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KINETIC STUDIES OF SOLVENT AND PRESSURE EFFECTS ON THERMAL ISOMERIZATIONS OF *N*-PHENYL- AND *N*-METHYLRHODAMINELACTAMS

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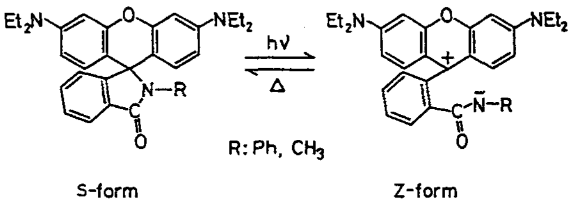
Solvent and pressure effects were examined for the isomerization rates of *N*-phenyl- and *N*-methylrhodaminelactams (RL-Ph and RL-CH_3) from their zwitterionic to the spiro forms. From the pressure dependence of the reaction rate, the activation volumes were estimated to be about 5 $cm^3\,mol^{-1}$ for RL-Ph and 3–10 $cm^3\,mol^{-1}$ for RL-CH_3. It is proposed that there are two rotameric isomers for the coloured zwitterionic forms, and the role of these rotamers in the kinetic effects of solvent and pressure is discussed. The results are consistent with a reaction mechanism involving heterolytic ring closure on activation.

INTRODUCTION

Photo- and thermochromism occur in a wide variety of inorganic and organic compounds, and these compounds have attracted attention for many years.[1] In the case of organic compounds, thermochromic behaviour is often associated with the reversible valence isomers. The mechanisms for thermochromic processes are roughly classified into the following types: (I) heterolytic bond cleavage and formation; (II) homolytic bond cleavage and formation; (III) *cis–trans* isomerization; and (IV) tautomerism. We have previously examined the solvent and pressure effects for various types of thermal isomerizations: spiropyrans[2] (Type I), spiro[1,8-*a*]dihydroindolizine[3] (DI) (Type II), azobenzenes[4] (Type III) and 4-phenylazo-1-naphthol[5] (Type IV).

Rhodamine derivatives are extensively used in dye lasers. It has been recognized that *N*-substituted rhodaminelactam is converted into a coloured zwitterionic structure (*Z*-form) by photochemically induced bond fission. In the dark, the *Z*-form reverts to the spiro form (*S*-form) as shown in Scheme 1.[6]



Scheme 1

Similarly, spiropyrans can exist with colourless spiro and coloured merocyanine structures.[2] The coloured merocyanine takes a planar form with delocalized π-electrons of the indoline and benzopyran fragments. From the kinetic solvent and pressure effects, we have established that the solvent-induced dipole through the conjugation of the π-electrons plays an important role in some cases.[2,4] For rhodaminelactam, the conjugation of π-electrons between isoindole and xanthene fragments in the *Z*-form is impossible as in the case of DI, and Willwohl *et al.*[7] have suggested that there are two coloured rotameric isomers for the *Z*-form. A detailed reaction mechanism involving the rotamers of the *Z*-form for the thermal isomerization has not been put forward. Therefore, it would be worth investigating the kinetic solvent and pressure effects on the isomerization rate and compare them with those for spiropyrans and DI. In this paper, the kinetic and thermodynamic quantities for the isomerizations of rhodaminelactams are presented, and the electronic structure of the transition state and the role of the rotamers are discussed.

EXPERIMENTAL

3′,6′-Bis(diethylamino)-2-phenylspiro[1*H*-isoindole-1,9′(9*H*)xanthene]-3(2*H*)-one (RL-Ph) and 3′,6′-bis-(diethylamino)-2-methylspiro[1*H*-isoindole-1,9′(9*H*)

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-xanthene]-3(2*H*)-one (RL-CH_3) were prepared by the reported method.[8] RL-Ph and RL-CH_3 were recrystallized from acetone, m.p. 227–228 °C (lit.[8] 222 °C) and 223–224 °C, respectively. Identification was made by melting points and ^1H NMR spectra. Solvents of reagent grade were stored over molecular sieves and distilled before use.

The instrumentation for the kinetic measurements under high pressures has been described elsewhere.[9] A sample solution (*ca* 10^{-4} mol dm^{-3}) deoxygenated by bubbling nitrogen gas was irradiated with a Toshiba H400-P mercury lamp through an interference filter (Toshiba UV-D33S) to produce the zwitterionic form. As far as we examined the electronic spectrum, the photo- and thermal isomerizations were quantitatively reproducible. The thermal return from the zwitterionic to the spiro form was followed by monitoring the change in the absorbance at *ca* 550 nm (the wavelength maximum of the band assigned to the absorption of the xanthene part[10]) using a Hitachi 139 spectrophotometer. The first-order rate constants, estimated by using the Guggenheim method, agreed within a 5% error.

RESULTS

The time dependence of the absorbance at λ_{max} (*ca* 550 nm) of the *Z*-forms of RL-Ph and RL-CH_3 was monitored in various solvents. The isomerization rate was followed at various pressures up to 1200 kgf cm^{-2} (1 kgf $cm^{-2} = 0{\cdot}981 \times 10^5$ Pa) in various solvents and the first-order rate constant k was estimated. The activation volume ($\Delta V^{\neq}$) at atmospheric pressure was estimated from the ln k vs pressure plot according to the following equations, and the values of $\Delta V^{\neq}$ are given in Tables 1 and 2:

$$\ln k = ap + b \tag{1}$$

$$\Delta V^{\neq} = -RT(\partial \ln k/\partial p)_T \tag{2}$$

In Table 3, the rate constants of RL-Ph at several

Table 1. Rate constants and activation volumes for the thermal isomerization of RL-Ph in various solvents at 40 °C

Solvent	λ_{max}(nm)	$10^3k(s^{-1})$				$\Delta V^{\neq}$ (cm^{-3} mol^{-1})	$10^{11}q_p$ (Pa^{-1})
		$p^a = 1$	$p = 300$	$p = 650$	$p = 1000$		
Chloroform	550	2·00	1·87	1·73	1·61	5·5	20·1
Chlorobenzene	554	54·5	48·9	45·5	42·7	5·1	10·7
1,2-Dichloroethane	558	5·42	5·27	4·60	4·53	5·6	14·4
Acetonitrile	556	3·71	3·19	3·16	3·03	4·7	2·17

[a] p in kgf cm^{-2}.

Table 2. Rate constants and activation volumes for the thermal isomerization of RL-CH_3 in various solvents at 40 °C

Solvent	λ_{max}(nm)	$10^2k(s^{-1})$					$\Delta V^{\neq}$ (cm^{-3} mol^{-1})
		$p^a = 1$	$p = 300$	$p = 600$	$p = 900$	$p = 1200$	
Chloroform	559	14·5	12·6	11·2	9·78	8·66	10·9
Chlorobenzene	561	9·35	8·55	7·93	7·29	6·66	7·0
1,2-Dichloroethane	556	10·4	9·44	8·56	7·76	6·98	8·4
Acetonitrile	554	11·1	11·0	10·4	9·89	9·70	3·1

[a] p in kgf cm^{-2}.

Table 3. Rate constants and activation parameters for the isomerization of RL-Ph at various temperatures

Solvent	$10^3k(s^{-1})$					E_a (kJ mol^{-1})	$\Delta S^{\neq}_{313\ K}$ (J K^{-1} mol^{-1})
	20 °C	25 °C	30 °C	40 °C	50 °C		
Chloroform		0·459	0·724	2·00	5·51	79·5	−50·8
Chlorobenzene		29·4	37·9	54·5	64·6	25·2	−198
1,2-Dichloroethane		1·78	2·59	5·42	10·5	56·7	−116
Acetonitrile	0·596	0·925	1·48	3·71		68·7	−80·9

temperatures are given, together with the activation parameters.

DISCUSSION

In a previous paper, we pointed out that the absorption band position of push–pull azobenzenes and spiropyrans having delocalized π-electron systems is sensitive to solvent polarity.[2,4] For instance, the absorption band position of 6-nitro-substituted spiropyran shifts from 585 nm in chloroform to 555 nm in acetonitrile. In contrast, as shown in Tables 1 and 2, the absorption band position of the *Z*-form of RL-Ph and RL-CH_3 is hardly sensitive to the solvent polarity, which suggests the localization of π-electrons on the xanthene and isoindole fragments.

Although the isomerization rate in chlorobenzene for RL-Ph is much larger than those in the remaining solvents (Tables 1 and 3), the linear free energy relationship for the isomerization of RL-Ph may be seen to hold (Figure 1). This suggests that a single interaction mechanism is involved.[11] For the isomerization from the bipolar *Z*-form of rhodaminelactam to the less polar *S*-form, large kinetic solvent effects due to a drastic change in polarity can be expected. However, as can be seen in Tables 1 and 2, significant solvent effects on the isomerization rate of RL-Ph and RL-CH_3 are not observed.

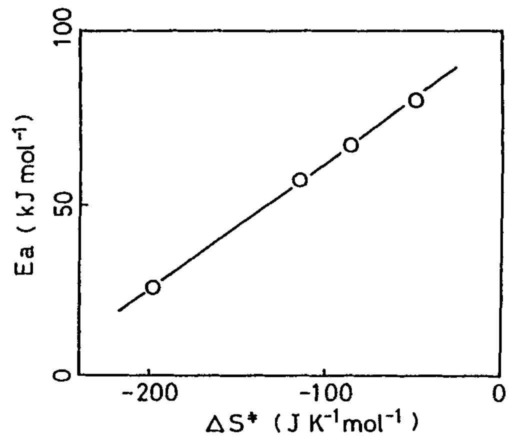
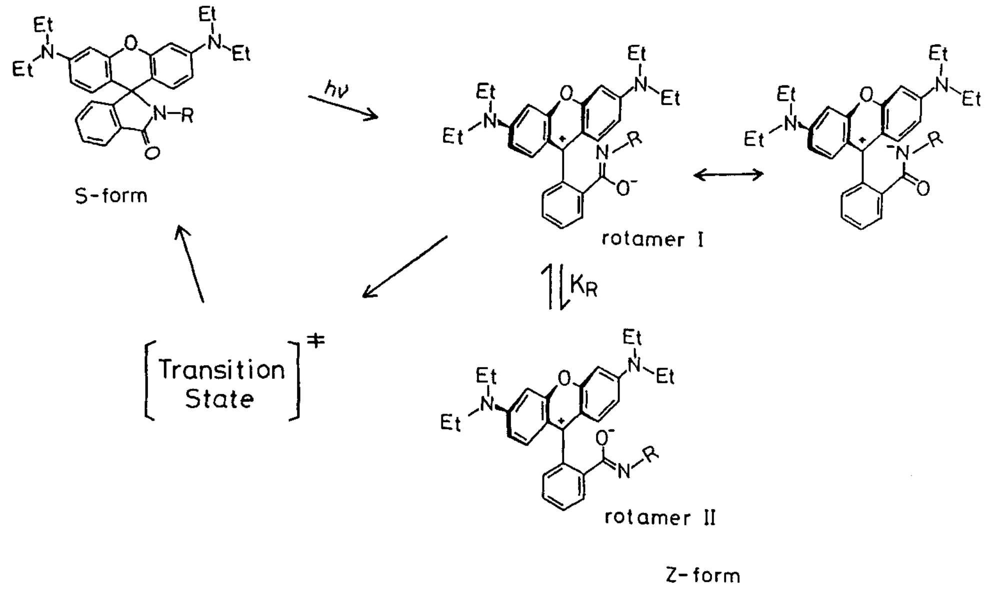


Figure 1. Relationship between E_a and $\Delta S_{313\,\mathrm{K}}^{\neq}$ for the thermal isomerization of RL-Ph

The two coloured rotameric isomers I and II[7] for the *Z*-form of rhodaminelactam are depicted in Scheme 2. The roamers will be in rapid equilibrium, and the dipole moment of rotamer I must be larger than that of rotamer II. According to Scheme 2, the observed rate constant k for the isomerization can be given by

$$k = K_R k_I/(1 + K_R) \qquad (3)$$

where K_R (= [rotamer I]/[rotamer II]) is the equilibrium constant between the two rotamers and k_I denotes the rate constant of the isomerization from the rotamer I to the *S*-form. In acetonitrile, a considerably polar solvent, it could reasonably be assumed that



Scheme 2

$K_R \gg 1$.[12] In this case, equation (3) reduces to

$$k = k_I \tag{4}$$

The rate constant k in the remaining solvents will be discussed later.

The rate constants given in Tables 1 and 2 decrease slightly with increasing external pressure. The estimated activation volumes are in the range 3–11 cm^3 mol^{-1}. It is noted that the activation volume estimated in acetonitrile corresponds to the volume change for the isomerization from the rotamer I to the *S*-form from equation (4). These values are 4.7 cm^3 mol^{-1} for RL-Ph and 3.1 cm^3 mol^{-1} for RL-CH_3 (Tables 1 and 2), and are similar to the activation volume for DI ($\Delta V^{\neq} = 3$–8 cm^3 mol^{-1}).[3] This suggests that the polarity of the *Z*-form decreases on activation but its extent is not as large as in the case of spiropyran.[2] Accordingly, the heterolytic ring closure mechanism may be acceptable for the thermal isomerization ($Z \rightarrow S$) as shown in Scheme 3. Since the isomerization of the rotamer I to the *S*-form starts from the polar *Z*-form and may proceed via the less polar transition state, the rate constant k_I decreases with increasing solvent polarity. On the other hand, the equilibrium constant K_R will increase with increasing solvent polarity, resulting in an increase in the $K_R/(1+K_R)$ value. Therefore, the insensitive nature of the observed rate constant may be due to the compensatory effect.

The activation volume ($\Delta V^{\neq}$) could be conventionally divided into two terms: an intrinsic volume change ($\Delta V_{int}^{\neq}$) and a volume change arising from reorganization of solvent molecules around the reactant on activation ($\Delta V_{sol}^{\neq}$):

$$\Delta V^{\neq} = \Delta V_{int}^{\neq} + \Delta V_{sol}^{\neq} \tag{5}$$

By means of the Kirkwood equation,[13] the solvation term $\Delta V_{sol}^{\neq}$ can be given by

$$\Delta V_{sol}^{\neq} = -N[(\mu^{\neq 2}/r^{\neq 3}) - (\mu_z^2/r_z^3)]q_p \tag{6}$$

where $q_p = [3/(2\varepsilon+1)](\partial\varepsilon/\partial p)_T$ and the other symbols have their usual meanings. Using available ε–p data,[14] q_p values were estimated. Although this is a simplified model in which the pressure dependence of the radius r is ignored, it could provide a convenient basis for a semi-quantitative comparison of solvent effects. In solvent effects on reactions involving dipoles, a linear relationship between the activation volume and q_p has been obtained, and the structure of the transition state has been discussed.[15]

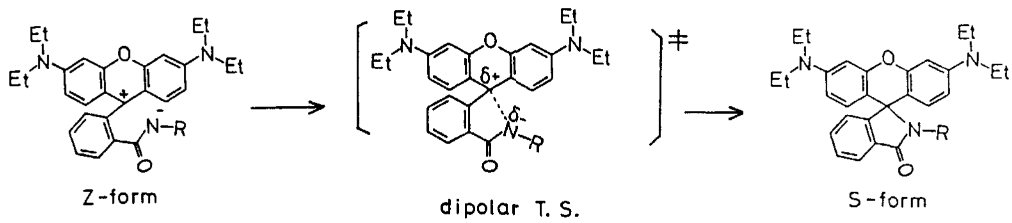
The activation volume in acetonitrile can be expressed from equation (4) as follows:

$$\Delta V^{\neq} \approx \Delta V_I^{\neq} = \Delta V_{I,int}^{\neq} + \Delta V_{I,sol}^{\neq} \tag{7}$$

where the subscript I denotes the isomerization of the rotamer I to the *S*-form. In order to estimate $\Delta V_{I,sol}^{\neq}$, we tentatively allotted $\mu_{z(\text{rotamer I})} = 15$ D for the dipole moment of the rotamer I, $\mu^{\neq} = 3{\cdot}0$D and $r_z = r^{\neq} = 0{\cdot}3$ nm, based on the dipole moment of the merocyanine form of spiropyran ($\mu \approx 13$ D) and previous studies for the isomerizations of spiropyrans and DI.[2,3] By substituting the above values into equation (6), the $\Delta V_{I,sol}^{\neq}$ value was estimated to be 10·4 cm^3 mol^{-1} in acetonitrile. The positive $\Delta V_{I,sol}^{\neq}$ value could be ascribed to the release of electrostricted solvent molecules. Using the $\Delta V_{I,sol}^{\neq}$ and $\Delta V^{\neq}$ values in acetonitrile, $\Delta V_{I,int}^{\neq}$ can be estimated to be −7·3 cm^3 mol^{-1} for RL-CH_3 and −5·7 cm^3 mol^{-1} for RL-Ph. It may be instructive to compare the $\Delta V_{I,int}^{\neq}$ values with those of similar reactions. For example, the Claisen rearrangement has been accepted as a typical reaction involving a cyclic transition state. Walling and Naiman[16] estimated the activation volumes for the Claisen rearrangement in several solvents, and found that the values of $\Delta V^{\neq}$ are −10 to −15 cm^3 mol^{-1} with no obvious solvent dependence. They interpreted these results as the intrinsic volume change for the ring-closure process on activation. The values of $|\Delta V_{I,int}^{\neq}|$ for RL-Ph and RL-CH_3 seem to be lower than those for the Claisen rearrangement, which may be ascribed to the similarity of conformations between the rotamer I and the activated complex. Using the above values, the volume profile for RL-Ph and RL-CH_3 is shown in Figure 2. It can be seen that the term $\Delta V_{I,sol}^{\neq}$ in equation (7) overwhelms $\Delta V_{I,int}^{\neq}$, resulting in small and positive $\Delta V^{\neq}$ values for the isomerization.

For the isomerization in the remaining solvents, the pressure effects can be expressed from equation (3) as follows:

$$\Delta V^{\neq} = \Delta V_I^{\neq} + \Delta V_R + RT[\partial \ln(1+K_R)/\partial p]_T \tag{8}$$



Z-form dipolar T.S. S-form

Scheme 3

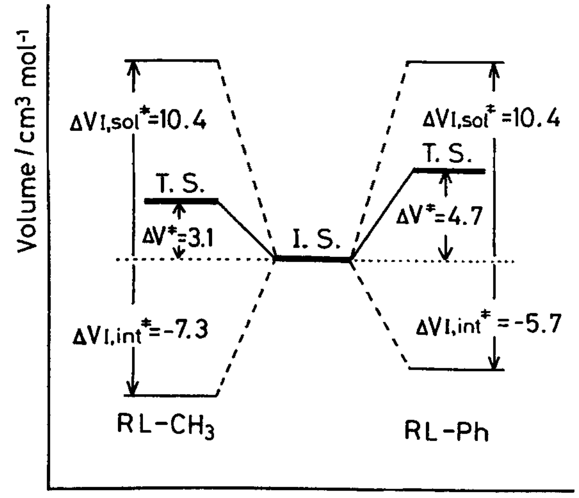


Figure 2. Volume profiles for the isomerization of RL-CH₃ and RL-Ph in acetonitrile

where $\Delta V_R (= \Delta V_{I,int} + \Delta V_{I,sol})$ is the difference in the molar volumes of the two rotamers. The equilibrium constant K_R may decrease with decreasing solvent polarity. In an extreme case for which $K_R \ll 1$, equation 8 reduces to

$$\Delta V^{\neq} = \Delta V_I^{\neq} + \Delta V_R \qquad (9)$$

The solvation term ($\Delta V_{I,sol}^{\neq}$) of the activation volume can be estimated as $\Delta V_{sol}^{\neq}$(RL-Ph) = $\Delta V_{sol}^{\neq}$(RL-CH$_3$) in a given solvent by substituting the q_p value into equation (6). Accordingly, the difference between the activation volumes of RL-Ph and RL-CH$_3$ in a less polar solvent such as chloroform can be given from equations (5) and (9) as

$$\begin{aligned}\Delta\Delta V^{\neq} &= \Delta V^{\neq}(\text{RL-Ph}) - \Delta V^{\neq}(\text{RL-CH}_3)\\ &= \Delta\Delta V_{I,int}^{\neq} + \Delta\Delta V_{R,int} \qquad (10)\end{aligned}$$

Since the $\Delta V_{I,int}^{\neq}$ value is independent of solvent polarity, $\Delta\Delta V_{R,int}$ is $-7{\cdot}0\ \text{cm}^3\,\text{mol}^{-1}$ using the $\Delta V_{I,int}^{\neq}$ values estimated in acetonitrile and $\Delta V^{\neq}$ in chloroform for RL-Ph and RL-CH$_3$. A conceivable reason for this difference is as follows. In the rotamer II, rotation of the CH$_3$ and Ph groups around the C—N single bond in the isoindole part is possible at ambient temperature, and the environmental situation of the CH$_3$ group will not change substantially between the rotamers I and II. However, the free rotation of the Ph group in the rotamer I will be restricted, which must give rise to a smaller exclusion of solvent molecules. This may be responsible for the difference in $|\Delta V_{R,int}|$ which is compared with the values reported for the isomerization of push–pull azobenzenes.[17]

In conclusion, the above findings suggest that the thermal isomerization proceeds via the dipolar transition state, and the small solvent effect on the isomerization is ascribed to the existence of the two rotameric isomers of the *Z*-form.

REFERENCES

1. G. H. Brown, *Photochromism*. Wiley, New York (1971), and references cited therein.
2. Y. Sueishi, M. Ohcho and N. Nishimura, *Bull. Chem. Soc. Jpn.* **58**, 2608 (1985).
3. Y. Sueishi, K. Danjo, S. Yamamoto and N. Nishimura, *Chem. Express* **6**, 459 (1991).
4. N. Nishimura, S. Kosako and Y. Sueishi, *Bull. Chem. Soc. Jpn.* **57**, 1617 (1984).
5. N. Nishimura, K. Danjo, Y. Sueishi and S. Yamamoto, *Aust. J. Chem.* **41**, 863 (1988).
6. K. H. Knauer and R. Gleiter, *Angew. Chem., Int. Ed Engl.* **16**, 113 (1977).
7. H. Willwohl, J. Wolfrum and R. Gleiter, *Laser Chem.* **10**, 63 (1989).
8. K. Beilstein, *Beilstein's Handbuch der Organischen Chemie*, Springer (Berlin) Vol. 27, p. 534 (1937); L. Cincotta and J. W. Foley, *US Pat.* 4,290,955 (1981).
9. Y. Sueishi and N. Nishimura, *Bull. Chem. Soc. Jpn.* **56**, 2598 (1983); N. Nishimura, S. Iga, M. Sato and S. Yamamoto, *Bull. Chem. Soc. Jpn.* **65**, 2437 (1992).
10. U. Kruger and R. Memming, *Ber. Bunsenges. Phys. Chem.* **78**, 679 (1974).
11. J. E. Leffler, *J. Org. Chem.* **31**, 533 (1966).
12. M. Moreno-Manas, A. Gonzalez, C. Jaime, J. Marquet, I. Hernandez-Fuentes, C. Salom and J. Bellanato, *J. Chem. Soc., Chem. Commun.* 1706 (1987).
13. J. Kirkwood, *J. Chem. Phys.* **2**, 351 (1934).
14. H. Hartmann, A. Neumann and G. Rinck, *Z. Phys. Chem., N. F.* **44**, 204 (1965); H. Hartmann and A. P. Schmidt, *Ber. Bunsenges. Phys. Chem.* **72**, 875 (1968); K. R. Srinivasan and R. L. Kay, *J. Solution Chem.* **6**, 357 (1977).
15. N. S. Isaacs, *Liquid Phase High Pressure Chemistry*. Wiley, Chichester (1981), and references cited therein.
16. C. Walling and M. Naiman, *J. Am. Chem. Soc.* **84**, 2628 (1962); E. Whally, *Adv. Phys. Org. Chem.* **2**, 93 (1964).
17. T. Asano, T. Yano and T. Okada, *J. Am. Chem. Soc.* **104**, 4900 (1982).