P_c = 60 atm (218 atm), V_c = 230 cm^3/mol (59 cm^3/mol), and T_c = 507 K (647 K), where the values in parentheses are experimental. It should be noted that this is to be viewed as giving qualitative information only, since the sum of terms beyond the $C(T)/V^2$ term in the virial equation of state is expected to be important near critical points. Furthermore, with $B(T)$ and $C(T)$ alone, the critical constants must always satisfy the relation $P_cV_c/RT = {}^1/_3$ regardless of the substances, whereas the experimental P_cV_c/RT_c for water is 0.242. As an indication of this problem, the critical constants calculated for water from *experimental* second and third virial coefficient are roughly P_c = 423 atm, V_c = 50 cm^3/mol, and T_c = 773 K.

To the best of our knowledge, there are only two other theoretical calculations of the third virial coefficients for steam. Both calculations employed semiempirical potential for the water-water interaction and assumed pairwise additivity in the potential. The earlier calculations were done by Rowlinson[17] using a Stockmayer potential, and the results are rather poor compared with the experiments: the $C(T)$ curve is closer than ours to the zero line, but it changes sign at much a lower temperature of about 380 K. More recently, Johnson and Spurling[18] have taken up a suggestion of Rowlinson by including the quadrupole moment of water, besides the polarizability and shape factor, in their potential. These authors reproduce almost exactly, within the experimental uncertainties, the experimental $B(T)$ and $C(T)$ coefficients. It is interesting to observe that their calculated values become too positive for temperatures below 550 K, where we find that the three-body correction begins to show up (about 6%). However, experimental uncertainties and the semiempirical nature of their potential rule out whether their values should be taken as suggesting the potential they used is to be considered as truly a two-body one. In fact, Johnson and Spurling have suggested otherwise.[18]

We also note that the nonadditive three-body contribution to $C(T)$ found in the present work for steam is much smaller than those reported by Sherwood and Prausnitz[19] for the Kihara and exp-6 potential functions. The reason for this difference is that their nonadditive potentials are valid only at separations where London forces predominate and are repulsive for most orientations (thus leading to very positive ΔC), which is not the case in our work.

Conclusion

The calculated $C(T)$'s in the temperature range studied are all too positive compared with the experiments, whereas the calculated $B(T)$'s are too negative.[15] Thus, the calculated $C(T)$ tends to correct the error in compressibility factor for steam predicted by the calculated $B(T)$ alone. However, as $B(T)$, the calculated $C(T)$ curve is far from satisfactory judging from the experimental data. Some of these difficulties are believed to be due to the assumption of rigid water molecule used in obtaining the interaction potentials; for example, the clustering mentioned earlier will likely require flexibility in the water geometry. The rigid assumption used so far is exacerbated by not allowing vibrations in the molecule. It is also noted that these assumptions are particularly poor for dimers and trimers constrained in small volumes. Recent improvements in our computational facilities[20] make it feasible to study these problems now in greater detail, and work is in progress in these directions.

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Registry No. Water, 7732-18-5.

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(17) J. S. Rowlinson, *J. Chem. Phys.*, **19**, 827 (1951).

(18) C. H. Johnson and T. H. Spurling, *Aust. J. Chem.*, **24**, 1567 (1971).

(19) A. E. Sherwood and J. M. Prausnitz, *J. Chem. Phys.*, **41**, 413 (1964).

(20) J. Detrich, C. Corongiu, and E. Clementi, *Int. J. Quantum Chem.*, in press.

Influence of Polar α Substituents in the Gas-Phase Pyrolysis Kinetics of Tertiary Chlorides. Correlation of Alkyl and Polar Groups

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The kinetics of the gas-phase pyrolysis of several polar α-substituted tertiary chlorides were determined in a static system over the temperature range of 339.5-420.1 °C and the pressure range of 46-221 torr. The reactions in seasoned vessels, and in the presence of a free-radical suppressor, are homogeneous and unimolecular and follow a first-order rate law. The variation of the rate coefficients with temperature is given by the following Arrhenius equations: for 1,2-dichloro-2-methylpropane, $\log k_1$ (s^{-1}) = (14.29 ± 0.53) - (207.6 ± 6.4) kJ mol^{-1} (2.303RT)$^{-1}$; for 2,2-dichloropropane, $\log k_1$ (s^{-1}) = (12.88 ± 0.53) - (199.0 ± 6.5) kJ mol^{-1} (2.303RT)$^{-1}$; for methyl 2-chloro-2-methylpropionate, $\log k_1$ (s^{-1}) = (13.81 ± 0.26) - (215.2 ± 3.3) kJ mol^{-1} (2.303RT)$^{-1}$. The $\log k_{\mathrm{rel}}$ of polar α substituents against the polar substituent constant σ^* values give an approximate straight line with $\rho^* = -0.73$, correlation coefficient $r = 0.912$, and intercept = -0.194 at 300 °C. This slope inflects at the point where $\sigma^*(\mathrm{CH_3}) = 0.00$ with another reported very good straight line derived by plotting $\log k/k_0$ vs. σ^* values for 2-chloro-2-alkylpropane pyrolyses ($\rho^* = -4.75$, $r = 0.993$, and intercept = 0.047 at 300 °C). The present result has been rationalized, as before, in terms of a slight alteration in the polarity of the transition state due to changes in electronic transmission at the carbon reaction center.

Introduction

The alkyl substituents in 2-chloro-2-alkylpropane pyrolyses have shown to affect the rate of elimination by electronic effects.[1] In this sense, plotting $\log k/k_0$ against σ^* values gave a very good straight line with $\rho^* = -4.75$, $r = 0.994$, and intercept = 0.048 at 300 °C. This result was found to be similar to those obtained with α- and β-alkyl-substituted ethyl chlorides,[2,3] thus supporting the polar effect of alkyl substituents in the gas-phase pyrolyses

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(1) Chuchani, G.; Martín, I. *J. Phys. Chem.* **1980**, *84*, 3188.

(2) Chuchani, G.; Martín, I.; Alonso, M. E. *Int. J. Chem. Kinet.* **1977**, *9*, 819.

(3) Chuchani, G.; Martín, I.; Rotinov, A.; Hernández A., J. A.; Reikonnen, N. *J. Phys. Chem.* **1984**, *88*, 1563.

0022-3654/85/2089-4134$01.50/0

of the said halides. Any consideration concerning steric acceleration in branched alkyl chloride pyrolyses was demonstrated to be unimportant, and furthermore the paramount factor which determines the rate of elimination is electronic in nature.[4] These finding suggested that, if the reaction center at the transition state of an organic molecule is markedly polar, the inductive electron-releasing effect of alkyls usually accelerates the gas-phase pyrolysis reactions.

In view of the few works done on the gas-phase pyrolyses of polar α-substituted tertiary chlorides,[5-8] it was thought to be of interest to study the effect of several polar substituents in these types of halides. A linear free energy relationship for a polar substituent is to be projected in order to obtain additional information with respect to the mechanism of tertiary chloride pyrolyses.

Experimental Section

2,2-Dichloropropane. This dihalide was prepared by treating acetone with phosphorus pentachloride as reported[9] (bp 69.0 °C 633 torr; lit.[9] bp 69.3 °C). It was fractionated several times, and the fraction of 97.5% purity as determined by GLC (FFAP (7%)–Chromosorb G AW DMCS, 80–100 mesh) was used. 2-Chloropropene was unequivocally identified by NMR and mass spectrometry analysis.

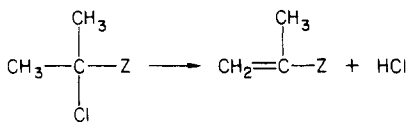
Methyl 2-Chloro-2-methylpropionate. Methyl 2-hydroxybutyrate (Aldrich) was treated with phosphorous pentachloride as described.[10] Several distillations of the product gave a boiling point at 36 °C (16 torr) [lit.[11] bp 133–135 °C (760 torr)] and a purity of 99.0% when analyzed by GLC (dinonyl phthalate (20%)–Gas Chromosorb Q, 80–100 mesh). Methyl methacrylate (Merck-Schuchardt) was analyzed in the same column.

1,2-Dichloro-2-methylpropane. This compound (Aldrich) was distilled several times, and the fraction of 99.5% purity as determined by GLC (diisodecyl phthalate (5%)–Chromosorb G AW DMCS, 80–100 mesh) was used (bp 95–96 °C at 630 torr). 3-Chloro-2-methyl-1-propene (Aldrich) was analyzed in the diisodecyl phthalate column.

Kinetics. The pyrolysis reactions were carried out in a static system[12] with the vessels seasoned by the decomposition products of allyl bromide.[12] The rate coefficients were determined by pressure increase and/or by the chromatographic analysis of the unreacted chloride substrate. The temperature was found to be within ±0.2 °C when measured with a calibrated platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel, and the substrate was injected directly into the vessel through a silicon rubber septum.

Results and Discussion

As a check on the stoichiometry of reaction 1, the pyrolyses



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-Z \longrightarrow CH_2=\overset{\displaystyle CH_3}{C}-Z + HCl} \qquad (1)$$

$Z = Cl, CH_2Cl, COOCH_3$

were carried out until no further increase in pressure was observed. The average ratio of the final pressure to the initial pressure, which should be equal to 2, was found to be at four different temperatures and 10 half-lives as follows: 2.04 for 1,2-dichloro-2-methylpropane, 1.82 for 2,2-dichloropropane, and 1.93 for methyl 2-chloro-2-methylpropionate (or methyl 2-chloroisobutyrate). The small departure of the stoichiometry was found to be due to a small polymerization of the corresponding olefinic product. As an additional verification of the above stoichiometry, up to 90% reaction of 1,2-dichloro-2-methylpropane, 35% reaction of 2,2-dichloropropane, and 70% reaction of methyl 2-chloro-2-methylpropionate are shown in Table I. The substrates, within the range of percentage decomposition carried out in this work, yielded only the corresponding olefinic product as described in eq 1. Some of these olefins were found to slightly polymerize in the presence of HCl gas.

TABLE I: Stoichiometry of the Reaction

1,2-Dichloro-2-methylpropane at 360.2 °C					
decomp, % (press.)	25.9	44.2	60.5	77.1	90.1
HCl, % titration	26.2	44.5	60.9	77.8	90.0
2,2-Dichloropropane at 359.5 °C					
decomp, % (press.)	15.0	20.1	24.5	33.2	
decomp, % (chrom)	14.9	19.9	23.1	30.9	
Methyl 2-Chloro-2-methylpropionate at 390.0 °C					
decomp, % (press.)	19.9	35.3	47.0	55.6	69.0
HCl, % titration	19.9	35.3	47.5	55.2	67.7

TABLE II: Variation of Rate Coefficients with Initial Pressure

1,2-Dichloro-2-methylpropane at 360.2 °C					
P_0, torr	46	71	106.5	129	187
10^4k_1, s^{-1}	14.26	14.59	14.52	14.63	14.20
2,2-Dichloropropane at 359.9 °C					
P_0, torr	88	97	124.5	134	221
10^4k_1, s^{-1}	3.02	3.11	3.12	3.00	3.44
Methyl 2-Chloro-2-methylpropionate at 390 °C					
P_0, torr	83.5	103.5	116	133.5	218
10^4k_1, s^{-1}	7.42	7.62	7.36	7.28	7.27

In order to check the effect of surface upon the rate of pyrolysis, several runs were carried out in a vessel packed with glass tubes. A 6-fold increase in surface-to-volume ratio indicated that the rates were unaffected in seasoned vessels, yet a significant effect was found in clean packed and unpacked Pyrex vessels. Consequently, these elimination reactions were performed in seasoned vessels at all times.

The kinetic runs had to be carried out with at least 2-fold of propene and/or toluene in order to suppress any possible free-radical process of the substrate and/or the products. Toluene as inhibitor does not affect the rates, and dibenzyl was not detected in the reaction products.

The rate coefficients of the chloride substrates calculated from $k_1 = (2.303/t) \log P_0/(2P_0 - P_t)$ have been found to be independent of the initial pressure (Table II). The plot of log $(2P_0 - P_t)$ vs. time t gave a straight line up to 90% decomposition of 1,2-dichloro-2-methylpropane, up to 35% decomposition for 2,2-dichloropropane, and up to 70% decomposition of methyl 2-chloro-2-methylpropionate. The temperature dependence of the reaction is shown in Table III. The rate coefficients are reproducible with a standard deviation not greater than ±5% at a given temperature.

Table IV shows the Arrhenius parameters obtained by using the least-squares procedure. The errors were estimated to 0.8 confidence coefficient.

As previously reported, the Taft plot of the alkyl substituents listed in Table V yielded a very good straight line ($\rho^* = -4.75$, $r = 0.993$, and intercept $= 0.047$ at 300 °C)[1] (Figure 1). However, plotting the log k_{rel} of the few electron-withdrawing substituents described in the present work (Table V) against σ^* values gives rise to an inflection point of the line at $\sigma^*(\mathrm{CH_3}) = 0.00$ into another approximate straight line with a slope $\rho^* = -0.73$, $r = 0.912$, and intercept $= -0.194$ at 300 °C (Figure 1). These results of one slope with electron-releasing groups and another slope at $\sigma^*(\mathrm{CH_3}) = 0.00$ with polar electron-withdrawing substituents are similar to the Taft correlation found in the gas-phase pyrolyses of α- and β-substituted ethyl chlorides.[2,3] A reasonable explanation of these facts, as already described,[2,3] is the belief that slight alteration in the polarity of the transition

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[4] Chuchani, G.; Rotinov, A. *React. Kinet. Catal. Lett.* **1979**, *12*, 333.
[5] Harding, C. D.; Maccoll, A. *J. Chem. Soc. B* **1969**, 634.
[6] Howlett, K. E. *J. Chem. Soc.* **1953**, 946.
[7] Young, B. C.; Swinbourne, S. E. *J. Chem. Soc. B* **1967**, 1181.
[8] Chuchani, G.; Hernández A., J. A. *J. Phys. Chem.* **1981**, *85*, 4139.
[9] Henne, A. L.; Renoll, M. W. *J. Am. Chem. Soc.* **1937**, *59*, 2435.
[10] Carman, R. M.; Shaw, I. M. *Aust. J. Chem.* **1976**, *29*, 133.
[11] Burns, R.; Trevor Jones, D.; Ritchie, P. J. *J. Chem. Soc.* **1935**, 714.
[12] Maccoll, A. *Chem. Rev.* **1969**, *69*, 33.
[13] Tsang, W. *J. Chem. Soc.* **1964**, *41*, 2487.
[14] Maccoll, A.; Wong, S. W. *J. Chem. Soc. B* **1968**, 1492.

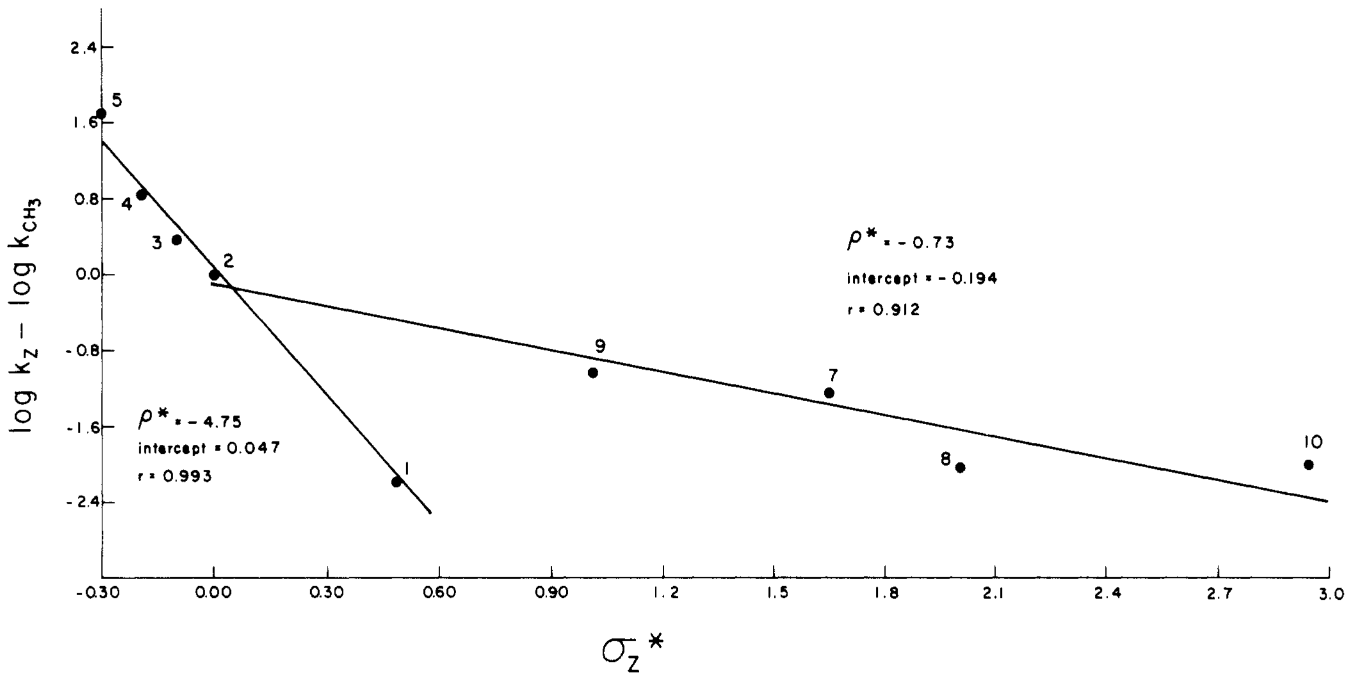


Figure 1. log k_Z/k_{CH_3} against σ^* values for electron-releasing and -withdrawing substituents in the pyrolysis of $Z(CH_3)_2CCl$ at 300 °C. The lines were drawn by the least-squares procedure.

TABLE III: Temperature Dependence of Rate Coefficients

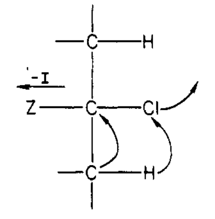
			1,2-Dichloro-2-methylpropane				
temp, °C	339.5	344.6	349.2	360.1	364.9	370.1	374.2
10^4k_1, s^{-1}	3.72	5.50	7.48	14.48	20.04	27.93	32.19
			2,2-Dichloropropane				
temp, °C	349.1	359.5	369.9	380.4	390.0	399.8	
10^4k_1, s^{-1}	1.40	3.00	5.28	9.11	15.71	27.02	
			Methyl 2-Chloro-2-methylpropionate				
temp, °C	360.1	370.1	380.1	390.0	400.0	410.0	420.1
10^4k_1, s^{-1}	1.09	2.06	4.03	7.38	12.65	21.77	37.95

TABLE IV: Arrhenius Parameters of the Halides

halide	log A, s^{-1}	E_a, kJ/mol
$CH_3C(CH_3)(Cl)CH_2Cl$	14.29 ± 0.53	207.6 ± 6.4
$CH_3C(Cl)_2CH_3$	12.88 ± 0.53	199.0 ± 6.4
$(CH_3)_2CClCOOCH_3$	13.81 ± 0.26	215.2 ± 3.3

state results from changes of electronic transmission at the carbon reaction center. Consequently, a simultaneous effect may be operating at the transition state during the process of pyrolysis, especially with polar electron-withdrawing substituents. This means that while the polar group destabilizes the reaction center, the hydrogen of the adjacent CH_3 groups to Z in Scheme I becomes more acidic and thus assists the leaving chloride atom. Because of this, pyrolysis rate is nearly similar or slightly higher with respect to unsubstituted compound of reference (**1**, Table V).

SCHEME I



The vinyl group, $CH_2{=}CH$ (Table V), directly attached to the α carbon (Scheme I), may delocalize its p electrons with the empty

TABLE V: Kinetic Parameters from Pyrolysis of $Z(CH_3)_2CCl$ at 300 °C

no.	Z	10^4k_1, s^{-1}	$10^4k_{CH_3}$, s^{-1} 1-olefin[a]	E_a, kJ/mol	log A, s^{-1}	log k_Z/k_{CH_3} 1-olefin	σ^{*b}	ref
1	H	0.017	0.017	213.8	13.64	-2.209	0.490	13
2	CH_3	4.13	2.75	188.2	13.77	0.000	0.000	14
3	CH_3CH_2	9.76	6.54	184.1 ± 2.6	13.77 ± 0.25	0.377	-0.10	1
4	$(CH_3)_2CH$	22.47	17.77	175.3 ± 1.9	13.33 ± 0.18	0.811	-0.19	1
5	$(CH_3)_3C$	147.19	147.19	171.5	13.80	1.729	-0.30	14
6	$CH_2{=}CH$	11.48	11.48	178.2 ± 0.5	13.30 ± 0.22	0.621	0.40	5
7	CH_3CO	0.15	0.15	190.8 ± 3.7	12.56 ± 0.31	-1.263	1.65	8
8	CH_3OCO	0.016	0.016	215.2 ± 3.3	13.81 ± 0.26	-2.235	2.00	this work
9	$ClCH_2$	0.23	0.23	207.6 ± 6.4	14.29 ± 0.53	-1.077	1.05	this work
10	Cl[c]	0.055	0.0275[d]	199.0 ± 6.5	12.88 ± 0.53	-2.000	2.94	this work

[a] The rate coefficient k_{CH_3} corresponds to the elimination of two methyl groups, i.e. $ZC(CH_3){=}CH_2$ as a product, thus allowing a determination of the effect of the Z substituent. [b] Hansch, C.; Leo, A. J. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979. [c] The pyrolysis of this substrate was previously reported (ref 6 and 7), but because the kinetic parameters from both works differ significantly, we have redetermined the kinetic of the said compound. [d] Effect of one Cl only.

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orbital of the adjacent positively charged carbon atom. Consequently, the point position of this substituent cannot be included in Figure 1 and it should be correlated with σ^+ values. However, σ^+ values have been defined for substituents on the benzene ring and not directly attached at the reaction site. Despite the fact that steric factors can simultaneously interfere with delocalization, the effect of $CH_2{=}CH$ substituent is polar in nature.

In conclusion, the results of the present work give additional support to Maccoll's theory on the heterolytic nature of the transition state for alkyl halide pyrolyses in the gas phase.[12]

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Registry No. $CH_3CCl_2CH_3$, 594-20-7; $CH_3C(Cl)(CH_3)CO_2Me$, 22421-97-2; $CH_3C(Cl)(CH_3)CH_2Cl$, 594-37-6.

Obtaining $\Delta C_p{}^\circ$ and Its Temperature Coefficients from Equilibrium Constants: A Tested Procedure

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An empirically justified pattern of the variation of $\Delta C_p{}^\circ$ with temperature ($\Delta C_p{}^\circ = \Delta a + \Delta bT + \Delta cT^2$) is used to establish the relationship $R \ln K^\circ(\beta) = \Delta S^\circ(\beta)_{298} - \Delta H^\circ{}_{298}K_1 + \Delta C_p{}^\circ{}_{298}K_2 + \Delta bK_3 + \Delta cK_4$ where K_1, K_2, K_3, and K_4 are temperature-dependent variables (TDV), tables of which are included, and β indicates which of the temperature-independent concentration scales is used. The equation is of general applicability. Although it has been developed for aqueous ionization reactions it has been profitably applied to high-temperature gas reactions, to the solubility product of ionic salts, and to the solution of gases in water. The number of terms in the $\Delta C_p{}^\circ$ function that is justified (often a matter of dispute) can be indicated graphically *by direct reference* to experimental values and their confidence limits established by means of the proposed method of intervals. Values of any of the thermochemical properties at 298.15 K obtained independently (e.g., calorimetrically) can, by adoption or adaptation, be incorporated into the processing procedure *during* the evaluation of the remaining properties. Sets of simulated results incorporating precisely stated thermochemical values at 298.15 K and processed to have differing and known levels of uncertainty in the resulting $R \ln K^\circ(m)$ values are used to assess the reliability of the proposed procedure by noting the adequacy of the recovery of the generating values.

1. Introduction

To obtain ΔH°, $\Delta S^\circ(m)$, and $\Delta C_p{}^\circ$ for a reaction from equilibrium information it is customary to fit $\ln K^\circ(m)$ to some reasonable and convenient function of T, and then to perform appropriate differentiations on the result.

We suggest that this treatment suffers from four weaknesses.

(i) The decision to use any specific equation for $\ln K^\circ(m)$ in terms of T imposes a form on the temperature dependence of $\Delta C_p{}^\circ$ irrespective of any calorimetric evidence. This point is discussed in detail by Timimi[1] and by Blandamer et al.[2] Of course, the converse is also true, but it is true to a lesser extent as is summarized in Chart I.

(ii) The form of the equation usually employed is

$$pK = A + B/T + C \log T + DT + ET^2$$

This will be referred to as the standard equation. Its form is a weakness in that it cuts itself off from other thermochemical measurements: any immediate significance of the coefficients is sacrificed to the simplicity of the temperature-dependent variables. For recall or interpolation of smoothed values at *any* temperature within a specified range, it is excellent. For obtaining thermochemical information, we suggest that there is a more convenient and reliable alternative.

(iii) The above characteristic also prevents independent thermochemical work from being simultaneously taken into account during data processing.

(iv) Lastly, the question of which and how many terms of the standard equation are used is usually controlled by statistical decisions built into the evaluating programs. Thus it can well happen that it is the uncertainties in the experimental results rather than any independent thermochemical evidence which impose a pattern on $\Delta C_p{}^\circ{}_T$.

The first two of these weaknesses are removed by the Clarke and Glew[3] treatment, but the last two remain. This paper attempts to alter the situation by two strategies: (a) by reversing, in two areas, the priorities on which the standard equation is based, namely, first by deciding on the form of an empirical equation for $\Delta C_p{}^\circ{}_T$ and *then* processing it to give an equation for $R \ln K^\circ{}_T(m)$, and second by doing this in such a way that the coefficients are values of clearly defined thermochemical properties while it is the temperature-dependent variables (TDV) which are the part whose immediate significance is sacrificed. (b) by developing a diagnostic procedure using a method of intervals whereby a plot of a $\Delta C_p{}^\circ{}_T$ function provides the basis for deciding on the number of terms to be incorporated into the formula for the temperature dependence of $R \ln K^\circ{}_T(m)$.

2. The Pattern of $\Delta C_p{}^\circ{}_T$

The behavior of $C_p{}^\circ$ for pure electrolytes and that of $\bar{C}_p{}^\circ$ for their dissolved species show extremely different pictures: the former always positive, showing a gently increasing value with near rectilinearity at high temperatures; the latter often markedly negative with a great rise and fall in value within the narrow range of 0–100 °C. The former, as Maier and Kelley[4] and Kelley[5]

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(1) Timimi, B. A. *Electrochim. Acta* **1974**, *19*, 149.

(2) Blandamer, M. J.; Burgess, J.; Robertson, R. E.; Scott, J. W. M. *Chem. Rev.* **1982**, *82*, 259.

(3) Clarke, E. C. W.; Glew, D. N. *Trans. Faraday Soc.* **1966**, *62*, 539.

0022-3654/85/2089-4137$01.50/0