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Chemical Reactions in the Medium Density Fluid. Anomaly in the Volume Profile of the Dimerization Reaction of 2-Methyl-2-nitrosopropane in Carbon Dioxide

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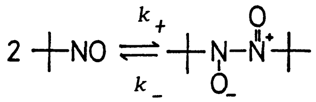
Pressure effects on the dimerization-dissociation reaction of 2-methyl-2-nitrosopropane in carbon dioxide were studied in the wide range of density. The volume profile of the reaction exhibited a remarkable difference between in the high and the medium density regions.

Most liquids commonly used for the study of chemical reactions can be considered as high density fluids and their structures are determined mainly by the repulsive forces between molecules.[1] In the medium density fluid, however, the attractive forces between molecules come to play an important role in determining the structure of the fluid. In such a fluid the thermodynamic behavior of solute is expected to be quite different from that in the high density fluid. In fact, it is known that the partial molal volume of solute has a large negative value in the medium density fluid.[2,3] We intend to clarify how the fluid structure which is dominated mainly by the attractive interactions between molecules influences chemical reactions, especially their volume changes, because the volume information reflects directly the correlation between molecules.[4] In the present work we have examined pressure effects on the equilibrium and the rate constants of the dimerization-dissociation reaction of C-nitroso compound in carbon dioxide.

The reaction scheme of the dimerization-dissociation reaction of 2-methyl-2-nitrosopropane (MNP) is given as follows:[5,6]



$$K = k_+/k_-, \qquad (1)$$

where K, k_+, and k_- denote the equilibrium constant, the rate constant of the dimerization, and that of the dissociation, respectively.

Dimeric MNP was prepared according to Stowell,[7] and purified by sublimation. Carbon dioxide (Nippon Tansan, 99.9%) was used without further purification. A schematic diagram of the apparatus is illustrated in Fig. 1. Before measurement carbon dioxide in the reservoir was directly introduced into the optical cell which was made of stainless steel (SUS 316). The reaction mixture was stirred by the magnetic stirrer in the optical cell. Pressure was measured by a strain gage

(Toyo Baldwin). The temperature was controlled by circulating water thermostated within ±0.05 °C and monitored by a thermocouple in the reaction cell. The density of carbon dioxide was calculated by an empirical equation of state.[8] Optical measurements were carried out at 25 °C. At this temperature, the density increases rapidly with an increase in pressure up to about 200 bar and then rather slowly. The density of carbon dioxide reduced by the critical density is about 2.0 at 200 bar, which is smaller than that of usual solvents (about 3.0). In this case the van der Waals picture will no longer be valid, and we need a new picture for carbon dioxide under 200 bar which is called here the medium density fluid.

MNP has absorptions around 291 nm mainly due to the dimer and around 673 nm due to the monomer. Kinetic measurements are made by observing the variation of the absorbance for the dimer with time. It obeyed the first-order rate law under the present conditions:[6,9]

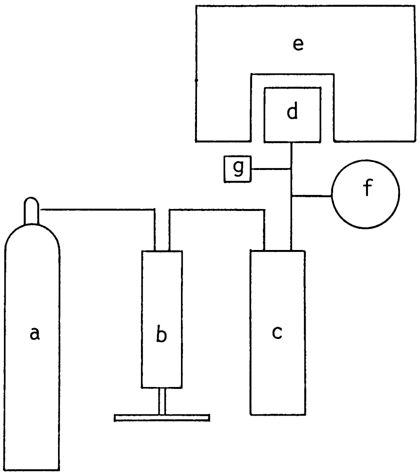


Fig. 1. Schematic diagram of the apparatus. a, Bomb; b, pump; c, pressure reservoir; d, optical cell; e, spectrophotometer; f, Heise bourdon tube gage; g, strain gage.

$$\frac{dA_{291}}{dt} = -k_{obsd}(A_{291} - A^{\infty}_{291}), \qquad (2)$$

where A, A^{∞} and k_{obsd} denote the absorbance, the absorbance in equilibrium and the apparent rate constant, respectively. The subscript for A denotes the wavelength. The apparent rate constant is expressed as follows:[9]

$$k_{obsd} = k_{-} + 4k_{+}[M]_e, \qquad (3)$$

where $[M]_e$ denotes the monomer concentration in equilibrium. The apparent rate constants are regarded as those for the dissociation, because they are found to be independent of the initial concentration of MNP. The logarithm of the rate constant k_{-} is plotted against the pressure in Fig. 2. The logarithm of the rate constant is not a linear function of pressure. Up to about 200 bar, it decreases rapidly with an increase in pressure and then decreases rather slowly. In the medium density region the activation volume of the dissociation, which is estimated from the slope of this plot, is very large (about +60 cm^3 mol^{-1}), whereas in the high density region it amounts only to +9 cm^3 mol^{-1}.

In the equilibrium state the following equation holds:

$$(\varepsilon^{D}_{291}/\varepsilon^{M\,2}_{673})K/\ell = (A_{291}/A_{673} - \varepsilon^{M}_{291}/\varepsilon^{M}_{673})/A_{673}, \qquad (4)$$

where ε and ℓ denote the molal extinction coefficient and the path length, respectively. The superscript M denotes the monomer, D the dimer. The band maximum and its shape of each spectrum do not change with an increase in the solvent density in our study. Since $\varepsilon^{M}_{291}/\varepsilon^{M}_{673}$ is negligibly small,[10] the pressure dependence of the equilibrium constant can be evaluated by that of

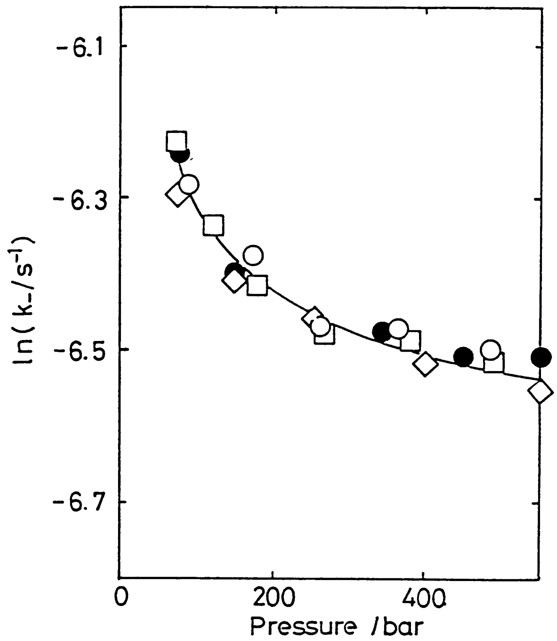


Fig. 2. Pressure dependence of the dissociation rate constant of the MNP dimer in CO_2 at 25 °C. The total concentration of MNP ([M]+2[D]): ◇, 1.58×10^{-2} M; ○, 2.33×10^{-2} M; □, 3.14×10^{-2} M; ●, 3.18×10^{-2} M. (1 bar = 10^5 Pa, 1 M = 1 mol dm^{-3})

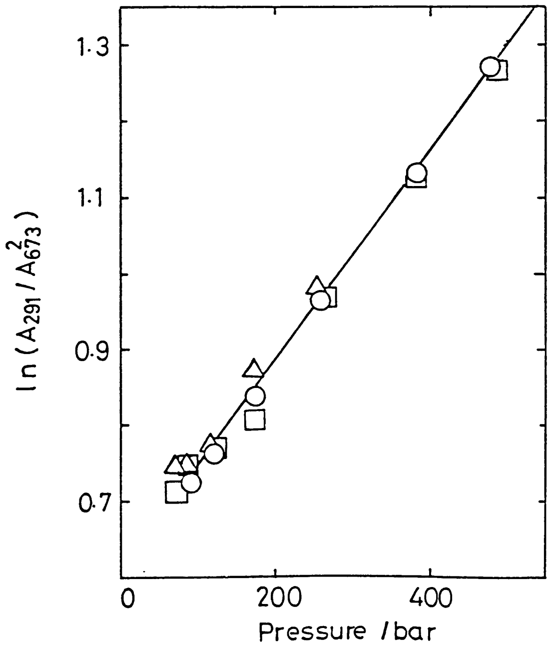


Fig. 3. Pressure dependence of the equilibrium constant of the dimerization-dissociation reaction of MNP in CO_2 at 25 °C. The total concentration of MNP: ○, 2.33×10^{-2} M; △, 2.63×10^{-2} M; □, 3.14×10^{-2} M.

A_{291}/A_{673}^2. The logarithm of A_{291}/A_{673}^2 is plotted against the pressure in Fig. 3. Though the pressure dependence of the solvent density is quite different between in the high and the medium density regions, the logarithm of the equilibrium constant is linear with respect to pressure. In the reaction system studied here, the configurational volume change for the dimerization,[11)] which is obtained from the slope of this plot as about -33 cm^3 mol^{-1}, is constant in the whole density region in contrast to the activation volume.

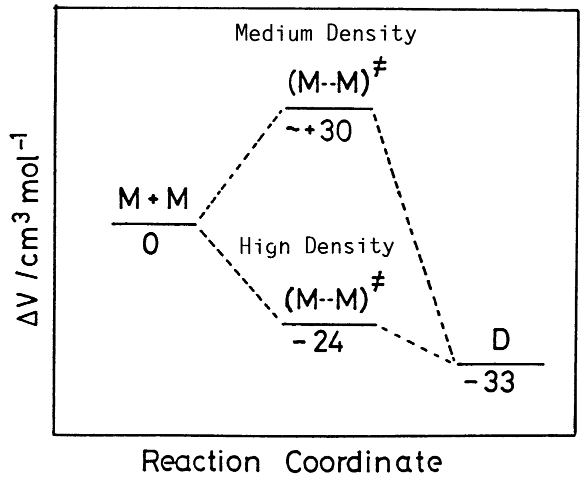


Fig. 4. Configurational volume profile of the dimerization reaction of MNP in CO_2 at 25 °C. The configurational volume change of the reaction is independent of the density of the solvent.

We can summarize these results in the profile of the configurational volume change during the dimerization as in Fig. 4. In the high density region the behavior of the volume change resembles that in carbon tetrachloride,[12)] which is interpreted on the basis of the van der Waals picture of liquid. In the medium density region, however, its behavior cannot be explained by the repulsive forces between molecules. As long as we believe in the transition state theory, the volume increase accompanied by the activation process is to be explained in terms of the desolvation due to the overlapping of the solvation shells of the monomers. On the other hand such effect was not observed in the configurational volume change for the dimerization; see Fig. 4. A theoretical treatment of this anomalous behavior of the volume profile will appear in the near future.

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9) According to Eq. 1, the time dependence of A_{291} is expressed as follows:

$$-\frac{dA_{291}}{dt} = \{k_-[1 + \frac{4K(A_{291} - A_{291}^{\infty})}{(\varepsilon_{291}^{D} - 2\varepsilon_{291}^{M})\ell}] + 4k_+[M]_e\}\times(A_{291} - A_{291}^{\infty}).$$

When $4K(A_{291} - A_{291}^{\infty})/(\varepsilon_{291}^{D} - 2\varepsilon_{291}^{M})\ell << 1$, the above equation is equivalent to Eqs. 2 and 3.
10) The value of $\varepsilon_{291}^{M}/\varepsilon_{673}^{M}$ is only 0.14 in carbon tetrachloride.[12)]
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