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THE REACTION OF NITRILE WITH α-HYDROGENS AT HIGH PRESSURE II

PRESSURE EFFECTS ON THE IMINOETHER FORMATION AND DEUTERIUM-HYDROGEN EXCHANGE REACTION OF PHENYLACETONITRILE IN METHANOL

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The rates of the nucleophilic attack of methoxide ion to phenylacetonitrile in methanol were studied at high pressure. The attack resulted in two different types of reactions, one being the elimination of α-hydrogens while the other the base-catalyzed methanol addition to C≡N triple bond. Positive ($+24\text{cm}^3\text{mol}^{-1}$ at 303.2K)and negative($-13.1\text{cm}^3\text{mol}^{-1}$ at 313.2K) activation volume changes were observed for the deuterium elimination and the nucleophilic attack of methoxide ion to C≡N triple bond, respectively. An expression which permits the distinction between the electrostatic volume change and the covalent volume change has been derived from a perturbed molecular-orbital theory combined with the Owen-Brinkley formula. Validity of the expression has been tested for various types of high-pressure reactions including those here studied.

Introduction

For the understanding of chemical dynamics in solution the interaction of solute with surroundings has to be unavoidably taken into account. The features of this interaction are informed by the knowledge of the effects of the surrounding conditions, such as solvent polarity, temperature and/or pressure on the thermodynamic activation parameter. In paraticular, the activation volume change which can be estimated from the pressure effect is well known to reflect the reaction coordinate from the viewpoint of the geometry change as well as the solvation change. However, such a macroscopic parameter often fails to account for relative reactivities of a molecule at different reaction sites; for example, the difference in reactivity of *meta*- and *para*- positions could not be explained successfully by considering only a single parameter. The molecular-orbital treatment has, on the other hand, succeeded in interpriting this kind of reactivity semiquantitatively, though the theoretically-derived reactivity indices do not incorporate the effect of the medium. In this paper the author has tried to derive a formula, which is generally applicable to the variation in reaction rate constants with pressure. Klopman's perturbation theory¹⁾ has been used, in which the charge density and the charge transfer between reacting sites are considered together with the solvation of charged atoms. The derived formula has been applied to several reactions which were studied by other researchers. The

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1) G.Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968)

nucleophilic reaction of methoxide ion to phenylacetonitrile, which involves the elimination of an α-hydrogen and the methoxide addition to the C≡N triple bond, has also been tested.

Experimental and Dielectric Constant at High Pressure

Phenylacetonitrile was distilled twice at reduced pressure of nitrogen atmosphere. Methyl phenylacetiminoether was prepared by the neutralization of methyl phenylacetiminoether hydrochloride which was synthesized according to Pinner's method[2] at 263K in order to prevent the "Pinner Cleavage." The mixture was extracted with carbon tetrachloride, and the extract was distilled twice at reduced pressure of nitrogen atmosphere. Phenylacetonitrile-d_2 was prepared by the base-catalyzed hydrogen-deuterium exchange in methanol-d_1. Methanol and triethylamine were purified in the same way as reported before[3]. The concentration of methoxide ion was determined by measuring the electrical conductivity, the way of which has an advantage to be able to correct the influence of carbon dioxide[3]. The elimination reaction could be easily quenched by blowing the carbon dioxide into the reaction mixture. At atmospheric pressure, the amine-catalyzed iminoether formation is too late to lead to serious errors during the evapolation of the solvent. The high-pressure generating systems and the reaction cell were reported elsewhere[4]. The yield of each product was determined from the NMR peak areas corresponding to the methylene protons.

The dielectric constants of pure liquids at high pressure were calculated by means of the Owen-Brinkley expression:[5] $1-D^{(1)}/D^{(P)}=A\ln(B+P)/(B+1)$, where $D^{(1)}$ and $D^{(P)}$ are the dielectric constant at 1 and P kg cm^{-2}*, respectively, and A and B are empirical constants[6].

Results and Discussion

Iminoether formation

Although phenylacetonitrile remained unreacted in methanol at pressure up to 7000 kg/cm^2 and 343K for 7h, the addition of triethylamine produced methyl phenylacetiminoether. It has been reported that in the presence of alkoxide ion nitriles convert partially to iminoether even at atmospheric pressure[7]. Thus the apparent amine-catalysis in methanol at high pressure is considered to be due to the promoted production of methoxide ion by proton transfer. The reaction scheme is represented as follows:

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*1atm = 1.033kg cm^{-2} = 1.013 × 10^5 pa, 1cal = 4.184J

2) A. Pinner, "Die Imidoäther und ihre Derivate,"Oppenheim, Berlin (1892)

3) H. Inoue, K. Hara, and J. Osugi, *This Journal*, **48**, 44 (1978)

4) H. Inoue, K. Hara, and J. Osugi, *This Journal*, **46**, 64 (1976)

5) B.B. Owen and S.R. Brinkley, *Phys. Rev.*, **64**, 32 (1943)

6) K.R. Srinivasan and R.L. Kay, *J. Solution Chem.*, **4**, 299 (1975); H. Hartmann, A. Neumann, and G. Rinck, *Z. Phys. Chem., Neue Folge* **44**, 204, 218 (1965); L.G. Schornack and C.A. Eckert, *J. Phys. Chem.*, 74, 3014 (1970); E. Schadow and R. Steiner, *Z. Phys. Chem., Neue Folge* **66**, 105 (1969)

$$N(Et)_3 + MeOH \overset{K_1}{\rightleftharpoons} HN(Et)_3^+ + MeO^-, \qquad (1)$$

$$PhCH_2CN + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhCH_2C(=N^-)OMe, \qquad (2)$$

$$\underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} (PhCHCN)^- + MeOH, \qquad (3)$$

$$PhCH_2C(=N^-)OMe + MeOH \overset{K_3}{\rightleftharpoons} PhCH_2C(=NH)OMe + MeO^- \qquad (4)$$

The ionic dissociation constants of triethylamine in methanol at high pressure were estimated by extrapolating the values which were determined from the measurements of electrical conductivities[3].

Time dependence of the formation of methyl phenylacetiminoether is shown in Figs. 1 and 2. The base-catalyzed hydrogen exchange (3) was confirmed by using MeOH-d_1 as the solvent. For some nitriles such a base-catalyzed α-hydrogen transfer in methanol has also been reported[8]. The hydrogen transfer(3) is fast as compared with the iminoether formation(2), the relaxation time being several minutes under our experimental condition. Therefore, step(3) can be regarded to be in equilibrium during the course of the iminoether formation, maintaining the relationship $[PhCH_2CN] \gg [(PhCHCN)^-]$[9, 10].

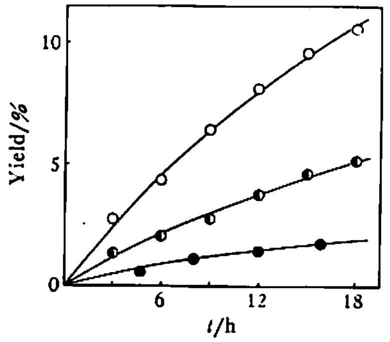

Fig. 1 Time dependence of the yield of $PhCH_2C(=NH)OMe$ in MeOH at 323.2K
$[PhCH_2CN]_0=0.05$ mol/kg,
$[N(Et)_3]=0.25$mol/kg
●: 1000 kg/cm², ◐: 2000 kg/cm²,
○: 3000 kg/cm²

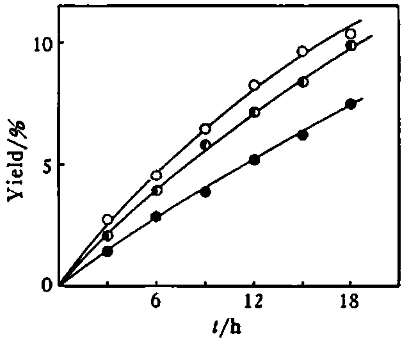

Fig. 2 Time dependence of the yield of $PhCH_2C(=NH)$ OMe in MeOH at 3000 kg/cm²
$[PhCH_2CN]_0=0.05$ mol/kg,
$[N(Et)_3]=0.25$mol/kg
●: 313.2K, ◐: 318.2K, ○: 323.2K

By applying the steady-state assumption to $PhCH_2C(=N^-)$ OMe, the iminoether formation can be expressed as a function of time:

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7) F.G. Schaefer and G.A. Peters, *J. Org. Chem.*, **26**, 412 (1961)

8) For example, N. -Å. Bergman and I. Källson, *Acta Chem. Scand.*, **A30**, 421 (1976): *ibid.*, **A30**, 411 (1976): R. Stewart, J.P. O'Donnell, D.J. Cram, and B.Rickborn, *Tetrahedron* **18**, 917(1962); D.J. Cram, C.A. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961)

9) J.R. Jones, "Progress in Physical Organic Chemistry," Wiley, 9, 241 (1972)

10) It has been reported that *p*-nitrophenylacetonitrile gave pink solution, $\lambda_{max}=530$ nm and $\epsilon=2.87\times10^4$, in MeO⁻-MeOH. See, for example, R.A. More O'Ferrall and J.H. Ridd, *J. Chem. Soc.*, **1963**, 5030. The absorbance of $(PhCHCN)^-$ was not observed from 290 to 800 nm within experimental error.

$$\ln\frac{X_e}{X_e-X}=(k_2'+k_{-2}')t, \tag{5}$$

where $k_2'=k_2[\mathrm{MeO^-}]$ and $k_{-2}'=k_{-2}K_3^{-1}[\mathrm{MeO^-}]$ are the pseudo-first order rate constants, X the molar concentration of iminoether at time t, and X_e its equilibrium value. In order to obtain the value of X_e, the mixture of the components whose concentration was approximately estimated from the intercept of the Guggenheim plot was kept at each pressure for a sufficiently long time. The exact equilibrium concentrations determined are listed in Table 1. Plots of $\ln[X_e/(X_e-X)]$ against t gave a satisfactory straight line at each pressure. Table 2 shows the values of the ionic dissociation constants of triethylamine and the rate constants of iminoether formation.

Table 1 Equilibrium conversion (%)*of $PhCH_2CN$ to $PhCH_2C(=NH)OMe$**

P/kg cm^{-2}	T/K		
	323.2	318.2	313.2
1	5.2	5.2	5.5
1000	8.3	8.6	9.5
2000	13.7	14.2	15.0
3000	18.8	22.4	23.2

* Theoretical yield based on $PhCH_2CN$
** Reaction time, 72-96h

Table 2 The values of K_1, k_2, and $k_{-2}K_3^{-1}$ at high pressures

P/kg cm^{-2}	T/K								
	323.2			318.2			313.2		
	$K_1\times10^6$*	$k_2\times10^3$*	$k_{-2}K_3^{-1}\times10^3$*	$K_1\times10^5$	$k_2\times10^3$	$k_{-2}K_3^{-1}\times10^3$	$K_1\times10^6$	$k_2\times10^3$	$k_{-2}K_3^{-1}\times10^3$
1	0.26	0.43	7.9	0.23	0.32	5.8	0.21	0.24	4.1
1000	1.4	0.67	7.3	1.3	0.51	5.4	1.3	0.36	3.4
2000	5.2	1.0	6.3	5.0	0.78	4.7	5.0	0.55	3.1
3000	16	1.4	5.5	16	1.2	4.2	17	0.78	2.6

* K_1/mol kg^{-1}, k_2/kg mol^{-1}s^{-1}

Deuterium-Hydrogen Exchange

The pressure effect on the nucleophilic attack to α-hydrogens was estimated for phenylacetonitrile-d_2 in methanol, because the reaction of phenylacetonitrile in MeO^--$MeOH$-d_1 was too fast to be followed at high pressure. The rate equations of the deuterium-hydrogen exchange are derived from the simplified reaction scheme;

$$PhCD_2CN+MeO^- \xrightarrow{2k_D} PhCDHCN+MeO^- \quad (6)$$

$$PhCDHCN+MeO^- \xrightarrow{k_D} PhCH_2CN+MeO^- \quad (7)$$

Since the deuterium-hydrogen exchange is very fast in comparison with the iminoether formation, the term of iminoether formation can be neglected. Hence, we can write

$$-\frac{d[PhCD_2CN]}{dt}=2k_D[PhCD_2CN][MeO^-]=2k_D'[PhCD_2CN] \quad (8)$$

$$\begin{aligned}\frac{d[PhCDHCN]}{dt}&=2k_D[PhCD_2CN][MeO^-]-k_D[PhCDHCN][MeO^-]\\&=2k_D'[PhCD_2CN]-k_D'[PhCDHCN] \quad (9)\end{aligned}$$

$$\frac{d[PhCH_2CN]}{dt}=k_D[PhCDHCN][MeO^-]=k_D'[PhCDHCN] \quad (10)$$

From Eqs. (8), (9), and (10), we obtain upon integration the following equation:

$$\frac{2[PhCH_2CN]+[PhCDHCN]}{2a}-1=\left(\frac{2[PhCH_2CN]_0+[PhCDHCN]_0}{2a}-1\right)\times\exp(-k_D't), \quad (11)$$

where $a=[PhCD_2CN]_0+[PhCDHCN]_0+[PhCH_2CN]_0$, the subscript 0 refers to the initial concentration, and $(2[PhCH_2CN]+[PhCDHCN])/2a$ is the quantity measured from the NMR spectral intensity. Plots of $\ln[1-(2[PhCH_2CN]+[PhCDHCN])/2a]$ against t seem to give a straight line, and the rates of the deuterium-hydrogen exchange was found to decrease with pressure, as is shown in Fig. 3 and Table 3.

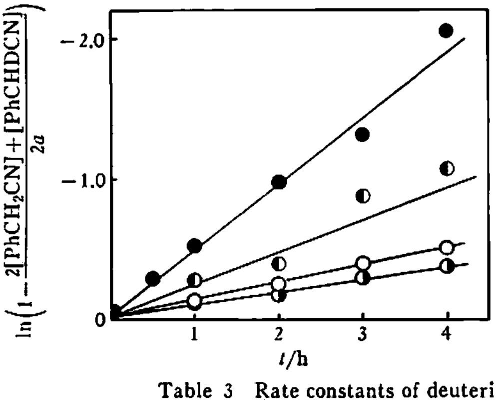

Fig. 3 Deuterium-hydrogen exchange of $PhCD_2CN$ in MeO^-—MeOH at 303.2K
$[PhCD_2CN]\cong0.07$ mol/kg,
$[MeOK]=0.31\times10^{-4}$ mol/kg
●: 1atm, ◐: 1000 kg/cm²,
○: 2000 kg/cm², ◑: 3000 kg/cm²

Table 3 Rate constants of deuterium-hydrogen exchange at 303.2 K

P/kg cm^{-2}	k_D/kg mol^{-1}s^{-1}
1	4.0
1000	2.0
2000	1.2
3000	0.9

Pressure dependence of the rate constants based on the perturbation theory

The molecular orbital theory has proved useful in explaining the relative reactivities of various reaction sites of organic compounds. The perturbation method has been especially successful, though its application is limited only to an early stage of the reaction. The energy contributions to the interaction energy can be divided into several terms including Coulomb (E_Q), exchange-repulsion (E_K), induction (E_I), and charge-transfer (E_{CT}) energies[11].

Klopman has introduced a simple perturbation theory taking account of only the Coulombic and electron-transfer effects in sophisticated solvent[1,12]. The interaction energy was roughly estimated from the solvation energy change produced by the partial electron transfer, neglecting the overlap integrals between the interacting orbitals, and the energy change due to the non-reactive sites:

$$\Delta G \sim q_r q_s F/D + \sum_{m}^{occ} \sum_{n}^{un} 2(C_r{}^m C_s{}^n \beta)^2/(E_m{}^* - E_n{}^*), \tag{12}$$

where q_r is the initial net charge of atom r, F a Coulombic intensity factor for the interaction between r and s, D a polarity parameter of the solvent, $E_m{}^*$ and $E_n{}^*$ the energies of the respective molecular orbitals m and n of molecules R and S under interaction in the medium. The second term of the right-hand side can be approximated by considering only the frontier orbitals[13];

$$\Delta G \sim q_r q_s F/D + 2(C_r^{HOMO} C_s^{LUMO} \beta)^2/(E^*{}_{HOMO} - E^*{}_{LUMO}) \tag{13}$$

where *HOMO* and *LUMO* represent the highest occupied and the lowest unoccupied molecular orbitals, respectively. Since the first term of the right-hand side of Eq. (13) expresses a rather long range energy where electron transfer does not occur, D is approximately considered to be a macroscopic dielectric constant of the medium. On the other hand, the solvent parameter involved in $E_m{}^*$ and $E_n{}^*$ should be a function of a local dielectric constant because the second term represents the energy due to the partial charge transfer in the vicinity of the sophisticated solvent molecules.

Assuming that only D and E^* are pressure dependent, we can derive from Eq. (13) the following relationship:

$$\Delta G^{(P)} - \Delta G^{(1)} = q_r q_s F(1/D^{(P)} - 1/D^{(1)}) + 2(C_r^{HOMO} C_s^{LUMO} \beta)^2 \times \\ [1/(E^*{}_{HOMO}^{(P)} - E^*{}_{LUMO}^{(P)}) - 1/(E^*{}_{HOMO}^{(1)} - E^*{}_{LUMO}^{(1)})]. \tag{14}$$

The first term of the right-hand side is analogous to that of Born's solvation theory if q_r and q_s are the integral charge and F is the function of reciprocal of distance. Following Nakahara's derivation in the case of the ionization equilibrium, it can be expressed as follows[14]:

$$q_r q_s F(1/D^{(P)} - 1/D^{(1)}) = \Delta V_{elect}{}^{(1)}(B+1)\ln(B+P)/(B+1), \tag{15}$$

where $\Delta V_{elect}{}^{(1)}$ refers to the electrostatic volume change at 1 atm and B is an empirical parameter in the Owen-Brinkley expression. The difference of energy lebels can be expanded as a power series

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[11] J.N. Murrell, M. Randić, and D.R. Williams, *Proc. Roy. Soc., Ser.* **A 284**, 566 (1965); T. Fueno, S. Nagase, K. Tatsumi, and K. Yamaguchi, *Theor. Chim. Acta,* **26**, 43 (1972); K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968)

[12] G. Klopman, *Chem. Phys. Letters*, **1**, 200 (1967); G. Klopman and R.F. Hudson, *Theor. Chim. Acta,* **8**, 165 (1967)

[13] K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); **22**, 1433 (1954)

[14] M. Nakahara, *This Journal* **44**, 57 (1974)

of pressure,

$$E^*{}_{HOMO}^{(P)}-E^*{}_{LUMO}^{(P)}=E^*{}_{HOMO}^{(1)}-E^*{}_{LUMO}^{(1)}+(\partial(E^*{}_{HOMO}-E^*{}_{LUMO})/\partial P)_{P=1,T}(P-1)+\cdots \quad (16)$$

Equation(16) could well be truncated by the term of the first order in $(P-1)$ if the operational pressure is low, and/or if the function of the local dielectric constant of the solvated molecules has a very small pressure dependence.*)

From Eqs. (14), (15), and (16), we obtain

$$\Delta G^{(P)}-\Delta G^{(1)}=\Delta V_{elect}{}^{(1)}(B+1)\ln[(B+P)/(B+1)]+\Delta V_{cov}{}^{(1)}(P-1), \qquad (17)$$

where $\Delta V_{cov}{}^{(1)}$ is the volume change at 1 atm for the structural change due to the formation of covalent bond and the desolvation change due to the partial electron transfer. It can be expressed as

$$\Delta V_{cov}{}^{(1)}\cong -\left[\frac{2(C_r^{HOMO}C_s^{LUMO}\beta)^2}{E^*{}_{HOMO}^{(1)}-E^*{}_{LUMO}^{(1)}}\right]\left(\frac{\partial(E^*{}_{HOMO}-E^*{}_{LUMO})}{\partial P}\right)_{P=1,T} \qquad (18)$$

If Eq. (17) can be expanded and applied to the transition states as such, the pressure dependence of the rate constant may be expressed as follows :

$$-RT\ln(k^{(P)}/k^{(1)})=\Delta V_{elect}{}^{\neq(1)}(B+1)\ln[(B+P)/(B+1)]+\Delta V_{cov}{}^{\neq(1)}(P-1). \qquad (19)$$

Thus the pressure dependence of the rate constant can be predicted qualitatively from the knowledges on the electronic properties of the isolated reactant molecules. When the difference between $E^*{}_{HOMO}$ and $E^*{}_{LUMO}$ is large, the pressure dependence of $\ln(k^{(P)}/k^{(1)})$ should show a curvature such as calculated from the Owen-Brinkley expression. On the other hand, when the frontier orbitals lie close, the contribution of the second term becomes appreciable. A formula starting from the Tait equation has never interpreted the linearity of the plot of $\ln(k^{(P)}/k^{(1)})$ against pressure, while such a tendency has been found so often for the reactions of neutral or weakly polarized species.

Several points may be raised against the present theoretical treatment; a) molecular structure deformations with the progress of reaction were precluded, b) overlap integrals were neglected between the interacting orbitals, c) the solvation model is extremely crude, d) the value of $\Delta V_{elect}{}^{\neq(1)}$ and $\Delta V_{cov}{}^{\neq(1)}$ cannot be calculated directly from the molecular orbitals of isolated reactants, and so on. In spite of these deficiencies, we believe that Eq. (19) can shed light on the physical meaning of the pressure dependence of rate constants.

From the viewpoint of practical use, the validity of Eq. (19) has been confirmed by usinng the experimental results of various types of reactions. Plots of the experimental values[15-18] for $[-RT/(P-1)]\ln(k^{(P)}/k^{(1)})$ against $[(B+1)/(P-1)]\ln[(B+P)/(B+1)]$ lie well on straight lines as shown in Fig. 4. The slope and intercept of the linearity are $\Delta V_{elect}{}^{\neq(1)}$ and $\Delta V_{cov}{}^{\neq(1)}$, respectively. It should be noted that these activation volumes at 1 atm can be correctly estimated even when the data are available

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*) $E_m{}^*=IP_m-q_s(C_r{}^m)^2F/\varepsilon-a^2[IP_m-EA_m+(C_r{}^m)^2(C_s{}^n)^2F(2/\varepsilon-1)]-\sum_r\frac{\chi_r(C_r{}^m)^2[q_r+2b^2\chi_r(C_r{}^m)^2]}{R_r}(1-1/\varepsilon)$

$E_n{}^*=IP_n-[q_r+2(C_r{}^m)^2](C_s{}^n)^2F/\varepsilon-b^2[IP_n-EA_n+(C_r{}^m)^2(C_s{}^n)^2F(2/\varepsilon-1)]-\sum_s\frac{\chi_s(C_s{}^n)^2[q_s-2b^2\chi_s(C_s{}^n)^2]}{R_s}(1-1/\varepsilon)$

Here, ε is the soluent parameter, and other various symbols have the shme meanings as in lit. 1).

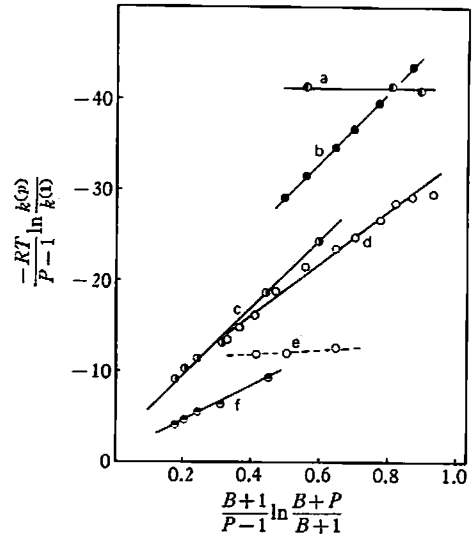

Fig. 4 Pressure dependence of the rate constants of various reactions

a) n-BuOCH=CH$_2$+TCNE in benzene[15]
b) n-BuOCH=CH$_2$+TCNE in acetone[15]
c) $C_6H_5N(CH_3)_2+CH_3I$ in methanol[16]
d) cyclopentadiene+dimethyl acetylenedicarboxylate in ethyl acetate[17]
e) $PhCH_2CN+MeO^-$ in methanol
f) $CH_3Br+MeO^-$ in methanol[18]

only at high pressure. After all, the pressure dependence of the rate constant has been expressed adequately by dividing the activation volume into two terms, $\Delta V_{elect}^{\neq}(1)$ and $\Delta V_{cov}^{\neq}(1)$, whose physical grounds could be clarified on a simple molecular-orbital interaction model. Starting from Born's solvation model, a similar expression was derived for the pressure dependence of the ionization constant[3,14]. It has been reported that both the electrostrictive volume change and other volume changes (crystal volume, void volume, *etc.*) play important roles in the pressure effect on the ionization in methanol.

Activation volumes of iminoether formation and deuterium elimination

Activation volumes have been evaluated by applying Eq. (19) to the reactions of phenylacetonitrile in methanol. The results are summarized in Table 4. The covalent volume change plays an important role in the case of the nucleophilic attack (k_2) to the C≡N triple bond as expected. Both

Table 4 Activation volumes of iminoether formation and deuterium-hydrogen exchange at 1 atm

T/K	B/kg cm^{-2}	$\Delta V^{\neq}_{cov}(2)$*	$\Delta V^{\neq}_{elect}(2)$*	$\Delta V^{\neq}_{cov}(-2)+\Delta V_{cov}(-3)$	$\Delta V^{\neq}_{elect}(-2)+\Delta V_{elect}(-3)$	$\Delta V^{\neq}_{cov}(D)$	$\Delta V^{\neq}_{elect}(D)$
323.2	750	−10.1	−3.0	+4.1	−2.2		
318.2	780	−10.9	−2.4	+3.6	−2.0		
313.2	817	−10.2	−1.0	+4.1	0		
303.2	853					~+4	~+20

* ΔV/cm^3 mol^{-1}

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15) F.K. Fleischmann and H. Kelm, *Tetrahedron Lett.*, **39**, 3773 (1973)
16) S.D. Hamann and D.R. Teplitzky, *Disc. Faraday Soc.*, **22**, 114 (1956)
17) R.A. Grieger and C.A. Eckert, *J. Am. Chem. Soc.*, **92**, 7149 (1970)
18) H.G. David and S.D. Hamann, *Trans. Faraday Soc.*, **50**, 1188 (1954)

$\Delta V_{elect}^{\neq(1)}$ and $\Delta V_{cov}^{\neq(1)}$ for step (2) are negative, and the magnitude of $\Delta V_{elect}^{\neq(1)}$ seems to indicate the fairly localized transition states. For the reverse process ($k_{-2}K_3^{-1}$) of iminoether formation, the covalent term is found to be positive, while the electrostatic term, negative. Since k_{-2} represents the rate constant for the bond cleavage of ion, both $\Delta V_{cov}^{\neq(1)}(-2)$and $\Delta V_{elect}^{\neq(1)}(-2)$would be positive. If $PhCH_2C(=N^-)OMe$ is assumed to have the most negative electrostrictive volume among those species in the course of the iminoether formation, the negative $\Delta V_{elect}^{\neq(1)}(-2)+\Delta V_{elect}^{(1)}(-3)$ can be understood; that is, the negative $\Delta V_{elect}^{\neq(1)}(-2)+\Delta V_{elect}^{(1)}(-3)$ comes mainly from the negative $\Delta V_{elect}^{(1)}(-3)$ term. Judging from the relative correlation of activation volumes, the transition state would be product-like, and the penetration of the van der Waals volumes between two reactants contribute largely to the volume contraction at the transition state for the iminoether formation.

Both $\Delta V_{cov}^{\neq(1)}(D)$ and $\Delta V_{elect}^{\neq(1)}(D)$ were positive for the deuterium-hydrogen exchange reaction. Since the large positive value of $\Delta V_{elect}^{\neq(1)}(D)$ reflects an extensive delocarization of the minus charge, the transition state of the deuterium-hydrogen exchange reaction is considered to be like a carbanion in which the α-carbon is nearly in the sp^2 structure. As $\Delta V_{cov}^{\neq(1)}$ in Eq. (19) involves not only the structural volume change of reactants but also the desolvation term produced by the electron transfer, it is dangerous to explain $\Delta V_{cov}^{\neq(1)}$ only in terms of the structural volume change. A small $\Delta V_{cov}^{\neq(1)}(D)$ value seems to indicate that a small amount of penetration of the van der Waals volume competes with the void volume change. The arguments delineated above can be represented diagrammatically by the volume profile as shown in Fig. 5. The enthalpy and entropy of activation for the iminoether formation were determined to be $\Delta H^{\neq}\sim 12$kcal/mol and $\Delta S^{\neq}\sim -5$e.u. The activation free energy of the deuterium elimination reaction was not determined, but it would be small compared with the value of $\Delta G_2^{\neq}$.

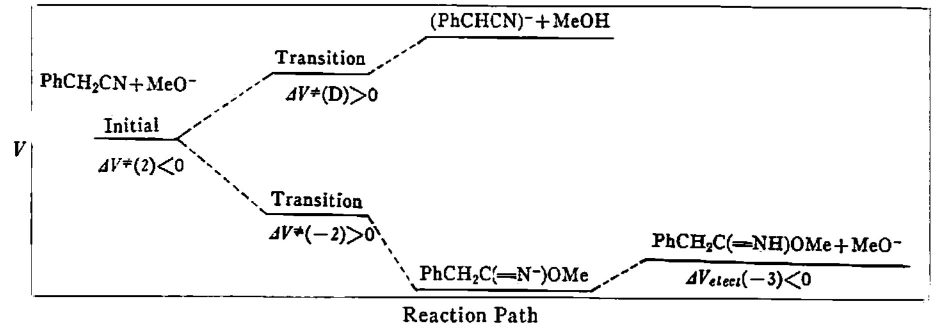

Fig. 5 Volume profile of the nucleophilic attack of methoxide ion to phenylacetonitrile

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