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Mechanism of the Photochemical Ring Expansion of *N*-Vinyl-2-pyrrolidone. Estimation of the Recombination-Time of Biradical

Haruo Shizuka, Toshio Ogiwara, and Toshifumi Morita
Department of Chemistry, Gunma University, Kiryu, Gunma 376

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The photochemical ring expansion of *N*-vinyl-2-pyrrolidone (NVP) has been carried out at 254 nm. The reaction quantum yield depends a great deal on the solvnet viscosity and temperature. The recombination time of the biradical of RP produced by Norrish type I fission was estimated to be $\approx 10^{-10}$ s by application of the Einstein and Smoluchowski-Debye equations. The spin inversion of the biradical in a solvent cage is also discussed according to Kaptein's theory of the radical-pair mechanism.

Geminate recombinations[1)] of primary products (radicals or free ions) produced in a solvent cage by irradiation have been studied experimentally and theoretically.[2–8)] Since the processes involved in cage effect reactions[9)] are in a range beyond the scope of conventional dynamic methods, the geminate recombination was monitored indirectly *via* the dependence of the products on the concentration of added scavengers.[10)] A more powerful experimental technique involves the application of pulsed excitation. Eisenthal *et al.*[5)] have carried out direct measurements of the geminate recombination of a radical-pair (iodine atoms) with picosecond pulses at 5300 Å, the recombination time τ being 70 and 140 ps in hexadecane and carbon tetrachloride, respectively. The fast reactions can be explained by a theory similar to that of the radical-pair mechanism for CIDNP and CIDEP.[11)]

According to the mechanism developed by Kaptein,[12)] the radical-pair model can be divided into two types depending upon the distance r between radicals in a solvent cage.

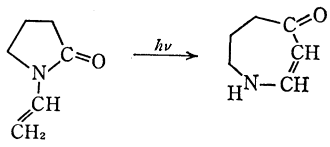
1) Closed Radical-pair $\overline{A\cdot\cdot B}$. The distance of r in this pair is shorter than that of r_0 (≈ 6Å)[13)] which is roughly given by the condition that the exchange integral J is of the order of the nuclear hyperfine interactions. In the region $r < r_0$, no Zeeman effects in CIDNP and CIDEP experiments can be detected from the pair except very high fields; no singlet-triplet mixing in the pair exists appreciably since the S-T energy gap ($2J$) is very large. The geminate recombination of the triplet closed radical-pair $^3\overline{A\cdot\cdot B}$ would therefore occur *via* a triplet separated radical-pair $^3\overline{A\cdot|\cdot B}$. In contrast, the geminate recombination of the singlet pair $^1\overline{A\cdot\cdot B}$ is very fast ($\approx 10^{-11}$ s).[6)]

2) Separated Radical-pair $\overline{A\cdot|\cdot B}$. The radicals in this pair are separated by solvent molecules[14)] to give the distance r ($\geq r_0$), but they are enclosed within a solvent cage. The $\overline{A\cdot|\cdot B}$ is produced from $\overline{A\cdot\cdot B}$ or diffusing radicals. The exchange term J becomes small[15)] in the region $r \geq r_0$, and the singlet-triplet mixing takes place due to the nuclear hyperfine and the spin-orbit interactions, resulting in the recombination of $^3\overline{A\cdot|\cdot B}$. In the presence of the external magnetic field, Zeeman terms also contribute to the S-T mixing in the pair, and CIDNP and CIDEP phenomena would be observed from $\overline{A\cdot|\cdot B}$ as has been proposed by Kaptein.[12)] As for the recombination of $^1\overline{A\cdot|\cdot B}$, its recombination probability may decrease with increasing S-T mixing.

Brocklehurst[2)] applied the radical-pair model to the rate of loss of spin correlation in geminate pairs of radical ions produced by radiolysis. Schulten *et al.*[16)] have recently studied the fast intersystem crossing in an exciplex due to the radical-pair mechanism.

In contrast to the cases of pair radicals and radical ions, the lack of recombination time of a biradical was pointed out.[17)] It seems that the behavior of the biradical in a solvent cage is similar to that of the radical-pair. However, the radical site of the biradical is always combined with a molecular chain: the structure allows a reversible change similar to $\overline{A\cdot\cdot B} \leftrightarrow \overline{A\cdot|\cdot B}$ without escape of the radicals from solvent cage. Thus, an appreciable S-T mixing may be expected, effecting the recombination of biradical. The kinetic behavior of a biradical has been studied from these viewpoints.

N-Vinyl-2-pyrrolidone (NVP) yields photochemically the ring expansion product (P) of 4-azacyclohepten-1-one in alcohols[18)] as follows:



NVP P (1)

In this ring expansion, α-cleavage (the Norrish type I fission) to give the biradical RP (Eq. 2) may be involved as considered from the other photochemical ring expansion.[19)] In the present work, the compound NVP was chosen in order to estimate the recombination time of biradical. We have measured the quantum yields for the intramolecular ring expansion of NVP at 254 nm as a function of η/T, where η and T denote viscosity and absolute temperature of solutions, respectively.

Experimental

N-Vinyl-2-pyrrolidone (E.P-grade, Tokyo Kasei Co., Ltd.) was purified by distillation before use. Ethanol (G.R.-grade, Tokyo Kasei Co., Ltd.) and spectrograde glycerol were used without further purification. The viscosity of sample solutions was adjusted with a mixed solvent (ethanol–glycerol system).[20)]

A low-pressure mercury lamp with a Vycor glass filter was used as the 254 nm radiation source. Actinometry was carried out using a ferric oxalate solution.[21] The quantum yields for the product formation were measured by spectrophotometry. For the measurement of temperature effect on the quantum yield, a quartz Dewar flask designed for spectrometry was used as a reaction cell, the temperature being controlled to within ±2 °C. In the measrements of degassed samples, the solutions were thoroughly degassed on a high-vacuum line by the freeze-pump-thaw method. Absorption and fluorescence spectra were measured with Hitachi 139 and 124 spectrophotometers and with a Hitachi MPF-2A fluorimeter, respectively.

Results

The spectrum of the degassed ethanol solution of *N*-vinyl-2-pyrrolidone (NVP) changed markedly upon irradiation with the 254 nm light at 293 K as shown in Fig. 1. The 235 nm band of NVP (ε: 1.68×10^4 M^{-1} cm^{-1}) and a new band with maximum at 308 nm (ε: 1.96×10^4 M^{-1} cm^{-1}) appeared. The spectral change shows the formation of ring expansion product of 4-azacyclohepten-1-one. The photochemical conversion from NVP into the photoproduct P in the initial stages of the reaction was very efficient (>90%). The photoproduct was separated by column chromatography and confirmed by UV, IR, and NMR, and comparison of its mp with that in the literature.[18]

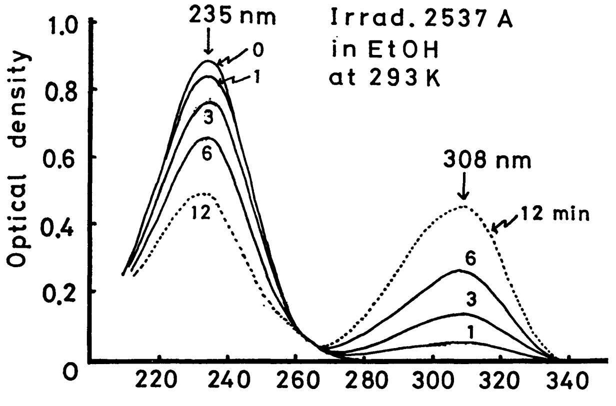


Fig. 1. The spectral change of ethanol solution of NVP with lapse of time at 254 nm. Numbers refer to time of measurement in minutes.

The quantum yields for the product formation Φ_R in ethanol [$\Phi_R=5.4$ $(\pm0.2)\times10^{-2}$ at 293 K, $\eta=12.2$ mp] did not change with variations of irradiation time (2—15 min), initial concentration of NVP (0.5×10^{-4}—1×10^{-2} M) and the addition of piperylene ($\leq2.2\times10^{-2}$ M). There was no dissolved oxygen effect on Φ_R. The results are shown in Fig. 2. However, significant effects of viscosity (η) and temperature (T) on Φ_R at 254 nm were observed (Table 1). The Φ_R values decreased with increase in η and decreased with fall in temperature. The dependence of Φ_R on η at 254 nm in ethanol or an ethanol–glycerol mixture is shown in Fig. 3. The difference between the two curves is due to the temperature effect on Φ_R.

No photochemical ring expansion of NVP was observed in a rigid EPA matrix at 77 K. Neither fluorescence (at 77 and 293 K) nor phosphorescence (at 77 K) could be observed. The emission quantum yields should be less than 10^{-4}. The photochemical ring expansion took place even in the gas phase. No quantitative work has been made.

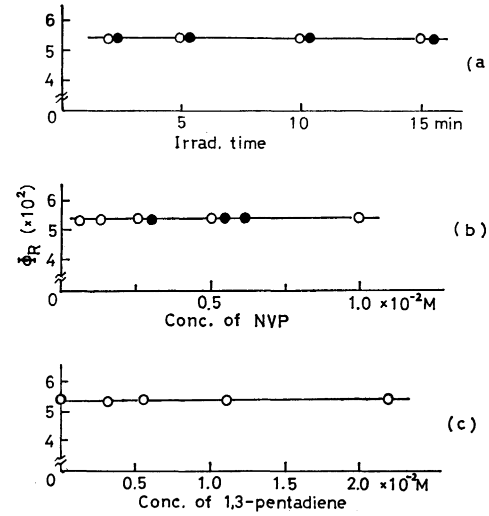


Fig. 2. Dependence of quantum yields for the product formation in ethanol at 254 nm and 293K.
(a) On irradiation time with initial concentration of 5×10^{-3}M.
(b) On concentration of NVP.
(c) On addition of 1,3-pentadiene.
○: In aerated ethanol.
●: In degassed ethanol.

Table 1. Viscosity and temperature effects on Φ_R at 254 nm

Solvent	$\frac{T}{K}$	η mpoise	Φ_R $\times10^2$
EtOH[a]	303	10.0	5.5(±0.2)
	293	12.2	5.4(±0.2)
	273	17.7	4.6(±0.2)
	263	22	4.3(±0.2)
	253	28	3.9(±0.2)
	233	48	3.0(±0.2)
	203	120	2.1(±0.2)
Gly Vol %[b]			
0	293	12.2	5.4(±0.2)
5	293	16.7	5.0(±0.2)
10	293	22.3	4.5(±0.2)
20	293	41.1	3.9(±0.2)
30	293	63.3	3.6(±0.2)

a) The data of viscosity of ethanol were taken from "Handbook of Chemistry and Physics," ed by R. C. Weast, The Chemical Rubber Co, Ohio (1969).
b) Taken from Ref. 20. Gly Vol % denotes the glycerol volume percent in ethanol.

Discussion

The Norrish Type I Dissociation. The Norrish type I fission (α-cleavage) of organic carbonyl compounds

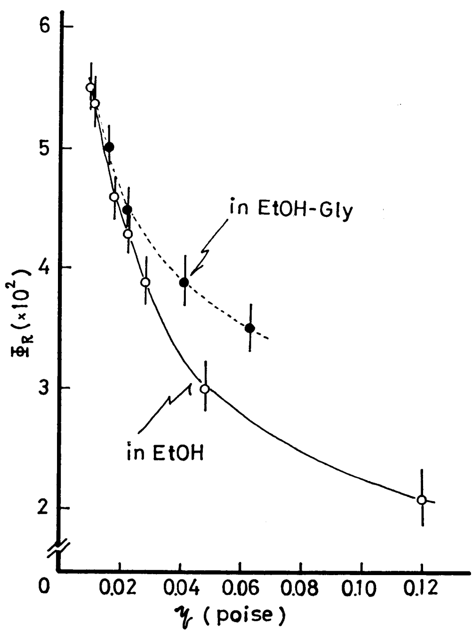


Fig. 3. The quantum yield for the product formation Φ_R as a function of viscosity η.

can be divided into three typical classes as follows:[22]

1) Photochemical fission of alkyl ketones occurs *via* both $^1(n, \pi^*)$ and $^3(n, \pi^*)$ states.[23,24]

2) Photochemical dissociation of aryl ketones[25] and some cyclohexanones[24] takes place *via* $^3(n, \pi^*)$, which might be due to the rapid intersystem crossing in the excited molecules.

3) Photochemical cleavages of aryl esters originate from $^1(\pi, \pi^*)$ $^1B_2$ states.[26]

The rate constants for the fissions are estimated to be 10^7—10^8 s^{-1} in case 1,[23,24] $\approx 10^{10}$ s^{-1} or more in case 2[25] and $\approx 10^9$ s^{-1} in case 3.[26] However, little is known about the reactive state responsible for photochemical ring expansions. The photochemical reaction of spiro[2.4]-heptan-4-one in methanol is an exception; the triplet state of the ketone ($\tau_T \simeq 2\times10^{-9}$ s) seems to be the reactive state from the result of the quenching experiment by 3 M 1,3-pentadiene.[27] The presence of triplet quenchers [1,3-pentadiene$\leq 2.2\times10^{-2}$ M[28a] and dissolved oxygen $\simeq 2.1\times10^{-3}$ M[29]] do not affect the Φ_R values. The results indicate that the photochemical ring expansion of NVP proceeds *via* a singlet precursor and/or very short-lived triplet state. The reactive state of $^3(n, \pi^*)$ is more likely than that of $^1(n, \pi^*)$, if we consider the allowed transition of $^1(\pi, \pi^*)\rightarrow{}^3(n, \pi^*)$ according to the El-Sayed rule.[30] The $^1(n, \pi^*)$ state in NVP lies energetically under the $^1(\pi, \pi^*)$ state, which was calculated by the CNDO/2 method.[28b] The $^1(n, \pi^*)$ band should be masked by the $^1(\pi, \pi^*)$ band at 235 nm.[31] The lack of emission from NVP shows that the excited state of NVP decays *via* rapid radiationless transitions [intersystem crossing, internal conversion, and the photochemical channel in part ($\leq 6.7\times10^{-2}$)]. Recent studies deal with the rapid radiationless processes in the excited molecules.[22,23]

Kinetics of Photochemical Ring Expansion of NVP. Viscosity and temperature dependence upon the reaction quantum yields Φ_R can be accounted for by the scheme shown in Fig. 4, which is simplified with respect to the processes of internal conversion and intersystem crossing, where NVP and NVP* are the ground and the electronically excited states of the staring material, respectively: RP the radical-pair (biradical) formed by the Norrish type I fission of NVP* (Eq. 2); and RP′ the biradical produced by rotational diffusion of RP resulting in the ring expansion product P (Eq. 3).

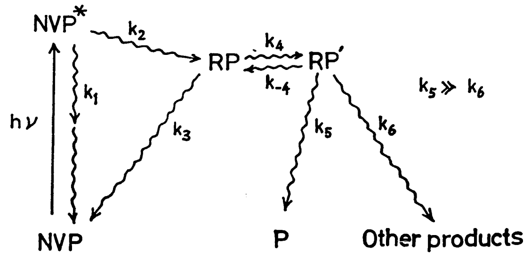
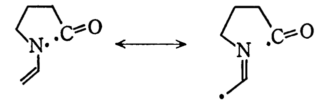
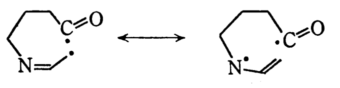


Fig. 4. A schematic energy state diagram for the photochemical ring expansion of NVP.

RP:

(2)

RP′:

(3)

By use of the usual steady-state approximation, the quantum yield for the product formation Φ_R is given by

$$\Phi_R = \left(\frac{k_2}{k_1+k_2}\right)\left\{\frac{k_4}{k_4+k_3\left(1+\frac{k_{-4}}{k_5+k_6}\right)}\right\}\left(\frac{k_5}{k_5+k_6}\right). \tag{4}$$

From the result of high efficiency (>90%) for the photochemical conversion NVP→P, the following should hold:

$$k_5 \gg k_6. \tag{5}$$

Using this we obtain

$$\Phi_R = \Phi_{RP}\left\{\frac{k_4}{k_4+k_3\left(1+\frac{k_{-4}}{k_5}\right)}\right\}, \tag{4'}$$

where Φ_{RP} is the efficiency for the RP formation from NVP*. From Eq. 4′, we obtain

$$\frac{1}{\Phi_R} = \frac{1}{\Phi_{RP}}\left(1+\frac{k_{-4}k_3}{k_4k_5}\right) + \frac{1}{\Phi_{RP}}\cdot\frac{k_3}{k_4}. \tag{6}$$

The rate constants k_4 and k_{-4} in the structural change between RP and RP′ seem to be diffusion-controlled, and should be proportional to $T\eta^{-1}$. Thus, Eq. 6 can be further simplified to

$$\frac{1}{\Phi_R} = a + b\frac{\eta}{T} \tag{7}$$

where a denotes the first term in Eq. 6 and b the term $\alpha k_3 \Phi_{RP}^{-1}$ (α: constant). The plot of Φ_R^{-1} *vs.* ηT^{-1} obtained experimentally, which agrees with Eq. 7, is shown in Fig. 5. The values of a and b are taken from the plot.

$$a = 15, \tag{8}$$

and

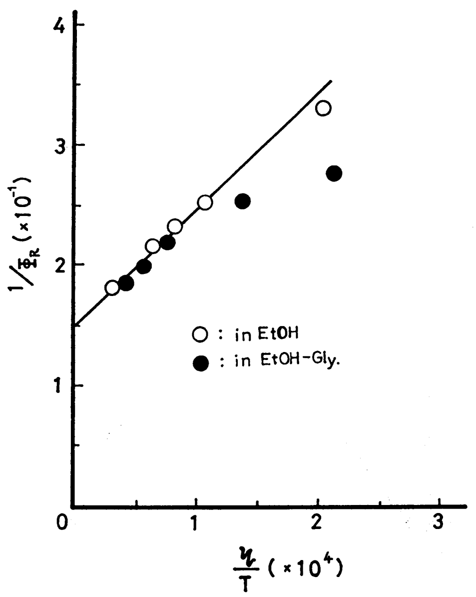


Fig. 5. Plot of Φ_R^{-1} as a function of ηT^{-1}.

$$b = 8.3 \times 10^4 (\text{dyn}^{-1}\ \text{s}^{-1}\ \text{cm}^2\ \text{deg}). \tag{9}$$

Deviations at high viscosity in the ethanol-glycerol system (Fig. 5) might be caused by inhomogeneity in the solvent.

Estimation of the Recombination Time of RP. Noyes's treatment[33] based on a random flight model is not applicable to the recombination of a biradical, since the radical sites of the biradical are combined with a molecular chain. Let us consider the recombination of the biradical of RP (or RP′) using the following approximations (Cases A, B, and C).

Case A: If we assume that the reversible process RP←RP′ is negligible, *i.e.* $k_{-4} \ll k_5$, Eq. 6 can be simplified to

$$\frac{1}{\Phi_R} = \frac{1}{\Phi_{RP}}\left(1+\frac{k_3}{k_4}\right) \tag{6$'$}$$

Using the experimental values a and Φ_R^{-1}, a linear plot of k_3/k_4 *vs.* η/T is obtained, showing that k_3/k_4 is less than unity in the range $\eta\ T^{-1} < 1.5 \times 10^{-4}$ poise deg^{-1}. This indicates that the diffusion rate constant k_4 (or k_{-4}) is greater than that of the recombination k_3 (or k_5). Thus, the assumption is not adequate.

Case B: If we assume that k_4 is approximately equal to k_{-4}, since both k_4 and k_{-4} are diffusion-controlled, we obtain from Eq. 6

$$\frac{1}{\Phi_R} = \frac{1}{\Phi_{RP}}\left(1+\frac{k_3}{k_5}+\frac{k_3}{k_4}\right). \tag{6$''$}$$

The value of k_4 (or k_{-4}) is related to the Debye rotational correlation time τ_0:[34]

$$\tau_0(\simeq k_4{}^{-1}) = \frac{4\pi a_0{}^3\eta}{3\kappa T}, \tag{10}$$

where a_0 is the radius of rotating particle and κ the Boltzmann constant. We thus get

$$k_4 = \frac{RT}{V\eta} \tag{11}$$

(*e.g.* $k_4 \simeq 4.0 \times 10^{10}\ \text{s}^{-1}$ in EtOH at 293K),

where R is the gas constant and V the specific volume of rotating sphere (the specific volume of rotating part ($C{-}N{-}CH{=}CH_2$) in RP is assumed to be about 50 ml).

Substituting Eq. 11 into Eq. 6″, we get

$$\frac{1}{\Phi_R} = \frac{1}{\Phi_{RP}}\left(1+\frac{k_3}{k_5}\right) + \frac{k_3 V}{\Phi_{RP} R}\cdot\frac{\eta}{T}, \tag{12}$$

where

$$\frac{1}{\Phi_{RP}}\left(1+\frac{k_3}{k_5}\right) = a, \quad \text{and} \quad \frac{k_3 V}{\Phi_{RP} R} = b.$$

The reaction quantum yield Φ_R at $\eta\ T^{-1} \rightarrow 0$ is found to be 6.7×10^{-2} (Fig. 5); *viz.*, $\Phi_{RP} \geq 6.7 \times 10^{-2}$ by means of Eq. 12. Thus, we can estimate the value of k_3 from Eqs. 8, 9, and 12 as follows:

$$k_3 \geq 9.2 \times 10^9\ \text{s}^{-1}. \tag{13}$$

If we assume that the rate constants k_3 and k_5 are approximately the same, the value of $(\Phi_{RP})^{-1}$ is equal to 7.5 from Eq. 12. We then obtain

$$k_3 \simeq 1.8 \times 10^{10}\ \text{s}^{-1}. \tag{14}$$

However, there are some problems in the approximations.

(1) The assumption $k_4 \simeq k_{-4}$ holds under the conditions that the potential energy and the frequency factor in the process k_4 are equal to those in the process k_{-4}. Strictly speaking, such conditions are unlikely, since there may be a difference in the steric hindrance between RP and RP′. Similarly, both k_3 and k_5 values may not be the same.

(2) The Debye equation is applicable to an entire molecule; the rotational diffusion in the present case is a restricted rotation.

Case C: We assume that the structural change of biradical (RP→RP′) occurs due to the Brownian movement of solvent molecules surrounding it. Einstein's theory of the Brownian movement can be applied to the diffusion of a molecule to an adjacent site.[35] When a solvent molecule adjacent to RP moves into a solvent hole with the rate constant τ_D^{-1}, an empty space may be

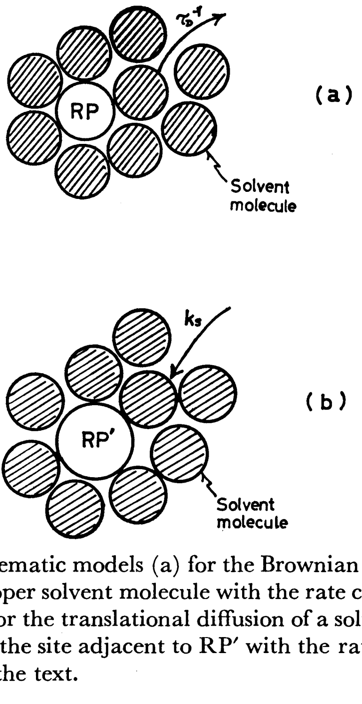


Fig. 6. Schematic models (a) for the Brownian movement of the proper solvent molecule with the rate constant τ_D^{-1} and (b) for the translational diffusion of a solvent molecule into the site adjacent to RP′ with the rate constant k_s. See the text.

produced as shown in Fig. 6(a). This makes the conformational change RP→RP′ possible. The value of k_4 may be equal to that of τ_D^{-1}. From the Einstein's equation for the Brownian movement, we have

$$k_4 \simeq \tau_D{}^{-1} = \frac{6(D_1+D_2)}{\bar{r}^2}, \tag{15}$$

where D_1 and D_2 are the diffusion constants of EtOH and RP respectively, and $\bar{r}$ is the average distance of the movement of the proper ethanol molecule ($\bar{r}=2\,a_1$, where a_1 denotes the radius of an ethanol molecule). The values of D_1 and D_2 can be determined by Stoke's formula for the translational diffusion:

$$D = \frac{\kappa T}{6\pi a_i \eta}, \tag{16}$$

where a_i is the radius of the corresponding species ($a_1 \simeq 2.85$ Å for EtOH; $a_2 \simeq 3.48$ Å for RP). From Eqs. 15 and 16, the value of k_4 can be estimated as a function of $T\eta^{-1}$:

$$k_4 = 8.6\times 10^5\, T\eta^{-1} \tag{17}$$

(*e.g.* $k_4 \simeq 2\times 10^{10}\,\mathrm{s}^{-1}$ in EtOH at 293K).

On the other hand, the rate constant k_{-4} can be evaluated by applying the Smoluchowski-Debye equation.[35,36] We assume that the conformational change RP′→RP is accomplished by the diffusion of a solvent molecule to an adjacent site with the rate constant k_s (Fig. 6(b)). The value of k_{-4} seems to be close to that of k_s:

$$k_{-4} \simeq k_s = \frac{4\pi P N\sigma(D_1+D_2)[\mathrm{solv}]}{1000}, \tag{18}$$

where D_1 and D_2 are diffusion coefficients in cm² s⁻¹; σ is the effective collision diameter in cm ($\sigma \simeq a_1+a_2 = 6.33\times 10^{-8}$ cm); N is Avogadro's number; P the steric factor (assumed to be unity); [solv] the concentration of neat EtOH (17.1 M). Thus, the value of k_{-4} is estimated from Eq. 18 to be

$$k_{-4} \simeq 5.4\times 10^{10}\,\mathrm{s}^{-1} \text{ at 293K.} \tag{19}$$

From Eqs. 6 and 17, we get

$$\frac{k_3}{\Phi_{\mathrm{RP}}} \geq 7.1\times 10^{10}\,\mathrm{s}^{-1}, \tag{20}$$

where $\Phi_{\mathrm{RP}} \geq 6.7\times 10^{-2}$. Thus

$$k_3 \geq 4.8\times 10^9\,\mathrm{s}^{-1}. \tag{21}$$

However, the value of k_3 should not exceed that of diffusion-controlled k_4 (*e.g.* $2\times 10^{10}\,\mathrm{s}^{-1}$ at 293 K). Thus, we can estimate the recombination time τ of RP as follows:

$$50\,\mathrm{ps} < \tau \leq 200\,\mathrm{ps}. \tag{22}$$

The τ value of the biradical RP is the order of $\approx 10^{-10}$ s, which is the same order of magnitude of the geminate recombination times between iodine atoms measured with picosecond pulses (70 ps in hexadecane and 140 ps in CCl_4).[5] The approximation in Case C seems to be the best.

Multiplicity and Spin Inversion of RP. The question arises as to the multiplicity of the biradical RP. If the singlet RP is produced *via* ^{1}(n, π^*), the direct back reaction ^{1}RP→NVP is faster than the recombination of ^{3}RP, since the recombination should occur after the spin inversion of ^{3}RP→^{1}RP. The time for the direct back reaction is the same as that ($\approx 10^{-11}$ s) of $\overline{{}^1\mathrm{A}\cdot\cdot\mathrm{B}}$. The processes ^{1}(n, π^*)→^{1}RP→NVP can not be observed in the present experiment, even if they are involved in the radiationless processes of NVP*. Judging from the recombination time of RP ($\approx 10^{-10}$ s) and the reactive state of NVP ^{3}(n, π^*), it is probable that the multiplicity of RP is triplet. The spin inversion time of ^{3}RP can be evaluated to be $\approx 10^{-10}$ s, since spin inversion is the rate-determining step in the recombination of ^{3}RP. The spin inversion of ^{3}RP needs time of $\approx 10^{-10}$ s to cause appreciable enhancement due to the radical-pair mechanism. Several re-encounters between the radical sites of ^{3}RP would occur before recombination. This supports Adrian's model[37] for the radical-pair mechanism.

The structure of biradical RP allows a reversible change similar to $\overline{\mathrm{A}\cdot\cdot\mathrm{B}} \leftrightarrow \overline{\mathrm{A}\cdot|\cdot\mathrm{B}}$ without further complete separation between radical sites, since the molecular chain joints them. The possibility for the formation of the $\overline{{}^3\mathrm{A}\cdot|\cdot\mathrm{B}}$ type of ^{3}RP is greater than that of freely diffusing radicals. The J value of a reorienting biradical fluctuates depending upon the distance between the radical sites [the correlation time of reorientation k_4^{-1} (or k_{-4}^{-1}) is $\approx 10^{-11}$ s in EtOH at room temperature], which decreases exponentially with increasing distance.[15] A small S-T energy gap ($2J$) of the triplet biradical gives rise to an efficient S-T mixing due to the nuclear hf and the spin-orbit interactions. The rapid spin inversion of ^{3}RP might be caused by the appreciable S-T mixing.

A similar fast spin inversion has been studied by Eisenthal *et al.*[5] using a picosecond laser at 5300 Å. At this frequency I_2 molecules are excited to the $^3\Pi_{0^+u}$ ($\nu' \simeq 33$) state. Only a small fraction of I_2 molecules are excited to the $^1\Pi_u$ state, dissociating directly. The I_2 molecules excited to the $^3\Pi_{0^+u}$ state undergo a predissociation induced by collision *via* the $^3\Pi_{1u}$ state leading to a pair of ground state, $^2P_{3/2}$, iodine atoms. According to the spin conservation rule, the radical-pair of iodine atoms in a solvent cage should be triplet. However, the geminate recombination time τ is very short (70—140 ps),[38] indicating that spin inversion takes place within τ. The fast geminate recombination of iodine atoms can be understood by the radical-pair mechanism resulting in the S-T mixing. The large spin-orbit coupling due to the heavy atom and the nuclear hf interactions may be involved in the system.

Conclusion

The mechanism of the photochemical ring expansion of NVP involving the Norrish type I dissociation at 254 nm in EtOH is shown in Fig. 4. The recombination time τ of the biradical RP was estimated to be $\approx 10^{-10}$ s. The spin inversion of the triplet biradical requires a time of about 10^{-10} s to cause efficient enhancement due to the radical-pair mechanism.

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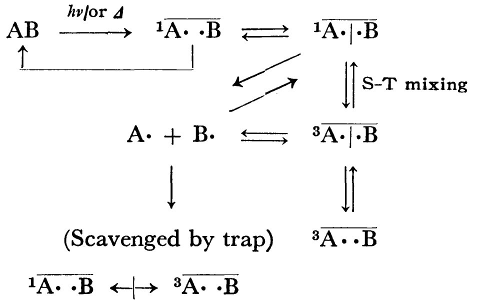
Appendix

The behavior of primary geminate and secondary recombination between radicals in fluid media schematically is shown as follows:

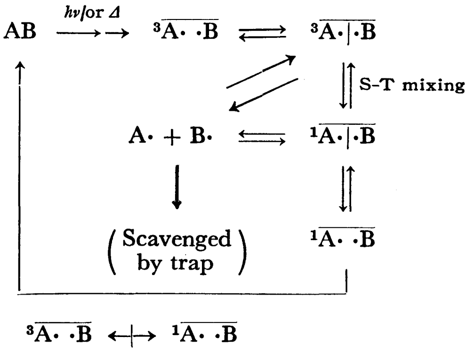
1) Radical-pair.

a) Singlet radical-pair:



(A1)

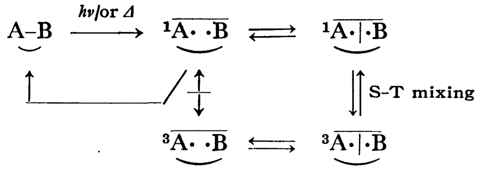
b) Triplet radical-pair.



(A2)

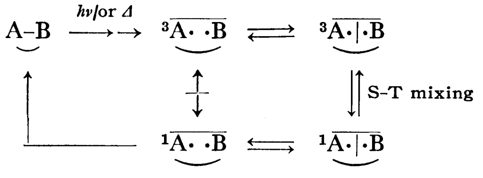
2) Biradical.

a) Singlet biradical:



(A3)

b) Triplet biradical:



(A4)

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