Table — C.V. and C.P.E. data[(a)] for the dinuclear carbene complexes $[\{(PPh_3)ClM(\mu\text{-}\overline{CYCH_2CH_2}N\text{-}\underline{C},\underline{N})\}_2]$ (1)

M	Y	E_p^{ox} (b) I	I'	II	III	C.P.E. I + I' n(e⁻)	n(H⁺) (c)	II n(e⁻)	n(H⁺) (c)
Pt	O	1.67 (d)				0.93 (d')	1.1		
Pt	NC_6H_4-p-OMe	0.98	1.13	1.60	1.88	2.0	2.0	4.0	3.4
Pd	NC_6H_4-p-OMe	0.96	1.10	1.58		1.8	1.8	4.1	3.4
Pd	NMe	0.80	1.12	1.44	1.80	1.9	1.7		

(a) At a Pt wire (C.V.) or gauze (C.P.E.), in NCMe (unless stated otherwise)/0.2 M $[Bu_4N][BF_4]$.

(b) Values in volt vs. s.c.e., measured by C.V. at 100 mVs^{-1}.

(c) Measured by acid-base titration of the electrolyzed solution.

(d) In CH_2Cl_2 due to insufficient solubility in NCMe

(d') In $NCMe/CH_2Cl_2$ (4:1 volume ratio).

VOLUME AND COMPRESSIBILITY CHANGES OF SOLVENTS IN IONIZING PROCESSES

by

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Volumic properties are of course volume dependent. Concentration is one of these properties and the ratio between the number of molecules and the volume is a very important property which must be taken into account in the study of solvolytic mechanisms.

In this respect two reactions, namely ter-butyl chloride and ethyl iodide/triethylammine in different alcohols are here analysed. The two mechanisms are essentially as follow[1,2]:

$$tBuCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\,tBu^{+\delta}\text{----}\,Cl^{-\delta}\,]^{\neq} \xrightarrow{k_2} Bu - O - Me + H^+ + Cl^- \qquad (1)$$

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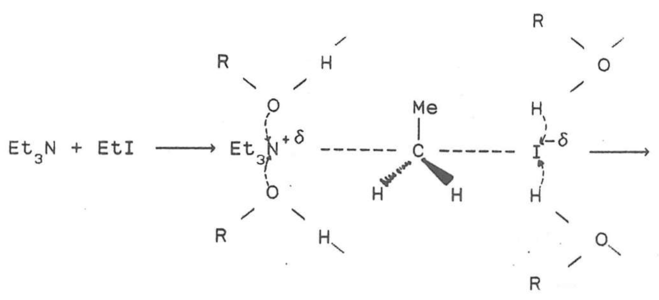
and

I II



III IV

$$\longrightarrow Et_4N^+I^-(ROH)_{m+n} \rightleftharpoons [Et_4N^+(ROH)I^-(ROH)_{m+n-1}]^{\neq} \rightleftharpoons$$

V

$$\rightleftharpoons (ROH)_mEt_4N^+ + I^-(ROH)_n \qquad (2)$$

Both reactions, S_N1 and S_N2 mechanisms respectively, are each time originating more ionic species as they get forward. So the solvations increasing on account of that and in particular, the number of the solvent molecules solvating the activated complex are in both cases higher than in initial state.

From the rate constant as a function of pressure the volumes of activation are obtained eventually as a function of

temperature, pressure and solvent. Such parameter can be dissected in two components as follows:

$$\Delta^{\neq}V^{o} = \Delta^{\neq}V^{o}_{1} + \Delta^{\neq}V^{o}_{2} \qquad (3)$$

where $\Delta^{\neq}V^{o}_{1}$ is concerned with intramolecular substrate volume changes and $\Delta^{\neq}V^{o}_{2}$ relates solvent volume change on account of substrate-solvent interactions. For these reactions $\Delta^{\neq}V^{o}_{2}$ values are larger than $\Delta^{\neq}V_{1}$ and the $\Delta^{\neq}V^{o}$ values are strongly negatives, wich suggest a strong involvement of the solvent in the activated complex.

The solvent molar volumes around the activated complex and in the bulk, $V^{\neq}_{2}$ and V_M, respectively are related trough equation

$$\Delta^{\neq}V^{o}_{2} = V^{\neq}_{2} - V_M \qquad (4)$$

These values are shown in tables 1 and 2.

As it can be seen the molar volumes around the activated complex are always much smaller than in the bulk which shows an increasing concentration of the solvent molecules as the change are developed over the substracta and as it can be proved by the values of the heat capacities of activation[2,3]. Equating the volume of activation in terms of the solvent free volume

$$V_F = V_M - V_S \qquad (5)$$

where V_F, V_M and V_S are the free volume, the liquid volume and the non-operable volume, it is possible to obtain[1-3]

Table 1 Activation volumes and molar volumes of *t*BuCl in MeOH as function of pressure (T = 313.15 K)

p/bar	$-\Delta^{\neq}V^{0}/cm^{3}mol^{-1}$	$-\Delta^{\neq}V_{2}^{0}/cm^{3}mol^{-1}$	$V_{M}/cm^{3}mol^{-1}$	$V_{2}^{\neq}/cm^{3}mol^{-1}$
1	26.7±1.2	30.7±2.2	41.47	10.8±2.2
500	20.7±0.1	24.7±1.1	39.31	14.6±1.1
1000	16.6±0.1	20.6±1.1	37.92	17.3±1.1
1500	14.4±0.1	18.4±1.1	36.89	18.4±1.1
2000	13.6±0.3	17.6±1.3	36.07	18.4±1.3

$\Delta^{\neq}V_{1}$ was determined on the basis described in reference (1)

Table 2 Activation volumes and molar volumes of a Menschutkin reaction as a function of solvent (T = 313.15 K , p = 1 atm)

Solvent	$-\Delta^{\neq}V^{0}/cm^{3}mol^{-1}$	$-\Delta^{\neq}V_{2}^{0}/cm^{3}mol^{-1}$	$V_{M}/cm^{3}mol^{-1}$	$V_{2}^{\neq}/cm^{3}mol^{-1}$	n
MeOH	29.8±0.8	21.3±2.5	41.47	20.2±2.5	3.7
EtOH	27.5±0.7	17.0±2.8	59.67	42.9±2.8	1.8
1-PrOH	25.7±0.7	12.6±2.7	76.32	63.7±2.7	1.2
1-BuOH	20.8±0.4	6.5±1.8	93.28	86.8±1.8	0.4
2-PrOH	28.7±1.0	19.9±1.9	78.22	58.3+1.9	1.5
2-BuOH	26.4±0.7	18.2±1.1	93.86	75.7±1.1	1.2

$\Delta^{\neq}V_{1}$ was obtained having in account the Kondo and col'equations[4] and the Asano and col'equations[5]

$$\Delta^{\neq}V^{o} = \Delta^{\neq}V_{1}^{o} + nV_{F} \qquad (6)$$

from which the extrasolvation number, n, on account of the activated complex formation, is obtained since $\Delta^{\neq}V_{1}^{o}$ can be considered constant in relation to $\Delta^{\neq}V_{2}^{o}$. So $(\partial\Delta^{\neq}V^{o}/\partial V_{M})_{T} = n$. Such derivative is determined through $(\Delta^{\neq}V^{o}, V_{M})$ variations which are always very approximately linear. An example of it is shown in Fig. 1[1,2] and the n values are as follow in table 2.

Having in consideration the equation (4) the following relationship

$$\chi_{2}^{\neq} = -\,(1\ /\ V_{2}^{\neq})\ \times\ (\partial V_{2}^{\neq}\ /\ \partial p)_{T} = -\ (\partial \ln V_{2}^{\neq}\ /\ \partial p)_{T} \qquad (7)$$

is obtained and from which the solvent compressibility of activation as well as the normal solvent compressibilities are obtained. Table 3 shows the normal solvent compressibility as well as the solvent compressibility of activation understood in both senses, the absolute value, $\chi_{2}^{\neq}$, and the variation of the solvent compressibility

$$\Delta^{\neq}\chi_{2} = \chi_{2}^{\neq} - \chi \qquad (8)$$

respectively, as a function of solvent.

As it can be seen the solvent compressibility decreases as the solvent carbon chain increases while the solvent compressibility of activation increases under similar conditions. This is in accordance to the larger sizes of solvent molecules which causes a smaller decreasing of solvent around the reaction sites as the solvent molecules increases.

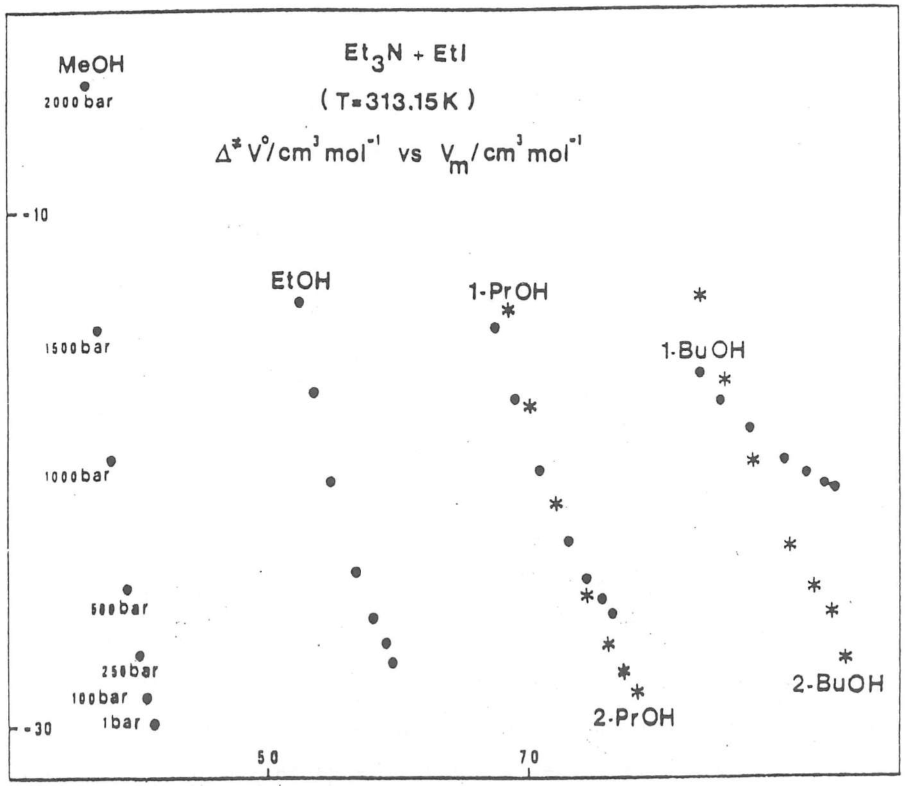


Fig. 1 Volumes of activation of ET_3N + EtI in different alcohols as a function of molar volumes

Table 3 Normal solvent compressibility and solvent compressibility of activation for a Menschutkin reaction as a function of solvent

(T = 313.15 K)

Solvent	$\chi_2^{\neq}\times10^4$/bar^{-1}	$\chi\times10^4$/bar^{-1}	$\Delta^{\neq}\chi_2\times10^4$/bar^{-1}
MeOH	-1.68±0.05	1.384	-3.06±0.05
EtOH	-0.43±0.06	1.272	-1.70±0.06
1-PrOH	0.19±0.05	1.120	-0.93±0.05
1-BuOH	0.42±0.04	1.039	-0.62±0.04
2-PrOH	-0.56±0.06	1.278	-1.84±0.06
2-BuOH	-0.31±0.04	1.103	-1.42±0.04
MeOH[a]	-2.6±0.7	1.384	-4.0±0.7

[a] Reaction of *t*BuCl (T = 313.15 K)

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STABILITY OF LIQUID JUNCTION POTENTIALS

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The widespread use of ion selective electrodes in the most varied fields - from environment to clinical chemistry, etc, as well as renewal of interest in transference data of electrolytes obtained from emf of cells with liquid-liquid junction make it crucial to have a trustworthy method of forming that junction.

The most recent transference data obtained by the determination of the electromotive force of cells with liquid-liquid junction refer to cell vessel designs which seem to be prone to instability. Several authors use the cell vessel design which is presented by F. King and M. Spiro (1) (e.g. (2), (3)), others use the one developed by Rupert (4) and adapted by Braun and Weingärtner (5) (e.g. (6), (7), cf. Fig. 1,2.

The cell vessel design used in our work, in which the junction is formed at the middle of a capillary tube of cylindrical symmetry, was developed to obtain operational pH values (8), (9) producing very steady and reproducible values, even though there was hydrogen bubbling in both compartments. However, wearing of the ground glass of the Y taps (which

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