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Volume of electrostriction of the solvate-separated ions of lithium perchlorate and contact ion pair of the transition state in sulfenyl insertion

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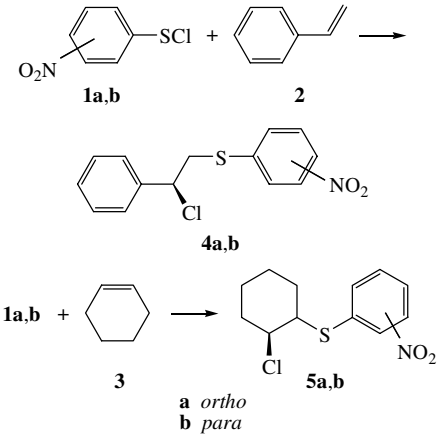
The volumes of electrostriction of the ions of lithium perchlorate are in a linear relation with the solvent electrostriction parameter $\partial(1/\varepsilon)/\partial p$ but the volume changes of ion pair transition state of electrophilic addition of aryl sulfenyl chloride to styrene and cyclohexene have the slope about 20 times less.

The high pressure effect on the rate and equilibrium of chemical reactions is of interest in pure and applied chemistry.[1–5] The nonpolar Diels–Alder reaction is convenient to elucidate volume changes in the absence of electrostriction.[3,6–8] Large electronic and steric effects of substitutions, as well as a solvent effect on the rate of the Menshutkin reaction at ambient and elevated pressure, have been intensively studied.[5] Here the charge separation can only grow during this reaction. On the other hand, a lot of substitution or addition processes have nonpolar initial and final states but a polar transition state. The substitution and solvent effects can be a reason for the transformation from polar nature of the transition state to nearly nonpolar one.[9] Sulfonium ion pair type of transition state was proposed for the electrophilic addition of sulfenyl halides to alkenes.[10] This assumption follows from the large solvent effect on the reaction rate and stereoselective *trans*-addition with formation of β-halide thioether. The transformation of the transition state from polar to nonpolar was proposed[11] for this reaction, when polar-type stabilization sharply decreases on going from polar to nonpolar media.



Scheme 1

If a polar transition state of the reaction is the same in polar and nonpolar media, solvent electrostriction should be in all solvents. But in this case the volume of activation in nonpolar solvents (*n*-hexane, carbon tetrachloride) should be more negative than that in polar ones.[2,5] On the other hand, if the transition state of the reaction is polar in a polar solvent but has a nonpolar type in a nonpolar medium, solvent electrostriction should be lack in the last case and the volume of activation in a polar solvent should be more negative. A polar solvent effect on the activation volume of Ad_E reaction (Scheme 1) was published recently.[12]

Lithium perchlorate with high solubility in organic *n*-donor solvents can be a suitable model of the ionic type of the transition state of chemical reactions. Solvent effect on the partial molar volume (PMV) of lithium perchlorate was measured for dilute solution.[13] The details of kinetic measurements under pressure were published elsewhere.[8,12] The rate constants of these reactions (Scheme 1) decrease in 10^6 times on going from acetonitrile to *n*-hexane. Long monitoring time (20–50 h) of the optical density change for *p*-nitrophenyl sulfenyl chloride was necessary because of the very slow reaction of **1b** with styrene **2** in *n*-hexane at 25 °C. The obtained rate constants were 1.80×10^{-5} at atmospheric pressure; 5.45×10^{-5} at 530 kg cm^{-2} and 1.16×10^{-4} dm^3 mol^{-1} s^{-1} at 960 kg cm^{-2}. From these data the apparent volume of activation in *n*-hexane was calculated as –49.3 cm^3 mol^{-1}.

$$-RT\left(\frac{\partial \ln k}{\partial p}\right)_T = \left(\frac{\partial G^{\neq}}{\partial p}\right)_T = \Delta V^{\neq}_{\text{exp}} \quad (1)$$

Because of the concentration of reagents (and the frequency of collision) growth under pressure due to the solvent compressibility, required correction for the second order reaction should be made.

$$RT\frac{\partial \ln k}{\partial V}\frac{\partial V}{\partial p} = \beta_T RT = -\Delta V^{\neq}_{\text{conc}} \quad (2)$$

The compressibility coefficient [$\beta_T = V^{-1}(\partial \text{V}/\partial \text{P})$] of *n*-hexane was measured in a special high pressure vessel up to 1000 bar at 20, 30, 40 and 50 °C. The Tait equation (3) has the best accuracy[2] in description of the V_p–p dependences.

$$\Delta V/V_0 = C\ln[(B + p)/B] \quad (3)$$

The coefficients C, B and β_T were obtained as 0.088123, 548.50 and 160.66×10^{-6} bar^{-1} at 20 °C; 0.088342, 501.69 and 176.09×10^{-6} bar^{-1} at 30 °C; 0.087517, 451.62 and 193.78×10^{-6} bar^{-1} at 40 °C and 0.088855, 415.10 and 214.06×10^{-6} bar^{-1} at 50 °C. From obtained dependence: $\beta_T = 137.22 + 0.93015T + 0.012125T^2$ ($R = 0.999997$), the value of β_{25} was calculated as 168.05×10^{-6} bar^{-1} at 25 °C. Using these data $\Delta V^{\neq}_{\text{conc}}$ [equation (2)] was calculated as –4.1 cm^3 mol^{-1}, and the corrected volume of activation ($\Delta V^{\neq}_{\text{exp}} - \Delta V^{\neq}_{\text{conc}}$) of the reaction (**1b** + **2**) in *n*-hexane at 25 °C was determined as –45.2 cm^3 mol^{-1}.

Table 1 Rate constants (k_2/dm^3 mol^{-1} s^{-1}) for the reaction of *o*-nitrophenyl sulfenyl chloride **1a** with cyclohexene **3** in a mixture of 1,2-dichloroethane and carbon tetrachloride at 25 °C.

Mole fraction of 1,2-dichloro-ethane	10^5k_2	ln k_2	ε_m[a]
0	1.60	–11.04	2.22
0.1398	20.4	–8.47	2.7
0.2898	60.3	–7.41	3.3
0.5521	624	–5.08	5.0
0.7850	2170	–3.83	7.2
1	5850	–2.84	10.02

[a]The values of ε for mixtures are taken from ref. 15.

It is well known[9] that the changes of the free energy of activation of polar reactions at ambient pressure are caused by the changes of solvation (ΔG_{solv}) of polar transition or initial states and described as:

$$\ln k = a + b(1/\varepsilon) \quad (4)$$

High pressure induces the growth of solvent permittivity ε:

$$\frac{\partial \ln k}{\partial(1/\varepsilon)}\frac{\partial(1/\varepsilon)}{\partial p} = b\frac{\partial(1/\varepsilon)}{\partial p} \quad (5)$$

With the known value of b it is possible to estimate the effect of the modified solvent properties, induced by pressure, on the rate constants and compare with the apparent volumes of activation. For the reaction of styrene with *o*-nitrophenyl sulfenyl chloride[12] the value of b is –22±2. Nearly the same value of b was obtained[14] for the reaction of styrene with phenyl sulfenyl chloride (–25±3). Solvent mixture effect of 1,2-dichloroethane and carbon tetrachloride on the rate constant of the reaction of *o*-nitrophenyl sulfenyl chloride with cyclohexene was studied at 25 °C (Table 1). Clear linear relation ln k_2 *vs.* $1/\varepsilon$ was obtained with the slope b equal to –22.3±0.9 (r = 0.997).

The values of equation (5) were calculated using b = –22 and known data for the $\partial(1/\varepsilon)/\partial p$.[2,16]

High level of correlation (r = 0.99) of the independent values $b\partial(1/\varepsilon)/\partial p$ and $V^{\neq}_{cor.} = \Delta V^{\neq}_{exp} - \Delta V^{\neq}_{conc}$ is in accordance with the assumption that the changes of free energy of activation under pressure ($\partial G^{TS}_{solv}/\partial p$) are produced by solvent permittivity growth. From this point of view a larger pressure effect on the rate constant, ln(k_p/k_0), in nonpolar medium can be caused by a larger change of baric coefficient of permittivity, $\partial(1/\varepsilon)/\partial p$, [equation (5)], or be a result of a larger contribution of mechanical work $p\Delta V^{\neq}$, caused by more negative value $\Delta V^{\neq}$. From the relation describing the pressure effect on free energy of a charged particle (q) solvation[2]

$$\frac{\partial \Delta G_{solv}}{\partial p} = \Delta V_{electr} = -\left(\frac{Nq^2}{2r}\right)\frac{\partial(1/\varepsilon)}{\partial p}, \quad (6)$$

it is clear that both these parameters should be indistinguishable. Nearly the same approach to the solvent effect on the volumes of activation of some polar reactions was discussed previously.[2,8,17,18]

The activation volume ($\Delta V^{\neq}$) refined from the solvent electrostriction effect ($\Delta V^{\neq}_{cor.} - V^{\neq}_{el}$) is nearly the same (–20.5±1.4 cm^3 mol^{-1}) for all of the test reactions (Scheme 1) and in all solvents under consideration, with the ratio $\Delta V^{\neq}/\Delta V_{reaction}$ = 0.92.

It is possible to compare the effects of the values of baric coefficient of permittivity of solvents, $\partial(1/\varepsilon)/\partial p$, as electrostriction parameter [equation (6)], on the change of PMV of the charge solute, lithium perchlorate (LP), and on the change of the activation volumes of studied reactions (Table 2, Figure 1).

Note that, for polar solvents with the dielectric constant ε higher than 20, [Figure 1, line *a*, solvents 1–7), there is a clear correlation (r = 0.96) of lithium perchlorate PMV and the electrostriction parameter $\partial(1/\varepsilon)/\partial p$:

$$V_{LP} = 51.3 + 8.83\times10^6\frac{\partial(1/\varepsilon)}{\partial p}. \quad (7)$$

In spite of a high solubility of LP in tetrahydrofuran (ε = 7.5), ethyl acetate (ε = 6.1) and, especially, in diethyl ether (ε = 4.3, solubility up to 6 mol dm^{-3} at 25 °C), the values of PMV of lithium perchlorate in dilute solutions of these solvents (no. 5, 7 and 9, Figure 1) deviate sharply from the common line (Figure 1, line *a*). From equation (7) it can be predicted that the values of PMV of separated ions of lithium perchlorate in EtOAc, THF and Et_2O are –100, –75 and –300 cm^3 mol^{-1}, respectively. This denotes a low degree of lithium perchlorate dissociation in these solvents under working conditions due to low polarity. In addition, all pressure-solvent effects on the studied reactions of aryl sulfenyl chloride with styrene and cyclohexene (Table 2) are in accordance with Kharasch' preposition[10] of zwitter-ionic type of transition state in the solvents under consideration. Because of small solvent effect on the PMV values of nonpolar reagents,[12] the differences in activation volumes can be accounted for electrostriction of transition state. Linear dependence (Figure 1, line *b*, solvents 11–17, r = 0.99) between the change of the volume of zwitter-ionic transition state and the electrostriction parameter of solvent $\partial(1/\varepsilon)/\partial p$) (Table 2) has the slope about 20 times less than that for separated ions of lithium perchlorate:

$$\Delta V^{\neq}_{cor.} = -20.5 + 0.49\times10^6\frac{\partial(1/\varepsilon)}{\partial p}. \quad (8)$$

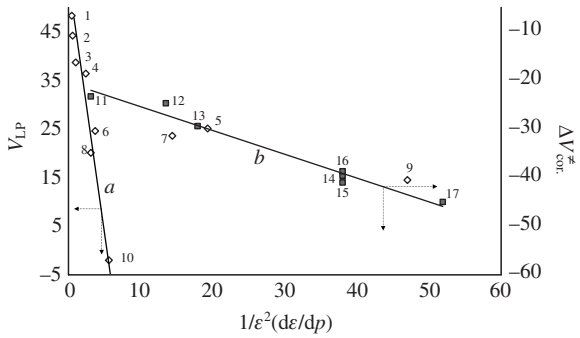


Figure 1 Effect of the electrostriction parameter of solvents $(1/\varepsilon^2)\partial\varepsilon/\partial p$ (*a*) on the partial molar volume (V_{LP}) of lithium perchlorate, and (*b*) on the volume of activation ($\Delta V^{\neq}_{cor.}$) of the studied reactions. For numeration of the solvents see Table 2.

Table 2 Partial molar volumes of lithium perchlorate (LP) in dilute solution (V/cm^3 mol^{-1}, no. 1–10), corrected activation volumes ($\Delta V^{\neq}_{cor.} = \Delta V^{\neq}_{exp} - \Delta V^{\neq}_{conc}$/ cm^3 mol^{-1}, no. 11–17) of studied reactions of sulfenyl chloride with alkenes and electrostriction volume ($\Delta V^{\neq}_{el}$/cm^3 mol^{-1}) at 25 °C.

No.	Solvent	V or $\Delta V^{\neq}_{cor.}$[a]	$-\Delta V^{\neq}_{el}$[b]	$(1/\varepsilon^2)\partial\varepsilon/\partial p$[c]	ε[d]	$10^6\beta$[e]
1	Formamide	48.3	3.0	0.45 (0.40)	100.5	39.9
2	H_2O	44.2	7.1	0.57 (0.57)	80.1	45.8
3	DMSO	38.7	12.6	— (1.0)	47.2	49
4	$MeNO_2$	36.4	14.9	2.4 (1.9)	37.3	71.7
5	EtOAc	25.1	26.2	19.3 (18.8)	6.08	113
6	MeOH	24.6	26.7	3.7 (3.7)	33.0	124
7	THF	23.6	27.7	14.4 (15.4)	7.52	116
8	MeCN	20.1	31.2	3.1 (3.1)	36.6	113
9	Et_2O	14.5	36.8	47 (44)	4.20	190
10	Me_2CO	–2	53.3	5.6 (6.4)	20.5	132
11	MeCN	–23.3 (**1a** + **2**)	2.8	3.1 (3.1)	36.6	113
12	Anisole	–24.7 (**1a** + **2**)	4.2	13.5 (15.8)	4.33	68.6
13	ClH_2CCH_2Cl	–29.4 (**1a** + **2**)	8.9	17.9 (7.6)	10.4	78.8
14	CCl_4	–39.6 (**1b** + **2**)	19.1	38 (48)	2.24	108.0
15	CCl_4	–41.0 (**1b** + **3**)	20.5	38 (48)	2.24	108.0
16	CCl_4	–37.8 (**1a** + **3**)	17.3	38 (48)	2.24	108.0
17	*n*-Hexane	–45.2 (**1a** + **2**)	24.7	51.9 (89)	1.88	167.4

[a]The values of PMV of lithium perchlorate are taken from ref. 13. [b]Calculated for solvents no. 1–10 from equation (7) and no. 11–17 from equation (8). [c]From refs. 2 and 16. Data in parentheses calculated from the ratio β/ε. [d]From ref. 16. [e]From refs. 2 and 19.

Note that the change of PMV of lithium perchlorate in the solvents of low polarity (no. 5, 7 and 9, Table 2) located with nearly the same slope on the zwitter-ionic line (Figure 2, line *b*).

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