

Dynamic Solvent Effects in the Degenerate Isomerization of a Hexafluoroacetone Anil Studied by High-Pressure ^{19}F NMR

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The rate of the degenerate isomerization of *N*-hexafluoroisopropylidene-*N,N'*-dimethyl-*p*-phenylenediamine was measured by high-pressure ^{19}F NMR spectroscopy in a viscous hydrocarbon, 2,4-dicyclohexyl-2-methylpentane. Pressure-induced retardations that cannot be rationalized within the framework of the transition state theory (TST) were observed, and it was concluded that the reaction was cast into the TST-invalid nonequilibrium conditions by high pressure.

Key words: High-pressure ^{19}F NMR; High-pressure Kinetics; Hexafluoroacetone Anil; Degenerate Isomerization; Dynamic Solvent Effect.

Introduction

In our previous studies [1 - 3], dynamic solvent effects were studied in the *Z/E* isomerization of substituted azobenzenes and benzaldehyde anils in their electronic ground state by a combination of high pressure and viscous liquids. The activation energy of the isomerization was as high as 70 kJ mol^{-1} , and the half life was as long as one second. In such slow unimolecular solution reactions it is almost certain that the reaction is in the equilibrium region [4] where the transition state theory (TST) can be applied at least approximately. To the best of our knowledge, TST seems to hold in relatively slow thermal unimolecular reactions even at high pressures of several hundred megapascals [5 - 7]. Namely, most of the pressure effects could be rationalized on the basis of the partial molar volume change of the reactant during the activation step [8, 9]. In some cases [10 - 13], the authors tried to rationalize their observations on the basis of a stochastic model. However, the experimental evidence for their rationalizations is not well-founded, we believe (*vide infra*) [14] because our results [1 - 3] clearly indicated that dynamic solvent effects appear only at highly viscous conditions [viscosity $\eta > 10 \text{ Pa s}$ ($1 \text{ Pa s} = 1000 \text{ cP}$)]. Although nobody had tried to exploit possibilities of kinetic studies at such high viscosities,

our results demonstrated that the experiments give new insights into the mechanism of solution reactions. One of the discoveries was a tendency of the isoviscosity activation energy to decrease with increasing viscosity in the TST-invalid region. This tendency can hardly be rationalized without assuming mutually independent chemical and solvent coordinates as in a model proposed by Berezhkovskii and Zitserman [15], or by Sumi and Marcus [16, 17]. In these models, it was assumed that the characteristic time scales for the chemical and the medium coordinate can be different, and reorganization of the solvation shell precedes the energy barrier crossing. In order to examine the versatility of such a model, it is highly desirable to extend the measurement to other reaction systems. As a part of our efforts in this direction, we decided to study dynamic solvent effects in the degenerate isomerization of *N*-hexafluoroisopropylidene-*N,N'*-dimethyl-*p*-phenylenediamine, hexafluoroacetone anil **1**, by ^{19}F NMR spectroscopy in 2,4-dicyclohexyl-2-methylpentane (DCMP). The reaction was selected because the effect of pressure had been studied by Asano and his co-workers [18] in acetonitrile- d_3 , and the reaction mechanism had been established. The isomerization proceeds *via* the nitrogen inversion, transition state **2**, with little change in the polarity during the activation. Another reason for the

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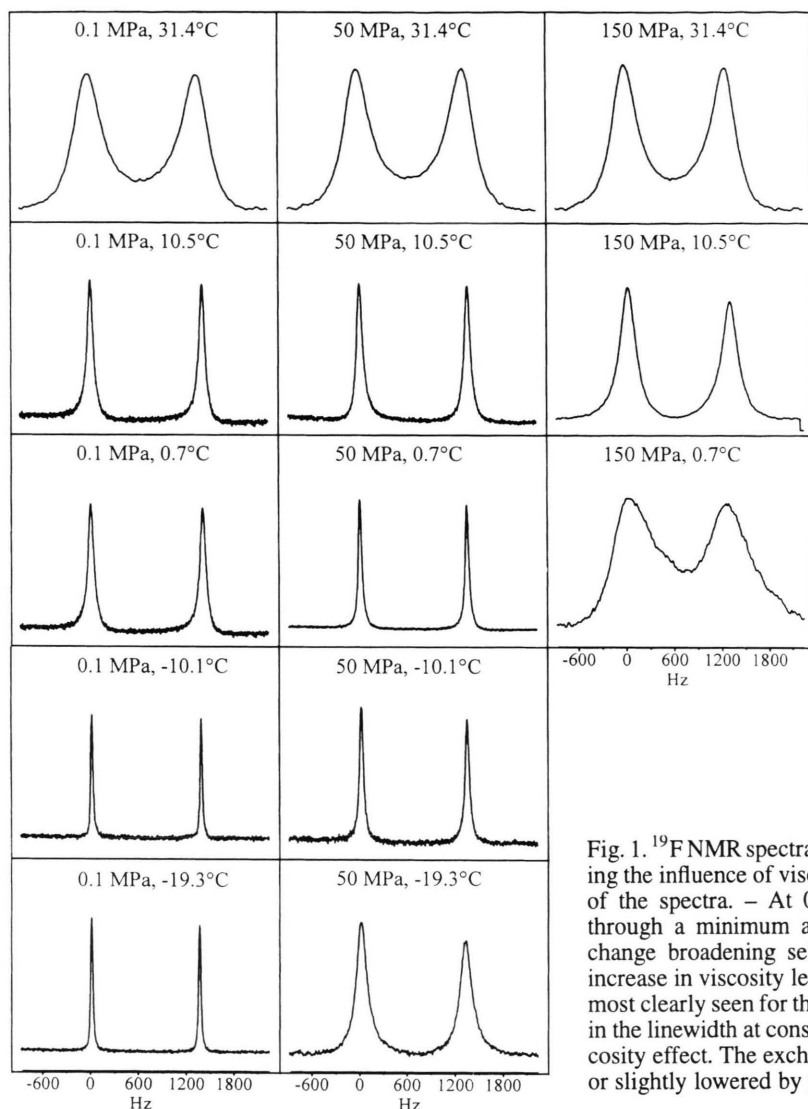


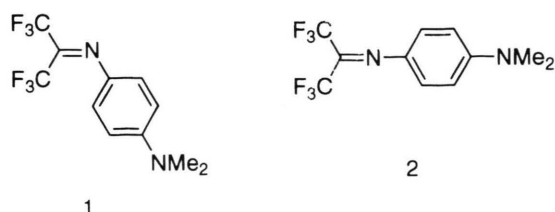
Fig. 1. ^{19}F NMR spectra of the hexafluoroacetone moiety, showing the influence of viscosity and exchange rate upon the shape of the spectra. – At 0.1 and 50 MPa, the linewidth passes through a minimum at -10°C . At higher temperatures exchange broadening sets in, while at lower temperatures the increase in viscosity leads to a larger natural linewidth. This is most clearly seen for the 50 MPa series. Obviously the increase in the linewidth at constant temperature is solely due to the viscosity effect. The exchange rate is either pressure independent or slightly lowered by pressure at low pressures (see text.).

selection of a degenerate isomerization was to explore the possibility to use NMR spectroscopy in the study of dynamic solvent effects.

Experimental

Material: The anil **1** was prepared as described previously [18]. DCMP was a product of Japan Energy Corporation with a purity of 98.65% (GLC) and was used without further purification.

NMR Measurements: Fluorine-19 NMR spectra were recorded with a Bruker MSL 300 spectrometer at 282.343 MHz with $15\ \mu\text{s}$ 90° rf pulses, acquisition time 5 s. DCMP solution which contains 3.2 w/w%



of the anil **1** and 1.8 w/w% of ethyl trifluoroacetate was filled into a homebuilt Yamada-type high pressure glass probe [19] with 0.8 mm i.d. and 7 mm o.d.. The details of the probe design and the operation procedures are given in [20]. Before filling the samples into the glass capillaries, they were degassed

by five freeze-pump-thaw cycles. The probehead was connected to a hand-operated high-pressure pump, and the pressure was determined by a "Heise" Bourdon tube gauge (Dresser Industries, Conn. U.S.A.) to ± 1 MPa. The temperature was determined by a thermocouple to ± 0.5 K.

Results and Discussion

Figure 1 shows a set of ^{19}F NMR spectra of **1** obtained at various temperatures and pressures. The spectra were similar to those reported in [18]. Because of the high viscosity of the solvent [3], the spin-spin relaxation time T_2 is shorter and the quartet structure is not resolved at low temperatures. Spectral simulations were performed by means of the DNMR5 program by assuming that the frequency difference between the two trifluoromethyl groups is linearly correlated to the temperature at a constant pressure and the line width at half height in the absence of exchange is proportional to the one of ethyl trifluoroacetate. The rate constants k_{obs} listed in Table 1 were obtained by visual comparison of the observed and the simulated spectra. The errors in k_{obs} are estimated to be 10 - 25%. The values were in reasonable agreement with the ones in acetonitrile- d_3 (150 s^{-1} at -1.2°C and 900 s^{-1} at 31.6°C) [18]. The Arrhenius plots were satisfactorily linear both at 0.1 and 50 MPa in the temperature ranges listed. The activation energies were 56 and 54 kJ mol^{-1} , respectively. These values were *ca.* 10 kJ mol^{-1} larger than that in acetonitrile- d_3 . At the present level of our knowledge, however, it is not possible to make any detailed analysis of this difference.

As can be seen clearly from Figs. 2 and 3, the pressure/viscosity effects were small at lower pressures/

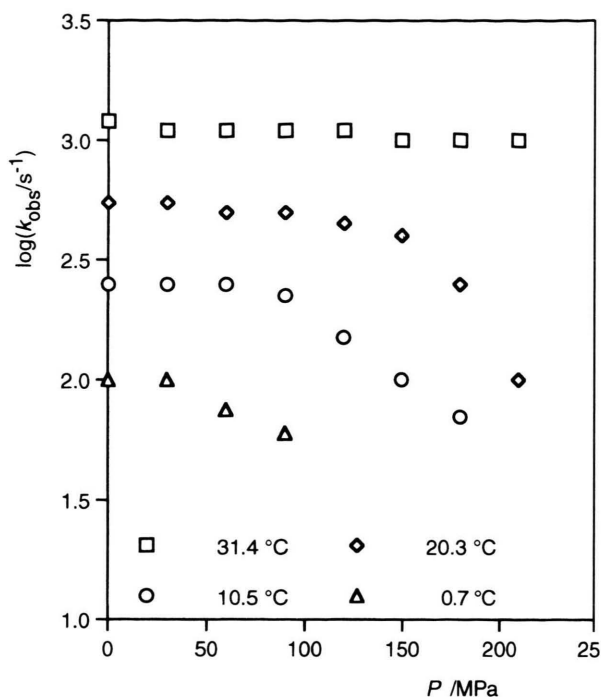


Fig. 2. Pressure dependence of the observed rate constant ($k_{\text{obs}}/\text{s}^{-1}$) in the isomerization of hexafluoroacetone anil **1** in DCMP.

viscosities. These results suggest strongly that the reaction is in the equilibrium region even in DCMP and the analysis based on TST will be valid. The activation volume $\Delta V_{\text{obs}}^\ddagger$ estimated by (1) and (2), where a and b are pressure independent parameters, were in the range of 0 and $2 \text{ cm}^3 \text{ mol}^{-1}$ in accordance with the inversion mechanism.

$$\ln k_{\text{obs}} = a + bP, \quad (1)$$

$$\Delta V_{\text{obs}}^\ddagger = -bRT. \quad (2)$$

At higher pressures/viscosities, however, relatively strong pressure-induced retardations were observed. This retardation appeared at higher pressures when the temperature was raised, and it was not observed in the pressure range studied at 30°C . An increase in pressure cannot induce a mechanistic change from the one with $\Delta V_{\text{obs}}^\ddagger \approx 0$ to a new mechanism with a large positive $\Delta V_{\text{obs}}^\ddagger$ because the latter becomes slower more rapidly than the former. Therefore, these pressure-induced retardations can hardly be rationalized without assuming an intervention of dynamic solvent effects at

Table 1. Rate Constants ($k_{\text{obs}}/\text{s}^{-1}$) for Fluorine Site Exchange in **1** in DCMP at Various Temperatures and Pressures.

P/MPa	$-T/^\circ\text{C}-$			
	0.7	10.5	20.3	31.4
0.1	100	250	550	1200
50	100	250	550	1100
100	75	250	500	1100
125	60	225	500	1100
150		150	450	1100
175		100	400	1000
200		70	250	1000
225			100	1000

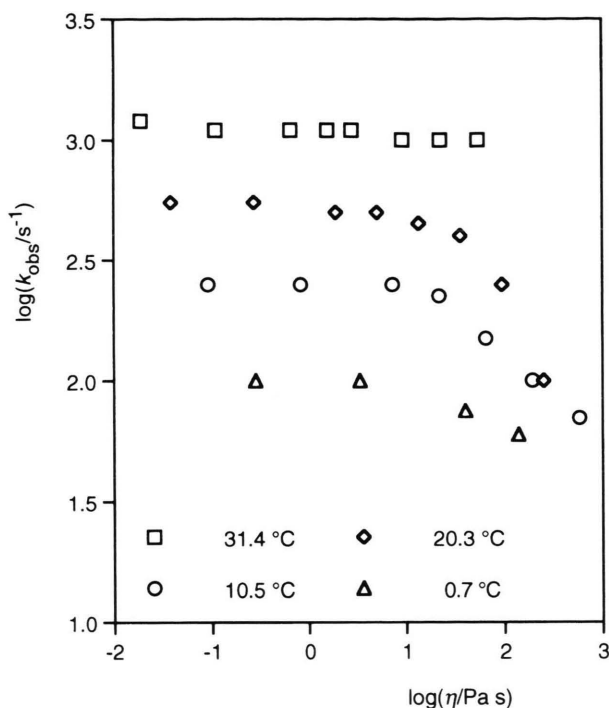


Fig. 3. Viscosity dependence of the observed rate constant ($k_{\text{obs}}/\text{s}^{-1}$) in the isomerization of hexafluoroacetone anil **1** in DCMP.

high pressures. The *Z/E*-type structural change must have been cast into the nonequilibrium (TST-invalid) region because of the high viscosity of the medium. As can be seen from Fig. 3, this shift to the nonequilibrium region seems to take place somewhere between 1 and 100 Pa s. In a pioneering work by Jonas and his co-workers [10, 11], pressure effects on the inversion of cyclohexane were studied by ^1H NMR in four different solvents. They tried to rationalize the results on the basis of a one-dimensional stochastic model. On the assumption that the partial molar volume change during the activation, i.e. $\Delta V_{\text{TST}}^\ddagger$, is $-1.5 \text{ cm}^3 \text{ mol}^{-1}$ and pressure independent, they calculated “the normalized transmission coefficient”

$$\frac{\kappa(\eta)}{\kappa(\eta_0)} = \frac{k(\eta)}{k(\eta_0)} \exp \left[\frac{(P - P_0)\Delta V_{\text{TST}}^\ddagger}{RT} \right], \quad (3)$$

where η_0 is the reference viscosity. The plot of $\kappa(\eta)/\kappa(\eta_0)$ against η reached a maximum at *ca.* 0.0025 Pa s and started decreasing with increasing η . This behavior was interpreted as an observation of a Kramers' turnover [21]. In another publication by the same group [12], the pressure-induced retardation of rotation of the dimethylamino group in *N,N*-dimethyltrichloroacetamide in pentane and methylcyclohexane at 9 °C were described as due to the viscosity dependence of the transmission coefficient. However, the solvent viscosities at 0.1 MPa were 3.5 and 8.8×10^{-4} Pa s for pentane and methylcyclohexane, respectively. Considering our previous [1 - 3] and the present results, it is difficult to believe that solvent thermal fluctuations are slow enough to cast the isomerization with a rate constant $k < 100 \text{ s}^{-1}$ to the nonequilibrium region. The inevitable conclusion from these considerations is that the experimental evidence for their claim of observation of dynamic solvent effects is, at least, fragile, and we would rather consider that the results presented here are the first unequivocal example of observation of dynamic solvent effects by NMR spectroscopy.

Since the present reaction is closely related to the *Z/E* isomerization of the benzaldehyde anils studied previously, it would be reasonable to assume that the results can be analyzed on the basis of a two-dimensional reaction coordinate model which treats the medium and the chemical coordinates separately. Unfortunately, however, further detailed analysis was not possible in the present case because the *T*, *P* ranges in which the simulations yield sufficiently precise k_{obs} were rather limited and the line broadening caused by high viscosities inevitably caused larger uncertainties in the estimation of the exchange rate. For further analysis, information on the viscosity dependence of T_2 is essential.

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