High-Pressure Study of the Viscosity Effect on the Ground-State Isomerization of 3,3'-Diethyloxadicarbocyanine Iodide (DODCI)

Kimihiko Hara* and Seiji Akimoto

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606, Japan
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The viscosity dependence on the ground-state isomerization of DODCI was studied as a model of one-dimensional barrier crossing by using a technique of high-pressure laser photolysis. The Kramers equation does not fit the data over the whole viscosity range examined. We show how our results are reproduced by the Grote and Hynes theory where frequency-dependent friction is considered for describing the influence of solvent friction. Solvent viscosity contributions to the apparent activation energy and apparent activation volume are discussed. The intrinsic activation energy of isomerization is 13.0 kcal/mol. The apparent activation volume can be explained exclusively by the volume change due to viscous flow. The intrinsic activation volume is found to be less than 1.0 cm³/mol.

Introduction

Recently there have been considerable experimental[1-7] and theoretical[8-10] studies on the dynamics of isomerization processes in solution where large-amplitude motion of a bulky aromatic group twisting around a molecular axis is involved. The rates of these processes, therefore, should substantially depend on the frictional force exerted by solvent molecules. Kramers' theory[11] is the best known and most widely used approach to this problem. The viscosity dependences on the formation rate of intramolecular excimer state in 1,3-di-1-pyrenylpropane (DPP)[12,13] and 1,3-di-2-naphthylpropane (DNP)[14] have been studied by using high-pressure techniques, and it was found that it was well expressed by the Kramers model of the intermediate friction regime. 1,1'-Binaphthyl is another case in which the applicability of this theory has been fully examined.[15]

A deviation from the Kramers expression, however, has been reported for various systems.[1,4,16] In this relation, various efforts have been made by various authors to understand the non-Kramers behavior. The representative approaches are those of (i) the frequency-dependent friction,[8] (ii) the extended Kramers equation introducing other parameters,[17] (iii) the breakdown of hydrodynamic friction law,[18] (iv) the breakdown of one-dimensionality,[10,19,20] and (v) the change of intrinsic activation energy with various solvents.[7]

The photoisomerization of the cyanine dye DODCI (3,3'-diethyloxadicarbocyanine iodide) has been extensively studied by

absorption and emission spectroscopy.[1,4,21,22] When excited to the S_1 state, it relaxes to the ground-state photoisomer (I form) with a yield of ca. 10%. There is experimental evidence from rotational diffusion measurements that the DODCI molecule in the ground state is normally in a coiled-up cis–cis conformation (N form), whereas the isomer (I form) molecule is in an elongated all-trans conformation.[22] The schematic potential energy diagram and both proposed molecular conformations are shown in Figure 1.

The high-pressure technique serves as an excellent method for the present purpose, since it is possible to achieve a continuous variation of solvent viscosity in a significant range without changing the potential property within the present pressure range. In the method of variation of the composition or the temperature of solvents, which is usually carried out for studying viscosity-dependent processes, the problem always arises of separating the viscosity dependence from purely temperature and/or solvent effects other than solvent friction.

In this paper we present the results of a high-pressure study of the ground-state isomerization rate for DODCI in a series of alcoholic solvents. The rates of ground-state isomerization from the I form to the N form were measured by means of a laser photolysis at high pressures up to 500 MPa.

Experimental Section

The laser grade dye DODCI (Kodak) was used without further purification. All experiments were performed in 10^{-5} M solution, low enough to ensure that dimerization was negligible.[23]

A technique of high-pressure laser photolysis was used to measure the ground-state isomerization rate at high pressures. For the excitation light source, a dye laser pumped by a flash lamp (UNISOKU LA-501) was used. The dye solution rhodamine 6G (Kodak) in methanol was employed as the excitation at 590 nm.

In this work the absorbance decay of the I form was probed with a pulsed xenon flash lamp at 630 nm. A transient memory (Graphtec TMR-80) was used to digitize the signal (50 ns/point,

TABLE I: Solvent Viscosity (η_s), Observed Rate Constant (k_{obs}) at 303 K, and Observed Activation Energy (E_{obs}) at 1 bar

solvt	η_s, cP	k_{obs}, s⁻¹	E_{obs}, kcal/mol
MeOH	0.51	720	14.4
EtOH	1.00	631	14.0
			14.1 (200 MPa)
			14.2 (500 MPa)
n-PrOH	1.72	520	14.1
n-BuOH	2.28	477	14.0

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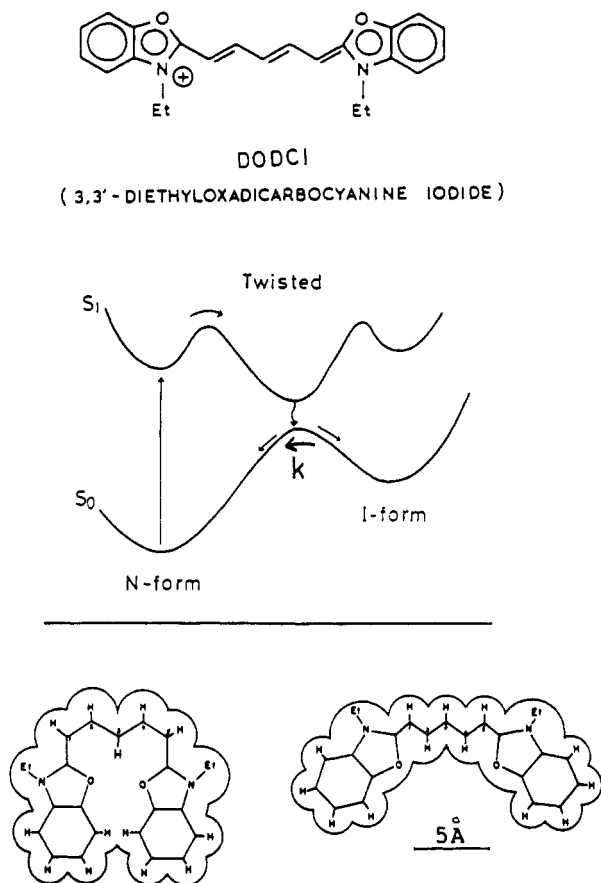(23) Sheppard, S. E.; Geddes, A. L. *J. Am. Chem. Soc.* **1944**, *66*, 2003.

DODCl

(3,3' - DIETHYLOXADICARBOCYANINE IODIDE)

Figure 1. Schematic potential diagram for DODCl photolysis and molecular drawings of N form (*all-trans*-DODCl) and I form (*cis,cis*-DODCl).

4096 points), and data were transfered to an NEC PC-9801VM computer for analysis.

The high-pressure optical apparatus and the experimental procedure have been previously described.[24]

Results

Rate Constant and Activation Energy at Atmospheric Pressure. The observed rate constant of isomerization is obtained from the measured lifetime (τ) by

$$k_{obs} = 1/\tau = F(\eta) \exp(-E_a/RT) \tag{1}$$

where E_a is the activation energy.

The values of k_{obs} at atmospheric pressure in various alcohols at 303 K and E_a obtained from the temperature dependence of k_{obs} are listed in Table I together with the solvent shear viscosity (η_s). These values are in agreement with those reported by Velsko et al.,[4] if the difference in the temperature is taken into account. Here, it should be noted that (i) k_{obs} is closely correlated with η_s and (ii) E_a is almost constant irrespective of the different characteristics of solvents. Namely, k_{obs} is independent of the polarity property of solvents.

Further, we measured the pressure dependence of E_a in EtOH solvent. As is also given in Table I, the resultant value of E_a is 14.0–14.2 kcal/mol. Thus, we can conclude that E_a is independent of pressure, just as it was independent of solvent polarity. Therefore, this supports the notion that the only relevant controlling factor is viscosity rather than other solvent properties. The analogous results observed for triphenylmethane dyes also support this idea.[25]

Effect of Pressure. Since the pressure dependence of the viscosity of the solvents is given by the literature,[26] the rate constant

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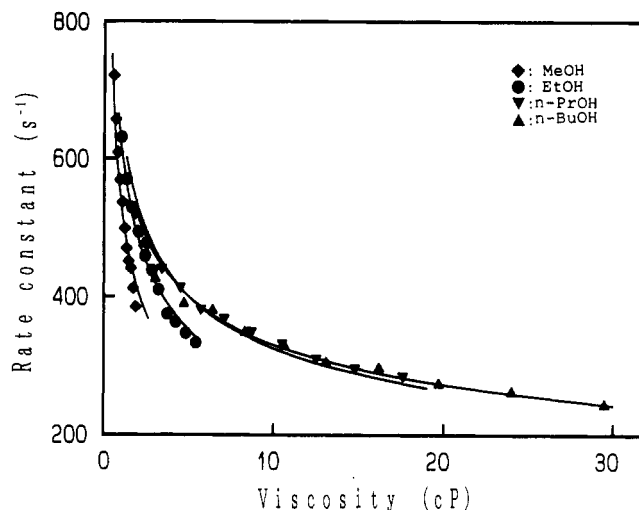(25) Brey, L. A.; Schuster, G. B.; Drickamer, H. G. *J. Chem. Phys.* **1977**, *67*, 2648.

Figure 2. Rate constant vs solvent viscosity in alcohols at 303 K. The solid lines represent the best fit of the Grote–Hynes equation, eq 5.
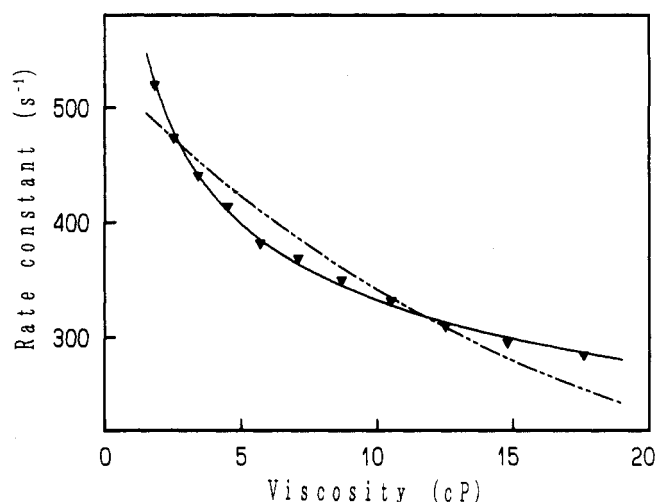

Figure 3. Rate constant against solvent viscosity in n-PrOH at 303 K. The solid line and dashed line represent the best fits to eqs 4 and 3, respectively.

was plotted against η_s, which is shown in Figure 2. The results clearly show a different viscosity dependence among different alcohols. The leveling-off behavior in the higher viscosity region becomes prominent with the order of MeOH < EtOH < n-PrOH < n-BuOH.

In such an isomerization process, which is independent of solvent polarity, the intrinsic volume change of activation (ΔV^*_i), defined by the pressure dependence of the rate constant due to transition-state theory, is expected to be quite small. So that the viscosity dependence of k_{obs} shown in Figure 3 can be mostly assigned to the viscosity dependence of preexponential term in eq 1.

This fact could also be demonstrated by an "iso-friction" plot, which measures the rate in some solvents at the same friction but at different pressures, if such plots were possible. It was found, however, that the intrinsic volume of activation obtained from the tentative "iso-viscosity" plots in this manner is small, that is, less than 1.0 cm³/mol.

Discussion

Kramers Theory and Frequency-Dependent Friction. The rate constant of chemical reaction in solution can be written by

$$k = \kappa k_{TST} \tag{2}$$

where k_{TST} is the rate constant defined by the transition-state theory. The influence of solvent frictional force on k is treated

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TABLE II: Calculated and Experimental α Parameters

solvt	$\alpha_{calc}{}^a$	α_{exp}
MeOH	0.42	0.48
EtOH	0.35	0.38
n-PrOH	0.30	0.26
n-BuOH	0.28	0.25

^{a}where $\omega_b = 8.0 \times 10^{12}$ s^{-1}.

as the viscosity dependence of the transmission coefficient (κ).

Therefore, the establishment of the explicit formalization for the viscosity dependence of $\kappa(\eta)$ is an essential problem. On this account, the Kramers theory of intermediate friction regime[11] provides a basic idea of the viscosity dependence to be examined at the outset. The Kramers transmission coefficient (κ_{KR}), which is obtained by solving the ordinary Langevin equation, assuming a model of the reactive motion as the passage of a solute particle over a one-dimensional potential barrier, is expressed by the following equation:

$$\kappa_{KR} = [1 + (\zeta/2\omega_b)^2]^{1/2} - \{\zeta/2\omega_b\} \qquad (3)$$

where ζ is the friction coefficient and ω_b denotes the barrier top frequency. To experimentally test the Kramers' equation, a linear dependence of friction on viscosity was supposed.

The dashed line in Figure 3 shows an example of the best fit to the Kramers equation for the case of n-PrOH. It is concluded that the hydrodynamic Kramers equation does not have the correct shape to fit our data. This is also the case for all other solvents examined although they are not shown.

On the other hand, all the results can be empirically fit to the following form:

$$\kappa(\eta) = A\eta^{-\alpha} \qquad (4)$$

where A and α are parameters. The solid line in Figure 3 represents the representative of least-squares fit to eq 4 with $\alpha = 0.26$. The resultant values of α for all the solvents examined are listed as α_{exp} in Table II. This power dependence on viscosity with $\alpha < 1$ has been observed previously for various types of molecules.[25,27,28] We found, however, that the present system has much smaller α values as compared with those of the intramolecular excimer formation for DPP ($\alpha = 0.74$)[12] and for some other TPM dyes in which an $\eta^{-2/3}$ relationship has been applied.[27]

To account for this non-Kramers behavior, we tried to apply an approach originally proposed by Grote and Hynes,[8] in which the generalized Langevin equation was exploited for the barrier crossing problem. The resultant Grote–Hynes transmission coefficient (κ_{GH}) can be ultimately written by

$$\kappa_{GH} = [1 + \{\hat{\zeta}(\lambda_r)/2\omega_b\}^2]^{1/2} - \{\hat{\zeta}(\lambda_r)/2\omega_b\} \qquad (5)$$

This expression looks just like Kramers' answer except the frequency-dependent friction $\hat{\zeta}(\lambda_r)$ replaces ζ, where

$$\hat{\zeta}(\lambda_r) = \int e^{-\lambda_r t}\zeta(t)\,dt \qquad (6)$$

For the calculation of $\hat{\zeta}(\lambda_r)$, the isomerization process in a molecule of DODCI can be modeled by the rotational motion of a sphere of hydrodynamic radius (r) around a molecule-fixed axis. The center of the sphere is at a distance ($r + l$) from the axis, where l is related to the C–C bond distance. On the basis of this model, we calculated the value of $\hat{\zeta}(\lambda_r)$ following the procedure of Bagchi and Oxtoby.[29] All the physical data necessary for the calculation, that is, the high-pressure data of zero-frequency shear viscosity ($\eta_s(0)$), bulk viscosity (η_v), solvent density (ρ), and sound velocity (C_s), were taken from literature.[30] The relaxation part of the solvent bulk modulous is given by $K_r = K_0 - K_\infty$, where $K_0 = \rho C_s^2$.
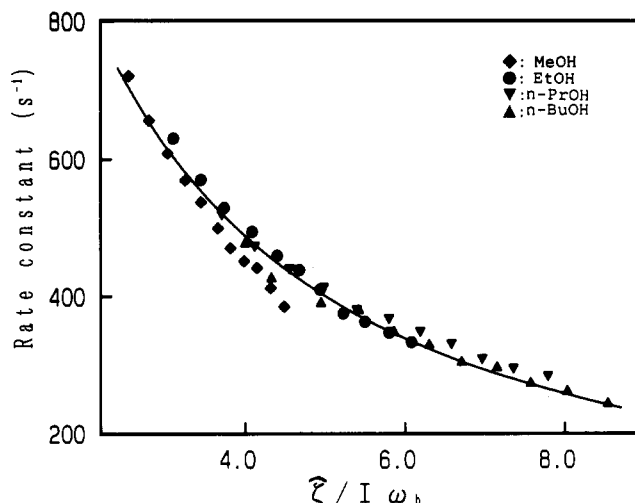

Figure 4. Rate constant against $\hat{\zeta}(\lambda_r)/I\omega_b$. See the text for details.

To compare the calculated result with that observed, we can use the exponent α of eq 4. The calculated values (α_{calc}) are compared with α_{exp} in Table II. Further, the solid lines in Figure 2 represent the fittings of calculated results to experimental data. It is concluded that the present calculated results excellently reproduce the experimental values over the full viscosity range for every solvent. In the course of the calculation we tried to change the value of ω_b in the range 10^{12}–10^{13} s^{-1}. The best fit to every result was obtained with $\omega_b = 8.0 \times 10^{12}$ s^{-1}. According to Velsko et al.,[4] a value of 2.45×10^{13} s^{-1} has been proposed, based on their experiment of temperature- and solvent-variation method.

Here we ask why the Grote–Hynes model using frequency-dependent friction, i.e., a non-Markovian model, appears to work for the DODCI ground-state isomerization in alcohols. The non-Markovian behavior is expected to be valid when the solvent motion is comparable to or slower than the reactive motion on the potential barrier.[8] That is, $\tau_s{}^{-1} \lesssim \omega_b$, where τ_s is the solvent correlation time. Our estimates of $\omega_b = 8.0 \times 10^{12}$ s^{-1} requires $\tau_s \gtrsim 0.13 \times 10^{-12}$ s. We find that this time-scale range could be attained for every alcohol, when we presume the solvent correlation time to be correlated with the longitudinal relaxation time of the solvent (τ_L),[31] which reflects orientational fluctuational motion of the solvent. Therefore, we can conclude that the present value of ω_b is quite reasonable to apply in the Grote–Hynes model.

In Figure 4 the rate constant is plotted against $\hat{\zeta}/I\omega_b$, where I denotes the moment of inertia. We obtain a single curve, which clearly reflects the isomerization being controlled by the frequency-dependent friction ($\hat{\zeta}(\lambda_r)$).

Activation Energy and Activation Volume. Differentiation of k_{obs} with respect to $1/T$ gives the apparent activation energy, i.e.

$$\frac{\partial \ln k_{obs}}{\partial(1/T)} = \frac{\partial \ln \kappa(\eta)}{\partial(1/T)} + \frac{\partial \ln k_{TST}}{\partial(1/T)} \qquad (7)$$

Thus, it follows by definition that

$$\Delta E_{obs} = \alpha\Delta E_\eta + E_a \qquad (8)$$

where ΔE_{obs} involves two contributions, i.e., the intrinsic activation energy (E_a) corresponding to the barrier height and the activation energy of the viscous flow (ΔE_η). The values of ΔE_η can be calculated from the literature data.[32] Thus, by using the values of α_{exp} and ΔE_η together with ΔE_{obs}, we obtain the value of E_a. The value of E_a is 13.0 kcal/mol. This is in good agreement with that by Velsko et al.[4]

The cause of the non-Kramers behavior is considered to have a connection with the large E_a value, since the larger E_a values commensurate with the sharper potential barrier.

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TABLE III: Barrier Top Frequency (ω_b), Intrinsic Activation Energy (E_a), and Form of Viscosity Dependence

	$10^{-12}\omega_b$, s^{-1}	E_a, kcal/mol	form of viscosity dependence	ref
	Ground-State Isomerization			
DODCI[a]	8.0	13.0	non-Kramers	present data[f]
	24.5	13.7	non-Kramers	4[g]
	10		non-Kramers	29[g]
	Excited-State Isomerization			
trans-stilbene	1.5	3.5	non-Kramers	16[h]
DPB[b]	6.0	4.7	non-Kramers	1, 29[h]
DODCI	4.7	2.9–3.1	non-Kramers	2[g]
BN[c]	23	1.3	Kramers	15[g]
	Intramolecular Excimer Formation			
DPP[d]	76	3.5	Kramers	12[f]
DNP[e]	95		Kramers	31[f]

[a] 3,3'-Diethyloxadicarbocyanine iodide. [b] 1,4-Diphenylbutadiene.
[c] 1,1'-Dinaphthyl. [d] 1,3-Di-1-pyrenylpropane. [e] 1,3-Di-2-naphthyl-propane. [f] By high-pressure method. [g] In alcohols. [h] In alkanes.

On the other hand, differentiation of k_{obs} with respect to pressure gives the apparent activation volume, which is written as

$$\frac{\partial \ln k_{obs}}{\partial P} = \frac{\partial \ln \kappa(\eta)}{\partial P} + \frac{\partial \ln k_{TST}}{\partial P} \quad (9)$$

By definition it follows that

$$\Delta V^*_{obs} = \alpha \Delta V^*_\eta + \Delta V^*_i \quad (10)$$

where the observed activation volume ($\Delta V^*_{obs} = -RT(\partial \ln k_{obs}/\partial P)$) involves the volume change due to diffusion ($\Delta V^*_\eta = RT(\partial \ln \eta/\partial P)$) as well as the intrinsic activation volume ($\Delta V^*_i = -RT(\partial \ln k_{TST}/\partial P)$). Using the value of α_{exp} and ΔV^*_η together with the value of ΔV^*_{obs}, we calculated the value of ΔV^*_i. Both ΔV^*_{obs} and ΔV^*_η change with pressure, but at around 100–300 MPa ΔV^*_i falls in the range 0.9–1.0 cm^3/mol. Therefore, we can conclude that ΔV^*_i is less than 1.0 cm^3/mol.

An important finding of this work is the success of the introduction of frequency-dependent friction in reproducing the experimental data by using reasonable parameter values. Table III summarizes the available barrier crossing data of ω_b and E_a, comparing with those of various isomerization and intramolecular excimer formation systems.

Note that a large barrier height is likely to have a non-Kramers behavior, implying a less strong dependence on solvent friction, which corresponds to a small α value. As the barrier becomes higher, ω_b is expected to get larger, since the barrier top curvature should get sharper if the forms of initial and final potential are not so different among the different systems. But such a correlation could not be found in the table. Among the numerous reasons for this, the most important will be a large uncertainty in the ω_b values in the case of non-Kramers behavior, which is mostly determined by means of the Grote–Hyes equation in which an introduction of various assumptions for molecular rotation and of various physical data is needed. Therefore, it may be impossible to compare the values obtained from the different models.

Concluding Remarks

The apparent non-Kramers behavior of the viscosity dependence of the ground-state isomerization of DODCI in a series of alcohol solvents can be understood by taking the frequency-dependent friction into consideration. This non-Markovian behavior could be expected from the comparatively slow motion of solvent relaxation as compared with the reactive motion.

The intrinsic activation volume is quite small, less than 1.0 cm^3/mol, so that the observed activation volume is explained by the viscosity term ($\alpha \Delta V^*_\eta$) appearing in eq 10. As for the previously reported activation volume in various isomerization systems,[33] it is mostly the case that the observed activation volume has been treated only as the intrinsic activation volume without discriminating the contribution of the viscosity term. It should be noted, however, that there are cases of even a larger contribution of the viscosity term to the observed activation volume. The accurate determination of $\alpha \Delta V^*_\eta$ is essential in order to evaluate the true intrinsic activation volume (ΔV^*_i).

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