PRESSURE AND SOLVENT EFFECTS ON THE KINETICS OF A MENSHUTKIN REACTION IN ALIPHATIC ALCOHOLS

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The kinetics of the Menshutkin reaction between triethylamine and iodoethane was studied at 313 K in seven primary and secondary alkanols. An accurate conductimetric method was employed to obtain second-order rate constants at pressures of 0·1–200 MPa. Volumes and isothermal compressions of activation were calculated by different model-based equations which are compared. Activation volumes at 0·1 MPa are in the range −26 to −33 cm^3 mol^{-1}. Procedures for dissecting intra- and intermolecular contributions to the volume of activation are discussed. A clear dependence of model parameters on the solvent volumetric properties was found.

INTRODUCTION

Menshutkin reactions are well characterized bimolecular nucleophilic substitution reactions. Their particular interest lies in the fact that an activated complex involving charge separation is formed from electrically neutral reactants. Menshutkin reactions are thus among the first choice for analysing solvent and pressure effects on kinetics in solution. Abboud et al.[1] have recently published a comprehensive and authoritative review on the Menshutkin reaction and a large compilation of activation volumes for reactions of organic compounds, including many Menshutkin reactions, can be found in Asano and Le Noble's review.[2] On the other hand, the reaction of triethylamine with iodoethane (the original Menshutkin reaction) has been studied at atmospheric pressure in a large set of mono- and dialkanols in order to establish initial and transition state solvation contributions[3] and to interpret medium effects by means of multi-parameter correlation analysis.[4] Therefore we focus this introduction on some models and equations for calculating activation volumes.

Volumes of activation

The volume of activation, $\Delta^* V$, is related to the pressure dependence of reaction rates, k, by

$$\Delta^* V = -RT(\partial \ln k / \partial p)_T \qquad (1)$$

The usefulness of this quantity of activation in discussing reaction mechanisms and solvent effects is enhanced if it is dissected into two contributions as follows:

$$\Delta^* V = \Delta_1^{\ddagger} V + \Delta_2^{\ddagger} V \qquad (2)$$

where $\Delta_1^{\ddagger} V$ is the result of intramolecular structural modifications in the substrates during the activation process and $\Delta_2^{\ddagger} V$ is an intermolecular term arising from solvent reorganization due to substrate-solvent interactions.

Activation volumes are generally pressure dependent. However, most authors consider the intramolecular term in equation (2) to be a reaction characteristic independent of external factors such as temperature, pressure and solvent, as long as the mechanism is not affected. This assumption leads to

$$\Delta^* K_T = -(\partial \Delta^* V / \partial p)_T = -(\partial \Delta_2^{\ddagger} V / \partial p)_T \qquad (3)$$

where $\Delta^* K_T$ is the isothermal compression of activation.

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The analysis of the intermolecular term requires further modelling. We recall the proposals advanced independently in the late 1960s by Kondo et al.[5] and by Hills and Viana.[6] Although using different approaches, they have derived equivalent expressions for the inter-molecular activation volume. It is rewritten here as

$$\Delta_2^{\ddagger} V = n(V_{m,s} - V_{m,A}) \tag{4}$$

where n represents the extra number of solvent molecules involved in an activation event and $V_{m,s}$ and $V_{m,A}$ are the molar volumes of the solvent in its solvating state (s) and in the bulk or pure state (A).

Assuming that the extra solvation number n does not change with pressure, it is clear that some information concerning this quantity would follow from combining equations (3) and (4) if independent knowledge of the solvent volumetric change could be obtained. With respect to this question, the two groups referred to followed divergent approaches.

Kondo et al.[5] introduced the approximation

$$V_{m,x} - V_{m,A} = -\delta p V_{m,A} \kappa_{T,A} \tag{5}$$

where $\kappa_{T,A}$ is the pure solvent isothermal compressibility, by assuming that the derivative $\partial V_{m,A}/\partial p$ may be approximated by the ratio $(V_{m,s} - V_{m,A})/\delta p$. Considering the bulk solvent at a pressure p, it follows from equation (5) that δp can be regarded as the extra pressure necessary to bring the solvent to the volumetric properties in its solvating state. In other words, Kondo and co-workers[5,7] equate $V_{m,s}$ at pressure p to $V_{m,A}$ at pressure $p + \delta p$. They obtained

$$\Delta_2^{\ddagger} V = -n \delta p V_{m,A} \kappa_{T,A} \tag{6}$$

However, no workable method to disentangle n and δp was found despite a proposal by Kondo et al.[8] based on the assumption that δp and n for a given reaction are the same in different solvents. In fact, considering these parameters to be independent of pressure from equations (3) and (6) one has

$$\Delta^{\ddagger} K_T = n \delta p V_{m,A} [(\partial \kappa_{T,A}/\partial p)_T - \kappa_{T,A}^2] \tag{7}$$

Hills and Viana[6] considered the solvent in its solvating state as a glassy state much less compressible than the bulk solvent. They obtained the equation

$$\Delta^{\ddagger} K_T = -n V_{m,A} \kappa_{T,A} \tag{8}$$

An advantage of this model is that it allows one to obtain n from the pressure dependence of activation volumes and pVT data for the solvent.

Interestingly, both approaches were the basis for new analytical equations proposed in the 1970s for describing the effect of pressure on the rates of reactions in solution and which make use of the Tait equation for liquid isotherms. In fact, combining equations (1), (2) and (4), we obtain

$$-RT(\partial \ln k/\partial p)_T = \Delta_1^{\ddagger} V + n(V_{m,s} - V_{m,A}) \tag{9}$$

Considering $\Delta_1^{\ddagger} V$, n and $V_{m,s}$ to be constant, Jones et al.[9] (for reaction rates) and North[10] (for equilibrium constants), independently of each other and of Hills and Viana, integrated equation (9) to obtain the equation

$$\ln k = \ln k_0 - (\Delta_1^{\ddagger} V/RT)p - (nV_{m,A,0}A/RT)p$$
$$\times [(1 + B/p)\ln(1 + p/B) - 1] \tag{10}$$

where the subscript 0 refers to zero (or atmospheric) pressure and A and B are constants independent of the pressure and appearing in the Tait's solvent isotherm:

$$V_{m,A} = V_{m,A,0}[1 - A \ln(1 + p/B)] \tag{11}$$

Later, based on Kondo et al.'s model,[5] Asano et al.[11,12] also integrated equation (9) for the case when $\delta p \ll B$ and assuming $\Delta_1^{\ddagger} V$, n and δp to be constant, which yields

$$\ln k = \ln k_0 - (\Delta_1^{\ddagger} V/RT)p$$
$$+ (n \delta p V_{m,A,0} A/RT)\ln(1 + p/B) \tag{12}$$

Now we note that, from equation (11),

$$V_{m,A} \kappa_{T,A} = V_{m,A,0} A/(B + p) \tag{13}$$

If this expression is used in equation (5) and the result is inserted into equation (9), then equation (12) is obtained on integration with $\Delta_1^{\ddagger} V$, n and δp constant. We can thus conclude that the approximation introduced by Kondo et al.[5] is equivalent to considering $\delta p \ll B$ as Asano[11] did.

Several other functions, either purely empirical or model based, for expressing the variation with pressure of the rate constants for reactions in solution are known. We mention the comparative studies of Lohmuller et al.,[13] Kelm and Palmer[14] and Asano and Okada.[15] Finally, we refer to Gavish,[16] who derived an expression equivalent to equation (12) if the parameter B is set adjustable to the kinetic data.

EXPERIMENTAL

Materials. Triethylamine and iodoethane were obtained from Fluka ($\geqslant$ 99.5%) and were used as received. Tetraethylammonium iodide was obtained from Merek ($\geqslant$ 99%). Alcohols were purchased from Merck ($\geqslant$ 99%) and their water content was kept lower than 0.2 %. The purification of the reactants and solvents has been described elsewhere.[17,18]

Apparatus. A Wayne Kerr B905 bridge (accuracy $\pm 0.05\%$) and glass conductivity cells with bright platinum electrodes and a rod and ring electrode configuration were used to obtain the conductimetric data from which rate constants were calculated. No differences were observed between measurements made using bright or light-grey electrodes.[19] Cell constants ranged from 0.2 to 0.3 cm^{-1}. High-pressure experiments were carried out in a stainless-steel vessel

Table 1. Rate constants for the reaction of Et_3N with EtI in different alcohols at $T = 313.15$ K

Solvent[a]	$k \times 10^5/(\text{mole fraction})^{-1} \text{ s}^{-1}$						
	1 bar	100 bar	250 bar	500 bar	1000 bar	1500 bar	2000 bar
MeOH	50·53 (0·24)	57·05 (0·24)	66·41 (0·08)	87·80 (0·12)	129·8 (0·70)	181·5 (0·10)	230·8 (0·90)
EtOH	25·46 (0·05)	28·61 (0·04)	32·64 (0·10)	42·68 (0·09)	64·23 (0·09)	91·49 (0·12)	124·2 (0·20)
1-PrOH	13·14 (0·03)	14·67 (0·02)	17·20 (0·04)	20·84 (0·08)	31·90 (0·11)	46·05 (0·15)	62·07 (0·17)
1-BuOH	10·91 (0·01)	11·98 (0·01)	13·82 (0·01)	17·16 (0·01)	25·77 (0·02)	36·81 (0·03)	49·58 (0·07)
1-PeOH	6·96 (0·01)	8·00 (0·02)	9·13 (0·02)	11·24 (0·01)	16·54 (0·02)	22·75 (0·03)	31·15 (0·06)
2-PrOH	18·89 (0·04)	21·49 (0·05)	25·46 (0·03)	32·41 (0·04)	50·54 (0·05)	71·04 (0·06)	99·69 (0·09)
2-BuOH	14·22 (0·02)	15·93 (0·03)	18·63 (0·01)	23·41 (0·07)	34·43 (0·07)	49·70 (0·06)	66·20 (0·12)

[a] MeOH = methanol; EtOH = ethanol; 1-PrOH = propan-1-ol; 1-BuOH = butan-1-ol; 1-PeOH = pentan-1-ol; 2-PrOH = propan-2-ol; 2-BuOH = butan-2-ol.

immersed in a thermostat similar to the apparatus described previously.[20] Pressure readings were better than ±20 bar (1 bar = 0·1 MPa) and temperature was maintained constant within ±0·01 K.

Kinetic procedure. The mole fraction vs time plots for the ionic reaction product, the tetraalkylammonium salt, were based on calibration graphs relating mole fractions, x_P, to experimental conductances, K, of the form $x_P = a + bK + cK^2$.[17,18] The calibration method has been exemplified before.[17,18] In this work at least eight different calibrating solutions were used with concentrations in the range $6·8 \times 10^{-5} - 7·5 \times 10^{-3}$ mol l^{-1}. All solutions were prepared by weight in solvents dried with oxygen-free nitrogen. Equal initial concentrations of both reactants varied from 0·02 to 0·05 mol l^{-1} depending on the solvent.

After thermal equilibration, the reaction mixtures were followed conductimetrically up to 8–15% conversion. Duplicate measurements of both calibrating and kinetic experiments were made at 40 °C and at all the working pressures for each solvent. Approximately 100 experimental points were obtained for each kinetic run.

RESULTS

Accurate rate constants for the reaction between triethylamine (Et_3N) and iodoethane (EtI) in seven different pure alkanols at 40 °C and at several pressures were obtained with standard deviations below 1% (with most of them below 0·5%) and are presented in Table 1. In their calculation a second-order rate law was assumed and the kinetic equation for equal initial concentrations of both reactants $x_P/x_R^0(x_R^0 - x_P) = kt$ (where x_P is the mole fraction of the product and x_R^0 is the initial mole fraction of either reactant) was used. Second-order rate constants were thus obtained in pressure-independent units to facilitate the calculation of activation volumes.[21] Such an analysis has been exemplified before.[18]

According to the values shown in Table 1, rate constants always increase with increasing pressure and decrease with increasing length of the alcohol carbon chain and the reactions in secondary alcohols have larger rate constants than in the corresponding primary alcohols.

By using a least-squares multilinear regression procedure, the high-pressure kinetic data listed in Table 1 were fitted to the following equations:

$$\ln k = a_0 + a_1 p + a_2 \ln(1 + p/B) \quad (14)$$

$$\ln k = a_0 + a_1 p + a_2 p[(1 + B/p)\ln(1 + p/B) - 1] \quad (15)$$

$$\ln k = a_0 + a_1 p + a_2 p^2 \quad (16)$$

We note that equations (14) and (15) are mathematically equivalent to equations (12) and (10), respectively, whereas equation (16) is the familiar quadratic law. Values for the parameter B together with other solvent properties used in calculations are given in Table 2. From the regression coefficients and their standard deviations, various quantities of activation and model parameters, and also the respective standard deviations

Table 2. Solvent properties at 313·15 K and 1 bar

Solvent[a]	$V_{m,0}$[b]/cm^3 mol^{-1}	B[c]/bar
MeOH	41·5	692
EtOH	59·7	753
1-PrOH	76·3	855
1-BuOH	93·3	922
1-PeOH	110·2	992
2-PrOH	78·2	749
2-BuOH	93·9	868

[a] For solvent abbreviations, see footnote to Table 1.
[b] From Ref. 23.
[c] The Tait parameter B was calculated by equation (13) with parameter A arbitrarily set equal to 0·0959 for all solvents, $K_{T,A,0}$ for methanol and primary alcohols from Ref. 24 and $\bar{K}_{T,A,0}$ for secondary alcohols from Ref. 25.

Table 3. Activation quantities and model parameters for the reaction of Et_3N with EtI at 313·15 K (activation volumes in $cm^3\ mol^{-1}$, δp in bar and activation isothermal compressions in $cm^3\ bar^{-1}\ mol^{-1}$)

Solvent[a]	Equation	$-\Delta^* V_0$	$-\Delta_1^* V_0$	$\Delta_2^* V_0$	$n\ \delta p$	n	δp	$-\Delta^* K_{T,0} \times 10^3$
MeOH	(14)	37·3 (1·7)	4·9 (1·5)	32·5 (3·1)	5640 (543)		1410	46·9 (4·5)
	(15)	33·1 (0·8)	15·4	17·7		4·00 (0·24)		23·0 (1·4)
	(16)	29·8 (0·8)						10·1 (0·8)
	(20)							15·4
EtOH	(14)	32·5 (1·3)	9·8 (1·2)	22·7 (2·5)	2996 (331)		1483	30·2 (3·3)
	(15)	29·7 (0·8)	17·2	12·6		2·02 (0·17)		15·3 (1·3)
	(16)	27·5 (0·7)						7·0 (0·7)
	(20)							10·2
1-PrOH	(14)	29·2 (1·5)	11·0 (1·5)	18·2 (3·0)	2124 (346)		1597	21·3 (3·5)
	(15)	27·3 (1·0)	17·0	10·3		1·33 (0·19)		11·4 (1·6)
	(16)	25·7 (0·7)						5·6 (0·7)
	(20)							7·4
1-BuOH	(14)	28·2 (1·0)	10·6 (1·1)	17·6 (2·0)	1814 (209)		1664	19·1 (2·2)
	(15)	26·5 (0·4)	16·5	10·0		1·09 (0·07)		10·6 (0·7)
	(16)	25·1 (0·1)						5·4 (0·1)
	(20)							6·8
1-PeOH	(14)	28·1 (1·2)	8·4 (1·5)	19·7 (2·7)	1844 (248)		1808	19·9 (2·7)
	(15)	26·2 (1·2)	14·9	11·2		1·02 (0·17)		10·9 (1·8)
	(16)	24·6 (1·2)						5·6 (1·2)
	(20)							7·0
2-PrOH	(14)	34·4 (0·8)	9·5 (0·8)	24·9 (1·6)	2482 (160)		1504	33·2 (2·1)
	(15)	31·2 (0·9)	17·5	13·6		1·65 (0·15)		16·5 (1·5)
	(16)	28·7 (1·0)						7·4 (1·0)
	(20)							11·0
2-BuOH	(14)	30·6 (0·9)	8·8 (0·9)	21·8 (1·7)	2107 (169)		1633	25·1 (2·0)
	(15)	28·2 (0·7)	16·0	12·3		1·29 (0·11)		13·4 (1·1)
	(16)	26·4 (0·7)						6·5 (0·7)
	(20)							8·7

[a] For solvent abbreviations, see footnote to Table 1.

when applicable, were calculated using standard equations and are presented in Table 3.

DISCUSSION AND CONCLUSIONS

Volumes of activation

For the Menshutkin reaction of triethylamine with iodoethane at 40 °C in each of the seven aliphatic alcohols used as solvents, the values for the activation volume at atmospheric pressure as calculated by equations (14), (15) and (16) (Table 3) are in the following order: $-\Delta^* V_0$ [equation (14)] $> -\Delta^* V_0$ [equation (15)] $> -\Delta^* V_0$ [equation (16)]. That the quadratic equation in pressure, equation (16), systematically underestimates the activation volume in compressible organic solvents has been noted before by Kelm and Palmer[14] and Asano and Okada.[15] Therefore, we focus this discussion on the difference between $\Delta^* V_0$ values calculated by the model-based equations (14) and (15), which in five out of seven cases exceeds the

expected experimental uncertainty. To this end we first examine the parameters n and δp.

Extra solvation numbers, n, as given by equation (15) are reported in Table 3. Their values are reasonably small and are of the same order as for solvolytic reactions in hydroxylic solvents.[6,22] More specifically, the variation of n with different structures and properties of the solvents shows up clearly. Thus, considering separately primary and secondary alcohols, one observes that n decreases as the chain length increases. On the other hand, displacing the OH group towards the middle of the chain leads to an increase in n. Both trends can be rationalized in terms of steric requirements to solvation of the transition state and the first trend follows the marked dependence of the rate constant on solvent dipolarity and polarizability found previously.[4] Lastly, the enhanced n value in methanol is consistent with a highly dipolar medium constituted by small and approximately spherical molecules.

Kondo and co-workers[5,7,8] have developed an analysis of the solvent effect on the volume of activation based

on the constancy of the product $n\delta p$ for a given reaction. However, our results in Table 3 do not support their view. Thus, in a series of similar solvents we found $n\delta p$ in the range $1\cdot8-5\cdot6$ kbar by direct application of Asano equation whereas Kondo et al.[7] claimed that, in a series of dissimilar solvents, $n\delta p$ for the same reaction is approximately equal to $2\cdot6$ kbar by using an indirect method.

To progress further, separating parameters n and δp becomes important. To this end, n values from equation (15) were used to estimate the δp values given in Table 3. The striking observation is that $\delta p \gg B$. In fact, although the approximation used to derive equation (15) may lead to underestimated n values, even for twice these values the requirement $\delta p \ll B$ introduced in both Kondo et al.'s model and Asano's equation would reduce their applicability to our reaction systems. It is interesting that the difference Δ^*V_0 [equation (15)] $-\Delta^*V_0$ [equation (14)] tends to decrease with increase in the product $nV_{m,A,0}$. This fact will be better understood following the discussion of the intermolecular contribution to activation volumes. Because equation (15) is based on the assumption that the solvent in its solvating state is much less compressible than in bulk, which amounts to consider $\delta p \gg B$, we conclude that Δ^*V_0 [equation (15)] is the most reliable of the activation volumes presented in Table 3. We remark that these activation volumes supersede preliminary results reported by us[18] and quoted in Table 26 in Ref. 1.

Analysis of $\Delta_2^\ddagger V$

From the knowledge of δp we can calculate the intermolecular term of activation volumes by means of equation (4), which is the common basis for the models of Hills and Viana and Kondo et al. In fact, Asano[11] has

shown that

$$V_{m,s} - V_{m,A} = V_{m,A,0}A \ln[(B+p)/(B+p+\delta p)]$$

Inserting this expression into equation (4) yields

$$\Delta_2^\ddagger V = -nV_{m,A,0}A \ln[1 + \delta p/(B+p)] \qquad (17)$$

which, at zero pressure, becomes

$$\Delta_2^\ddagger V_0 = -nV_{m,A,0}A \ln(1 + \delta p/B) \qquad (18)$$

Since Asano's approximation consists in taking $\ln(1 + \delta p/B) \approx \delta p/B$, the resulting expression for the intermolecular term is

$$\Delta_2^\ddagger V_0 = -n \, \delta p V_{m,A,0}A/B \qquad (19)$$

The above equation can also be obtained by inserting equation (13) at $p=0$ into equation (6). Hence, the $\Delta_2^\ddagger V_0$ values in the row for equation (14) in Table 3 correspond to equation (19). Those calculated from equation (18) are given in the row for equation (15). We observe that the former values are much larger than the latter, which we believe to be more accurate. We note further that the ratio $\Delta_2^\ddagger V_0$ [equation (19)]/$\Delta_2^\ddagger V_0$ [equation (18)] is approximately constant in all solvents (Table 4). In view of equations (18) and (19), this ratio is equal to $(\delta p/B)/\ln(1 + \delta p/B)$. Hence $\delta p/B$ should be insensitive to solvent changes. In fact, we found for this quantity in the seven solvents used a mean value (m.v.) of $1\cdot91$, a mean deviation (m.d.) of $4\cdot1\%$ and a largest deviation (l.d.) of $6\cdot5\%$. Moreover, because parameter B is related to the solvent isothermal compressibility through equation (13) and since the Tait parameter A is constant for all the solvents, we can conclude that δp for this reaction in a series of similar solvents is approximately proportional to $1/\kappa_{T,A}$. Therefore, the quantity δp appears to be linked to the mechanical properties of the solvating medium and is probably independent of the particular reaction in that solvent.

Table 4. Comparison of $\Delta_2^\ddagger V_0$ given by equations (18) and (19)

Solvent[a]	$\dfrac{\Delta_2^\ddagger V_0 \text{[equation (19)]}}{\Delta_2^\ddagger V_0 \text{[equation (18)]}}$	Solvent contraction due to solvation (%)	
		Equation (18)	Equation (19)
MeOH	1·83	10·7	19·5
EtOH	1·81	10·4	18·9
1-PrOH	1·77	10·1	17·9
1-BuOH	1·75	9·9	17·3
1-PeOH	1·76	9·9	17·5
2-PrOH	1·82	10·6	19·2
2-BuOH	1·78	10·2	18·0
Mean value	1·79	10·2	18·3
Mean deviation (%)	1·6	2·5	4·1
Largest deviation (%)	2·6	4·0	6·5

[a] For solvent abbreviations, see footnote to Table 1.

These regularities allow us to probe deeper into the models under analysis. Thus, comparing equations (4) and (18) leads to interpreting the quantity $A \ln(1 + \delta p/B)$ as the percentage contraction in the bulk solvent molar volume due to solvation at atmospheric pressure. However, when equation (19) is used, the percentage contraction is given by $A \; \delta p/B$. Their values and respective statistics are given in Table 4. We note that a 10% contraction estimated from the non-approximate model for $\Delta_2^{\ddagger}V_0$ is acceptable but that a 18% contraction suggested by the approximate model seems exaggerated.

Additionally, this analysis offers an explanation for the aforementioned variation of the difference between $\Delta^{\ddagger}V_0$ [equation (15)] and $\Delta^{\ddagger}V_0$ [equation (14)] with the solvent. If $\Delta_2^{\ddagger}V_0$ calculated by equation (19) is associated with $\Delta^{\ddagger}V_0$ [equation 15)] values, then from equations (18) and (19) a term of the form $-nV_{m,A,0}$ $[A \ln(1 + \delta p/B) - A \; \delta p/B]$ should contribute to the difference under analysis. Since the quantity in brackets is fairly constant in this series of solvents (m.v. 0·081; m.d. 6%; l.d. 10%) the greater is the product $nV_{m,A,0}$, the larger the difference in calculated activation volumes according to equations (14) and (15) should be, just as found experimentally.

Analysis of $\Delta_1^{\ddagger}V$

Asano's equation has the merit of allowing the direct estimation of intramolecular activation volumes. For a given reaction in a series of similar solvents, one might expect to find constant $\Delta_1^{\ddagger}V$. However, the values for this quantity calculated by equation (14) and given in Table 3 are strongly solvent dependent. Alternatively, combining $\Delta_2^{\ddagger}V_0$ calculated by equation (18) with $\Delta^{\ddagger}V_0$ from equation (15) by means of equation (2), new values for $\Delta_1^{\ddagger}V$ have been derived. They are given in Table 3 in the row for equation (15). We note that $\Delta_1^{\ddagger}V$ [equation (15)] is not markedly dependent on the solvent and that it is very different from $\Delta_1^{\ddagger}V$ [equation (14)]. In fact, for $\Delta_1^{\ddagger}V$ [equation (14)] one has m.v. $-9 \cdot 0 \text{ cm}^3 \text{ mol}^{-1}$, m.d. 16% and l.d. 46%, whereas for $\Delta_1^{\ddagger}V$ [equation (15)] the statistics are m.v. $-16 \cdot 3 \text{ cm}^3 \text{ mol}^{-1}$, m.d. 5% and l.d. 9%. For the reaction of triethylamine with iodoethane at 50 °C in nitrobenzene and in propanone, Asano[11] calculated intramolecular activation volumes of $-8 \cdot 7$ and $-9 \cdot 5 \text{ cm}^3 \text{ mol}^{-1}$, respectively, in agreement with our results from equation (14).

An independent test of the constancy of $\Delta_1^{\ddagger}V$ in different solvents is suggested by equation (2). If a straight line is obtained when $\Delta^{\ddagger}V_0$ is plotted *versus* $\Delta_2^{\ddagger}V_0$, then one is allowed to conclude that $\Delta_1^{\ddagger}V$, which is given by the intercept, is constant. Figure 1 shows two such plots from the data in Table 3. Although the correlation coefficient for both cases is modest, the estimates of $\Delta_1^{\ddagger}V$ are very similar: $-16 \cdot 9 \text{ cm}^3 \text{ mol}^{-1}$

when $\Delta^{\ddagger}V_0$ and $\Delta_2^{\ddagger}V_0$ are calculated by equation (14), and $-17 \cdot 4 \text{ cm}^3 \text{ mol}^{-1}$ when $\Delta^{\ddagger}V_0$ is calculated by equation (15) and $\Delta_2^{\ddagger}V_0$ by equation (18). Moreover, they are in very good agreement with the previous mean value of $-16 \cdot 3 \text{ cm}^3 \text{ mol}^{-1}$ and with the value of $-18 \cdot 4 \text{ cm}^3 \text{ mol}^{-1}$ obtained by Kondo *et al.*[7] for this reaction in a different set of solvents.

The obvious conclusion is that equation (14) grossly underestimates the intramolecular term of the activation volume, a situation which may be a consequence of overestimating the intermolecular term as discussed above.

Isothermal compressions of activation

Activation isothermal compressions at atmospheric pressure, $\Delta^{\ddagger}K_{T,0}$, calculated by means of the three equations employed to fit kinetic data are given in Table 3. Now, in view of equation (3), a fourth estimate of $\Delta^{\ddagger}K_{T,0}$ can be obtained from partial differentiation of equation (17), leading to

$$\Delta^{\ddagger}K_{T,0} = -n \; \delta p V_{m,A,0} A/B(B + \delta p) \qquad (20)$$

The resulting values, believed the most reliable, are also given in Table 3.

The relative order of the four different estimates of $\Delta^{\ddagger}K_{T,0}$ is identical in every solvent tested, namely $-\Delta^{\ddagger}K_{T,0}$ [equation (14)] $> -\Delta^{\ddagger}K_{T,0}$ [equation (15)] $>$ $-\Delta^{\ddagger}K_{T,0}$ [equation (20)] $> -\Delta^{\ddagger}K_{T,0}$ [equation (16)]. It is interesting that these values are in the same order as the corresponding activation volumes. Similarly, the quadratic equation in pressure leads to the smallest, underestimated, values whereas Asano's equation yields clearly overestimated quantities. Model-based quantities are best analysed in terms of their expressions. Thus, for Kondo *et al.*'s model, we find from equation (7) that

$$\Delta^{\ddagger}K_{T,0} = -n \; \delta p V_{m,A,0} \; A/B^2 \qquad (21)$$

which alternatively could be obtained by partial differentiation of equation (19) with respect to pressure. Hills and Viana's model yields, from equation (8),

$$\Delta^{\ddagger}K_{T,0} = -n \; \delta p V_{m,A,0} A/B \qquad (22)$$

Equations (21) and (22) can be seen as approximate expressions of equation (20). In fact, if in this equation the approximation $B + \delta p \approx B$, valid for $\delta p \ll B$, is introduced, then Kondo *et al.*'s model equation (21) is obtained. In turn, Hills and Viana's model equation (22) results from equation (20) in the case $B + \delta p \approx \delta p$, valid for $\delta p \gg B$. Differences in numerical values for model-based isothermal compressions of activation are therefore a direct consequence of these approximations. Since we found experimentally that $\delta p \gg B$ for these systems, it is now fully explained why equation (22) leads to values much closer to those from equation (20) than does equation (21).
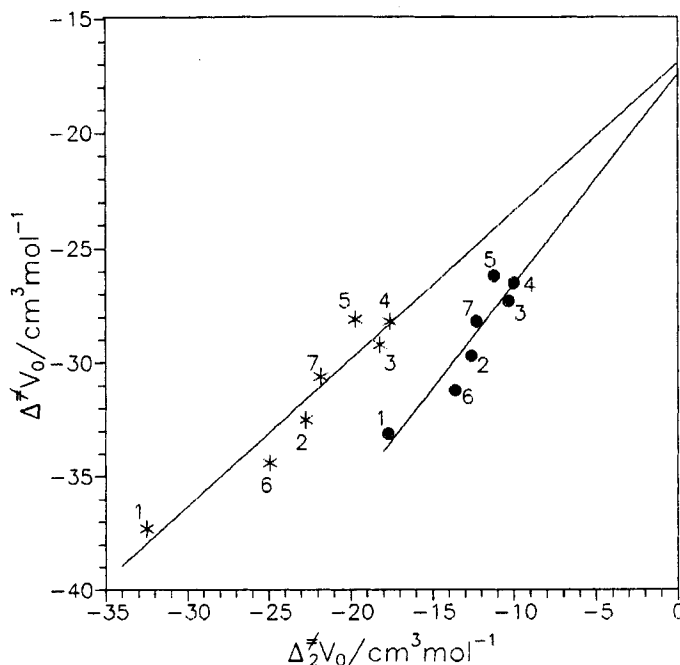
Figure 1. Plot for estimating Δ_i^*V for the reaction of Et_3N with EtI. (*) Data from equation (14); (•) Δ^*V_0 from equation (15) and $\Delta_2^*V_0$ from equation (18). 1, MeOH; 2, EtOH; 3, 1-PrOH; 4, 1-BuOH; 5, 1-PeOH; 6, 2-PrOH; 7, 2-BuOH

Finally, we enquire into the relationship between the volume and the isothermal compression of activation. Inspection of equations (18) and (20) allows us to write

$$\Delta^*V_0 = \Delta_1^*V_0 + B(1 + B/\delta p) \ln (1 + \delta p/B) \Delta^*K_{T,0} \quad (23)$$

which in the case $\delta p \ll B$ simplifies to

$$\Delta^*V_0 = \Delta_1^*V + B \Delta^*K_{T,0} \quad (24)$$

and in the case $\delta p \gg B$ has the form

$$\Delta^*V_0 = \Delta_1^*V + B \ln (1 + \delta p/B) \Delta^*K_{T,0} \quad (25)$$

From equation (23), the conditions for observing a linear relationship between both quantities of activation are a constant intramolecular activation volume and a constant solvent, even though $\delta p/B$ is insensitive to the solvent. These conditions can only be met by a series of similar reactions having the same Δ_1^*V in a given solvent. In fact, a linear relationship between $\Delta_r V_0^0$ and $\Delta_r K_{T,0}^0$ has been observed by Lown et al.[26] for a wide range of acid–base equilibria in water. However, the apparent linearity between $\Delta^*K_{T,0}$ and Δ^*V_0 reported by Kondo et al.[8] for a Menshutkin reaction in a series of solvents is probably an artefact finding no support from either equation (23) or even from approximate equations (24) and (25).

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