{I})$  calculated from the polynomial equation.

#### DISCUSSION

Previously,<sup>1</sup> the negative values for the heat capacities of activation,  $\Delta C_p^\ddagger(\text{I})$ , were understood in terms of the need to destroy enhanced water structure around the

hydrophobic initial state. It might be anticipated, therefore, that the magnitude of  $\Delta C_p^\ddagger(\text{I})$  would be dependent on the size of RX or at least show some gradual change as R was varied through a series with a common leaving group X. No such simple pattern emerges. Indeed it is difficult to accept that local reorganisation of water structure can lead to the often large negative values<sup>1</sup> for  $\Delta C_p^\ddagger(\text{I})$ . The problem now becomes more intractable if  $\Delta C_p^\ddagger(\text{I})$  is markedly temperature dependent. These and related observations lead us to

conclude that the interpretations previously advanced<sup>1</sup> are flawed. Indeed, a mechanistic scheme along the lines suggested by Albery and Robinson provides a more satisfactory explanation of the experimental observations, the curvature in the plot of  $\ln[k(\text{obs})]$  against  $T^{-1}$ . In these terms the complexities in the patterns shown by  $\Delta C_p^\ddagger(\text{I})$  stem from a number of features: (i) the relative positions of the temperature range over which  $k(\text{obs})$  is measured and the temperature at which  $\alpha = 1$ , (ii) the temperature at which  $\Delta C_p^\ddagger(\text{app})$  is a minimum, and (iii) the magnitude of  $\Delta C_p^\ddagger(\text{app})$  at this minimum. All these factors play their part in determining the magnitude of  $\Delta C_p^\ddagger(\text{I})$  calculated from the Valentiner and the Polynomial equations. A similar consideration is involved in the calculation of  $\Delta H^\ddagger(\text{I})$ . Thus it is apparent that the spread of values for  $\Delta H_1^\ddagger$  and  $\Delta\Delta H^\ddagger$  exceeds that for  $\Delta H^\ddagger(\text{I})$ .<sup>1</sup> In other words  $\Delta H_1^\ddagger$  and  $\Delta\Delta H^\ddagger$  are more discriminating between solvolytic reactions. In all cases  $\Delta\Delta H^\ddagger$  is negative, indicating that the process leading to products has a lower enthalpy barrier. This is eminently reasonable for solvolysis in water if the intermediate is more polar than the initial state. Finally we note that the dependence of  $\Delta C_p^\ddagger(\text{app})$  on temperature (Figure) follows the trend predicted by Robertson and Scott<sup>6</sup> although in that paper their conclusion appears to favour model I as the most satisfactory explanation. However, this conclusion was based on the argument that  $\Delta C_p^\ddagger(\text{I})$  is not dependent on temperature. We now see that this is not the case. Indeed the dependence is complex and more in keeping with model II.

We thank the S.R.C. for a maintenance grant to P. P. D.

[0/770 Received, 21st May, 1980]

## REFERENCES

- <sup>1</sup> R. E. Robertson, *Prog. Phys. Org. Chem.*, 1967, **4**, 213.
- <sup>2</sup> S. Valentiner, *Z. Phys. Chem.*, 1907, **42**, 253; D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.
- <sup>3</sup> M. J. Blandamer, R. E. Robertson, and J. M. W. Scott, *J. Chem. Soc., Perkin Trans. 2*, 1981, 447.
- <sup>4</sup> M. J. Blandamer, R. E. Robertson, and J. M. W. Scott, *Can. J. Chem.*, 1980, **58**, 772.
- <sup>5</sup> W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, 1969, **65**, 980.
- <sup>6</sup> R. E. Robertson and J. M. W. Scott, *Can. J. Chem.*, 1972, **50**, 167.
- <sup>7</sup> M. J. Blandamer, R. E. Robertson, J. M. W. Scott, and A. Vrieling, *J. Am. Chem. Soc.*, 1980, **102**, 2585.
- <sup>8</sup> S. Glasstone, K. J. Laidler, and H. Eyring, 'The Theory of Rate Processes', McGraw-Hill, New York, 1941.
- <sup>9</sup> E. A. Moelwyn-Hughes, R. E. Robertson, and S. E. Sugamori, *J. Chem. Soc.*, 1965, 1965.
- <sup>10</sup> R. L. Heppollette and R. E. Robertson, *Can. J. Chem.*, 1966, **44**, 677.
- <sup>11</sup> R. L. Heppollette and R. E. Robertson, *Proc. R. Soc. London Ser. A*, 1959, **252**, 273.
- <sup>12</sup> R. E. Robertson, *Can. J. Chem.*, 1957, **35**, 613.
- <sup>13</sup> P. W. C. Barnard and R. E. Robertson, *Can. J. Chem.*, 1961, **39**, 881.
- <sup>14</sup> R. E. Robertson and J. M. W. Scott, *J. Chem. Soc.*, 1961, 1596.
- <sup>15</sup> R. E. Robertson, A. Stein, and S. E. Sugamori, *Can. J. Chem.*, 1966, **44**, 685.
- <sup>16</sup> G. A. Hamilton and R. E. Robertson, *Can. J. Chem.*, 1961, **39**, 881.
- <sup>17</sup> M. J. Blandamer, H. S. Golinkin, and R. E. Robertson, *J. Am. Chem. Soc.*, 1969, **91**, 2678.