

MECHANISM OF THE PHOTOINDUCED RING OPENING REACTION OF 1-(2-NAPHTHOYL)AZIRIDINE IN VARIOUS HALOALKANES

S. NISHIMOTO, T. IZUKAWA and T. KAGIYA

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

(Received July 14, 1983)

Summary

Quantum yields for the photoreactions of 1-(2-naphthoyl)aziridine (NAz) to *N*-(2-chloroethyl)-2-naphthamide (CENA), *N*-(2-bromoethyl)-2-naphthamide (BENA) and 2-(2-naphthyl)-2-oxazoline (NOz) in various chloroalkanes and bromoalkanes were determined together with the yields for the fluorescence emission and intersystem crossing of NAz. The quantum yields for both CENA formation in chloroalkanes and NOz formation in bromoalkanes increased, whereas the quantum yield for fluorescence emission decreased, with increased halogen substitution in the solvent molecule. The influence of haloalkane solvents on the quantum yield for intersystem crossing was relatively small. The Stern-Volmer plot for quenching of the CENA or BENA formation by 1,3-pentadiene first increased rapidly and then asymptotically approached a straight line. A reaction mechanism via both the lowest excited singlet and triplet states of NAz accounts for the formation of both CENA and BENA.

1. Introduction

We have previously reported that 1-(2-naphthoyl)aziridine (NAz) undergoes photochemical ring opening at the C-N bond of the three-membered aziridine moiety to give *N*-(2-chloroethyl)-2-naphthamide (CENA) in chlorinated solvents and *N*-(2-bromoethyl)-2-naphthamide (BENA) together with the rearranged product 2-(2-naphthyl)-2-oxazoline (NOz) in brominated solvents [1, 2]. More recently, it has been demonstrated that the photorearrangement to NOz occurs via electron transfer quenching of the lowest excited singlet state of NAz by brominated hydrocarbons in non-polar benzene solution [3]. In this paper we report the quantum yields for the formation of CENA, BENA and NOz in various chloroalkanes and bromoalkanes together with those for the fluorescence emission and intersystem crossing of NAz. The mechanism of the photoinduced ring opening reaction is discussed on the basis of quenching experiments with 1,3-pentadiene.

2. Experimental details

2.1. Materials

NAz was prepared and purified as reported previously [1]. *tert*-butyl chloride, propyl bromide and dibromomethane were purified by distillation before use. Dichloromethane, chloroform and carbon tetrachloride were of spectroscopic grades and were used without further purification. 1,3-cyclohexadiene and 1,3-pentadiene (*cis-trans* mixture) were distilled before use.

2.2. Spectra and analyses

Fluorescence spectra were recorded on a Jasco FP-550A fluorescence spectrophotometer. ^1H nuclear magnetic resonance (NMR) spectra were measured using a JEOL PMX-60 spectrometer with tetramethylsilane as the internal standard. High performance liquid chromatography (HPLC) analysis was performed using a TOYO SODA HLC-802UR high performance liquid chromatograph with the same column conditions as reported in ref. 1.

2.3. Reaction quantum yield

Monochromatic light at 334 nm was isolated from a Philips high pressure mercury arc (SP-500) using a Toshiba UV-33 glass filter and an aqueous solution filter of path length 1 cm containing nickel sulphate (0.3 g ml^{-1}). This combined filter had a maximum transmittance of 35.8% at 334 nm and a bandpass halfwidth of 29.5 nm. The intensity of incident light was determined as $2.11 \times 10^{-6} \text{ einstein ml}^{-1} \text{ min}^{-1}$ using a ferrioxalate actinometer ($\Phi_{\text{Fe}^{\text{II}}} = 1.23$ at 334 nm) [4]. Solutions of 2.5 mM NAz in various haloalkanes (4 ml) placed in a glass finger tube attached to an optical flat quartz cell (1 cm path length) were deaerated by repeated freeze-pump-thaw cycles under reduced pressure (less than 40 mPa), sealed and then irradiated using the 334 nm mercury line at room temperature. When the solution had been irradiated for an appropriate time it was evaporated under reduced pressure. The resulting photoproducts were subjected to HPLC analysis. The quantum yield Φ_{R} for the photoreaction was obtained as the ratio of the number of specified products to the number of quanta absorbed by NAz over the period of irradiation. Less than about 20% of the aziridine was converted.

2.4. Fluorescence quantum yield

The fluorescence spectra of 0.4 mM NAz in a series of haloalkanes were measured at room temperature under deaerated conditions ($\lambda_{\text{ex}} = 334 \text{ nm}$). The quantum yield Φ_{F} for the fluorescence emission was determined by reference to a standard solution of 0.5 mM quinine sulphate in aqueous sulphuric acid (0.5 M) [5].

2.5. Triplet quantum yield

The quantum yield Φ_{ST} for the intersystem crossing of NAz from the lowest excited singlet state S_1 to the lowest triplet state T_1 was estimated from the triplet energy transfer to 1,3-cyclohexadiene and analysis of the resultant diene dimer [6, 7]. A deaerated solution containing 87 mM NAz and 0.42 M 1,3-cyclohexadiene in various haloalkanes (3 ml) was placed in a Pyrex glass cell (1 cm path length) and was irradiated at $\lambda_{ex} = 334$ nm for less than 250 min. The direct excitation of 1,3-cyclohexadiene was ruled out under these conditions because the diene showed no absorption band at 334 nm. The dimerization of 1,3-cyclohexadiene due to photosensitization by NAz was confirmed by the 1H NMR spectrum of the resulting reaction mixture after evaporating the solvent and dissolving in $CDCl_3$. In each run the conversion of 1,3-cyclohexadiene did not exceed 10% and the self-photoreaction of NAz as a triplet sensitizer was negligible (less than 0.2% conversion). The extent of the dimerization was derived from the decrement in either the vinylic protons ($\delta = 5.90$ ppm) or the allylic protons ($\delta = 2.23$ ppm) of 1,3-cyclohexadiene relative to the virtually unchanged aziridinyl protons ($\delta = 2.54$ ppm) or naphthoyl protons ($\delta = 7.64$ ppm, $\delta = 7.95$ ppm and $\delta = 8.64$ ppm) of NAz. In the evaluation of the triplet yield we assumed that the concentration of 1,3-cyclohexadiene (0.42 M) was high enough to quench completely the triplets of NAz and that the singlet quenching of NAz by the diene made only a minor contribution [8].

3. Results and discussion

3.1. Quantum yields for the photochemical ring opening and rearrangement of 1-(2-naphthoyl)aziridine in haloalkanes

Photoirradiation of a deaerated solution of NAz in a series of haloalkanes at $\lambda_{ex} = 334$ nm and room temperature led to the same reaction characteristics as reported previously [1], *i.e.* CENA was obtained in *tert*-butyl chloride, dichloromethane, chloroform and carbon tetrachloride whereas BENA and NOz were obtained in *n*-propyl bromide and dibromomethane (Table 1). Photorearrangement of NAz to NOz did not occur in chlorinated solvents.

Neither solvent molecule is photoexcited under these conditions. It follows that photoexcitation of NAz to the S_1 state ($^1(\pi, \pi^*)$; $E_S = 353$ kJ mol $^{-1}$) [1, 3] is a primary process involved in the ring opening and rearrangement reactions (Fig. 1).

In a representative experiment, the yield of CENA produced in the photoreaction of 2.5 mM NAz in deaerated chloroform solution (4 ml) was found to increase linearly with irradiation time up to a conversion of about 20% of the aziridine (Fig. 2, curve a). In view of this linear dependence, the initial rate of formation of a given product was estimated from the corresponding yield over the irradiation period in which the overall conversion of NAz was not more than 20%. The ratio of the initial rate to the initial

TABLE 1

Quantum yields Φ_R , Φ_F and Φ_{ST} for photoreactions, fluorescence emission and intersystem crossing respectively of NAz in various haloalkanes at room temperature^a

Solvent	Irradiation time (min)	Product		Φ_F	Φ_{ST}^b	Φ_{ST}/Φ_F^c	$\{1 - (\Phi_F + \Phi_{ST})\}/\Phi_F^c$		
		CENA or BENA	NOz						
		Yield (%)	Φ_R	Yield (%)	Φ_R				
<i>tert</i> -C ₄ H ₉ Cl	490	11	0.0016	0	0	0.26	0.56	2.2 (1.0)	0.69 (1.0)
CH ₂ Cl ₂	370	19	0.0036	0	0	0.13	0.34	2.6 (1.2)	4.1 (5.9)
CHCl ₃	325	21	0.0042	0	0	0.035	0.32	9.1 (4.1)	19 (28)
CCl ₄	87	9.7	0.0075	0	0	0.013	0.22	17 (7.7)	59 (86)
<i>n</i> -C ₃ H ₇ Br	89	14	0.010	3.8	0.0028	0.012	0.28	23 (10)	59 (86)
CH ₂ Br ₂	70	7.8	0.0074	9.6	0.0091	0.007	0.33	47 (21)	94 (140)

^a Irradiated at $\lambda_{ex} = 334$ nm under deaerated conditions.

^b Estimated from the photosensitized dimerization of 1,3-cyclohexadiene.

^c The relative values are given in parentheses.

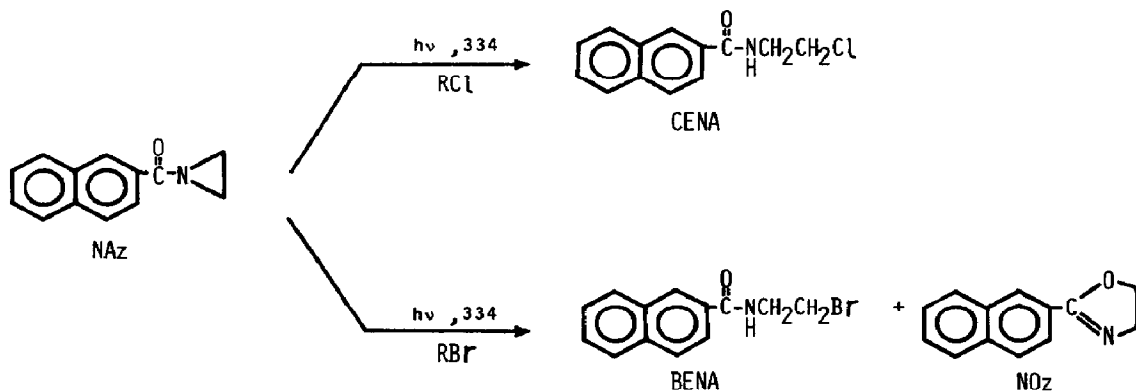


Fig. 1.

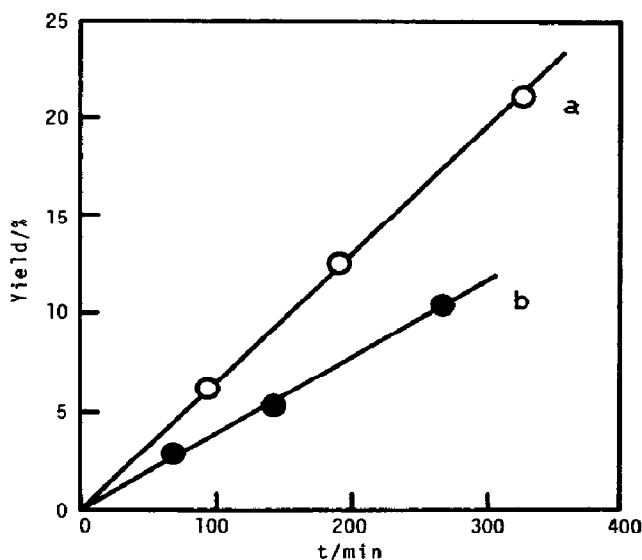


Fig. 2. Time-dependent yields of CENA (○) in the photoreaction of 2.5 mM NAz in chloroform (curve a) and of the diene dimer (●) in the photodimerization of 0.42 M 1,3-cyclohexadiene sensitized by 87 mM NAz in chloroform (curve b) on irradiation at 334 nm under deaerated conditions.

number of quanta absorbed by NAz in haloalkane solvents was used to obtain the quantum yields Φ_R for the formation of CENA, BENA or NOz as summarized in Table 1.

It is seen from Table 1 that the value of Φ_R for the formation of CENA in the chloroalkanes investigated increases by a factor of about 5 with increased chlorine substitution in the solvent molecule. In contrast, increasing bromine substitution tends to enhance the rearrangement of NAz to NOz in preference to the ring-opened BENA formation. The selectivity of the photorearrangement in dibromomethane was evaluated as 55%, which is much lower than that (82%) observed previously [3] in non-polar benzene containing 0.09 M NAz and 0.2 M dibromomethane. This difference appears

to be closely associated with the photochemical behaviour of NAz in the presence of 1,3,5-tribromobenzene in a mixed benzene–acetonitrile solvent, *i.e.* the selectivity of the rearrangement to NOz falls from 91% in benzene to 65% in acetonitrile as the polar acetonitrile content increases [3].

3.2. Quantum yields for fluorescence emission and intersystem crossing of 1-(2-naphthoyl)aziridine in haloalkanes

Figure 3 illustrates representative electronic absorption and fluorescence spectra of NAz in benzene, chloroform and dibromomethane. A distinct red shift in the absorption band of NAz in the 310 - 360 nm wavelength range was observed in dibromomethane relative to the benzene solution, while only a small spectral change occurred in the chloroform solution. This is the result of the formation of a contact charge transfer complex between the ground states of NAz and dibromomethane [3]. Such a ground state interaction is considered to be relatively unimportant in chloroform solution.

The fluorescence intensities of NAz in benzene, chloroform and dibromomethane solutions decreased in that order (Fig. 3). This order parallels that of the magnitude of the change in the spectral absorption as a result of the ground state interaction between NAz and the solvent molecule. Figure 3 also indicates that the decreased fluorescence intensity is not accompanied by an appreciable change in the profile of the emission spectrum. It follows that on weak interactions with haloalkane solvents NAz

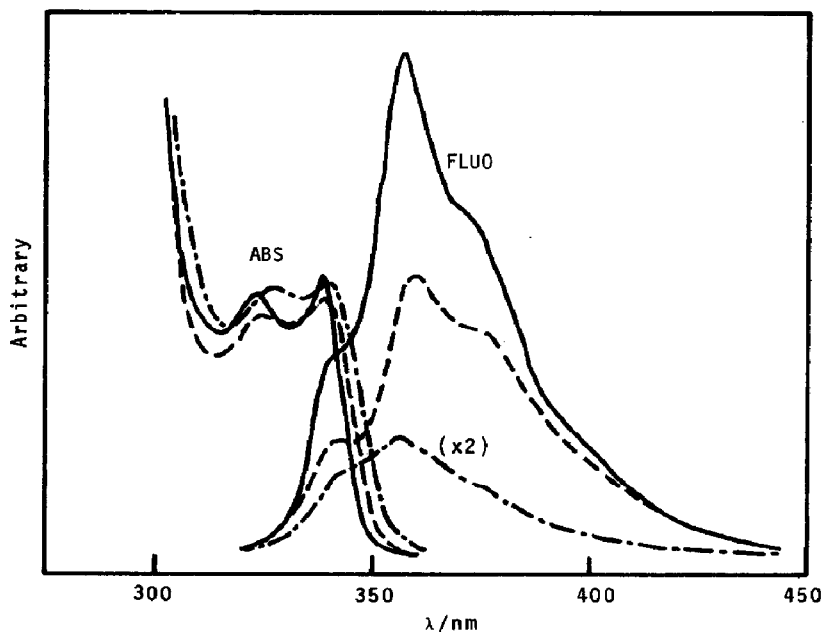


Fig. 3. Representative electronic absorption and fluorescence spectra of deaerated solutions of 0.4 mM NAz in benzene (—), chloroform (---) and dibromomethane (-·-).

is locally excited to the S_1 state and is deactivated via quenching by the solvents in competition with the fluorescence emission. The formation of a ground state complex of NAz with the haloalkane solvent would also account for the apparent fluorescence quenching.

Table 1 summarizes the quantum yields Φ_F for the fluorescence emission in various haloalkanes under deaerated conditions. The value of Φ_F in the chloroalkane series changed over a twentyfold range, decreasing with increasing chlorine substitution. Bromoalkanes reduced the Φ_F value much more effectively than chloroalkanes. For example even mono-substituted *n*-propyl bromide was comparable with carbon tetrachloride with respect to the fluorescence quenching efficiency (see Table 1).

The quantum yield Φ_{ST} for the $S_1 \rightarrow T_1$ intersystem crossing of NAz was estimated using a conventional method based on the sensitized photodimerization of 1,3-cyclohexadiene [6, 7] since the T_1 energy level of NAz ($^3(\pi, \pi^*)$; $E_T = 245 \text{ kJ mol}^{-1}$) [3] lies sufficiently above that of cyclohexadiene ($E_T = 224 \text{ kJ mol}^{-1}$) [9]. Thus the selective photoexcitation of NAz (87 mM) as a triplet sensitizer in this experiment induced dimerization of 1,3-cyclohexadiene (0.42 M) at $\lambda_{ex} = 334 \text{ nm}$ in deaerated haloalkane solutions. Typically, the dimer yield in CHCl_3 increased linearly with irradiation time up to a conversion of about 10% of the cyclohexadiene as shown in Fig. 2, curve b. Under these conditions the conversion of NAz to CENA was less than 0.2% at the dimer yield of 10.4%. The reduced yield of CENA appears to be due to the reaction between the S_1 state of NAz and chloroform because the added 1,3-cyclohexadiene would quench the T_1 state of NAz by triplet-triplet energy transfer and dimerization would occur at such a high concentration of the diene.

Table 1 shows the Φ_{ST} values obtained from the yield of cyclohexadiene dimer over the irradiation period in which the conversion of cyclohexadiene did not exceed 10%. The procedure used was similar to the evaluation of the reaction quantum yields. The Φ_{ST} value appeared to change only slightly in the series of haloalkane solvents investigated, ranging from 0.22 to 0.56. However, it should be noted that the ratio Φ_{ST}/Φ_F , which is equal to the ratio k_{ST}/k_F of the rate constant of intersystem crossing to the rate constant of fluorescence emission, increases by about a factor of 20 with the increased halogen substitution and the alternation in the solvent substituent from chlorine to bromine. This enhanced intersystem crossing of NAz is partly attributable to a normal heavy atom effect [10] of the haloalkanes (Fig. 4, where the quencher Q is 1,3-pentadiene).

The increase in the ratio $\{1 - (\Phi_F + \Phi_{ST})\}/\Phi_F$, which is equivalent to the ratio $(k_{IC} + k_{SE} + k_{SR})/k_F$ in Fig. 4, is more marked than that of Φ_{ST}/Φ_F (Table 1). This indicates that quenching of the S_1 state of NAz by the haloalkane solvents leads to enhanced internal conversion and/or the formation of an exciplex [3] more efficiently than does intersystem crossing to the T_1 state, *i.e.* $k_{IC} + k_{SE}$ is greater than k_{ST} in all solvents except *tert*-butyl chloride. It is clear from the smaller quantum yields for the formation of CENA and BENA ($\Phi_R \leq 0.010$) that the rate constant k_{SR} of the singlet

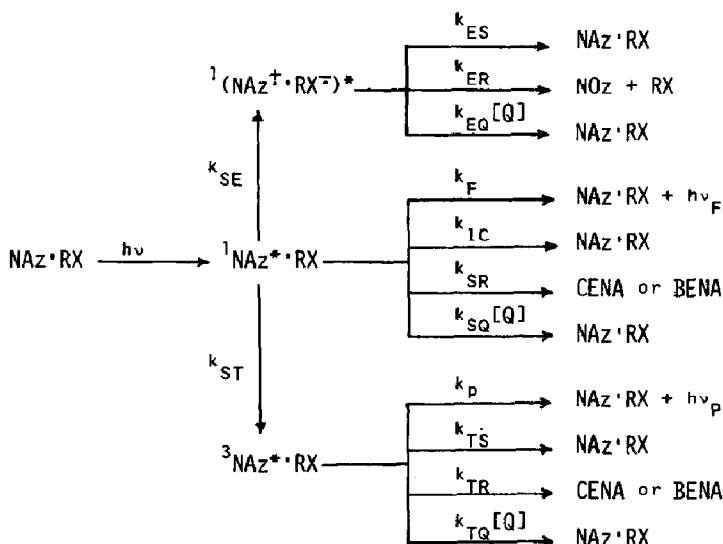


Fig. 4.

reaction is much less than the rate constants k_{IC} and k_{SE} of internal conversion and exciplex formation respectively.

3.3. Quenching of the ring opening reaction of 1-(2-naphthoyl)aziridine by 1,3-pentadiene in chloroform and dibromomethane

The yields of both CENA and BENA were reduced in the presence of 1,3-pentadiene which is a well-known quencher of both the excited singlet and triplet states of a variety of reactants [11]. Such quenching behaviour was determined in further detail for the deaerated chloroform and dibromomethane solutions. The Stern-Volmer plots of Φ_R^0/Φ_R against [1,3-pentadiene] for the quenching of the formation of CENA in chloroform and of BENA in dibromomethane are shown in Fig. 5. It is apparent in each plot that Φ_R^0/Φ_R first increases rapidly and then approaches asymptotically a straight line with a slope smaller than the initial slope on increasing the concentration of 1,3-pentadiene. This type of Stern-Volmer plot is characteristic of kinetics in which reaction and quenching occur from both the S_1 and the T_1 states of a reactant [12]. We therefore concluded that the reactions of Naz in both the S_1 and T_1 states with chloroform and dibromomethane lead to the formation of CENA and BENA respectively.

The mechanism of the formation of CENA and BENA can be represented as in Fig. 4, in which local photoexcitation of a weak interaction of Naz with a haloalkane (RX) occurs and produces primarily the S_1 state. Photoexcitation of the ground state complex would make a minor contribution relative to this local excitation of Naz [3]. In accord with the previous result [3], the production of NOz via the singlet exciplex state of Naz is also involved in this scheme. Furthermore the ring opening reaction of Naz from both the S_1 and T_1 states to give halogen-substituted CENA or BENA is assumed to be pseudo first order

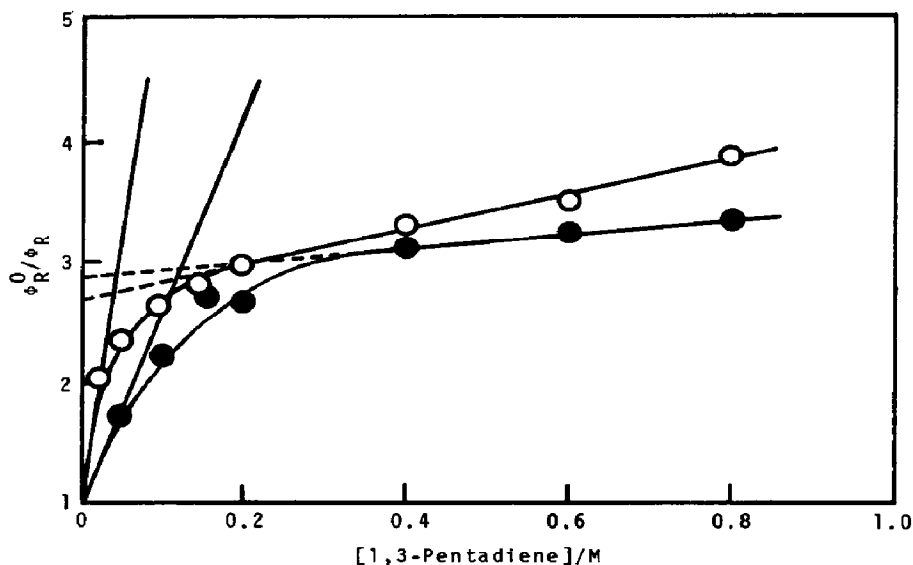


Fig. 5. Stern-Volmer plots for the quenching by 1,3-pentadiene of the formation of CENA in chloroform (○) and of BENA in dibromomethane (●) on irradiation of 2.5 mM NAz at 334 nm under deaerated conditions.

($k_{SR}[^1\text{NAz}^*\cdot\text{RX}]$ and $k_{TR}[^1\text{NAz}^*\cdot\text{RX}]$) because the excited NAz would react most efficiently with the nearest-neighbour haloalkane solvent molecule.

According to this scheme, the Stern-Volmer expression for quenching of the ring opening reaction is given by [12]

$$\frac{\Phi_R^0}{\Phi_R} = \frac{(\Phi_{SR}^0 + \Phi_{TR}^0)(1 + k_{SQ}\tau_S^0[Q])(1 + k_{TQ}\tau_T^0[Q])}{\Phi_{SR}^0 + \Phi_{TR}^0 + \Phi_{SR}^0 k_{TQ}\tau_T^0[Q]} \quad (1)$$

where

$$\Phi_{SR}^0 = k_{SR}\tau_S^0 = \frac{k_{SR}}{k_F + k_{IC} + k_{ST} + k_{SE} + k_{SR}} \quad (2)$$

$$\Phi_{TR}^0 = k_{ST}\tau_S^0 k_{TR}\tau_T^0 = \frac{\Phi_{ST}^0 k_{TR}}{k_P + k_{TS} + k_{TR}} \quad (3)$$

The initial slope at a quencher concentration [Q] of zero can be derived from eqn. (1) as follows:

$$\text{initial slope} = k_{SQ}\tau_S^0 + \frac{\Phi_{TR}^0/\Phi_{SR}^0}{1 + \Phi_{TR}^0/\Phi_{SR}^0} k_{TQ}\tau_T^0 \quad (4)$$

The final slope and intercept of the asymptote as [Q] increases to infinity are given by

$$\text{final slope} = \left(1 + \frac{\Phi_{TR}^0}{\Phi_{SR}^0}\right) k_{SQ}\tau_S^0 \quad (5)$$

TABLE 2

Kinetic parameters derived from quenching data^a for the formation of CENA in chloroform and of BENA in dibromomethane

	<i>CENA formation</i>	<i>BENA formation</i>
Initial slope (M ⁻¹)	45	12
Final slope (M ⁻¹)	1.5	0.63
Final intercept	2.7	2.8
$k_{\text{SQ}}\tau_{\text{S}}^0$ (M ⁻¹)	0.56	0.22
$k_{\text{TQ}}\tau_{\text{T}}^0$ (M ⁻¹)	70	18
$\Phi_{\text{TR}}^0/\Phi_{\text{SR}}^0$	1.7	1.8
$k_{\text{TR}}\tau_{\text{T}}^0/k_{\text{SR}}\tau_{\text{S}}^0$	5.3	5.6

^aSee the Stern-Volmer plots in Fig. 5.

$$\text{final intercept} = \left(1 + \frac{\Phi_{\text{TR}}^0}{\Phi_{\text{SR}}^0}\right) \left(1 - \frac{\Phi_{\text{TR}}^0 k_{\text{SQ}}\tau_{\text{S}}^0}{\Phi_{\text{SR}}^0 k_{\text{TQ}}\tau_{\text{T}}^0}\right) \quad (6)$$

Kinetic parameters for the formation of CENA (k_{SE} is neglected in this case) and BENA obtained from the quenching data shown in Fig. 5 using eqns. (4) - (6) are listed in Table 2. It can be seen that the quenching efficiencies $k_{\text{SQ}}\tau_{\text{S}}^0$ and $k_{\text{TQ}}\tau_{\text{T}}^0$ of 1,3-pentadiene for the S₁ state and the T₁ state of NAz in chloroform are greater by factors of 2.5 and 3.9 respectively than those in dibromomethane. This suggests that the singlet and triplet lifetimes τ_{S}^0 and τ_{T}^0 in the absence of a quencher are both reduced in dibromomethane solution compared with those in chloroform solution. It is also interesting that the ratio $\Phi_{\text{TR}}^0/\Phi_{\text{SR}}^0$ has almost the same value (about 1.8) for the formation of both CENA and BENA. This implies that the quantum yield for the ring opening reaction from the T₁ state of NAz is about twice that of the reaction from the S₁ state regardless of whether the solvent is chloroform or dibromomethane. Substitution of the quantum yield Φ_{ST}^0 for intersystem crossing (see Table 1) in $\Phi_{\text{TR}}^0/\Phi_{\text{SR}}^0$ (which is equivalent to $\Phi_{\text{ST}}^0 k_{\text{TR}}\tau_{\text{T}}^0/k_{\text{SR}}\tau_{\text{S}}^0$) gives the estimates of $k_{\text{TR}}\tau_{\text{T}}^0/k_{\text{SR}}\tau_{\text{S}}^0$ listed in Table 2. These values show that the intrinsic reactivity $k_{\text{TR}}\tau_{\text{T}}^0$ of NAz in the T₁ state is about five times higher than the reactivity $k_{\text{SR}}\tau_{\text{S}}^0$ in the S₁ state for ring opening of the aziridine moiety to produce CENA in chloroform and BENA in dibromomethane.

References

- 1 S. Nishimoto, T. Izukawa and T. Kagiya, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1484.
- 2 S. Nishimoto, T. Izukawa and T. Kagiya, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2937.
- 3 S. Nishimoto, T. Izukawa and T. Kagiya, *J. Chem. Soc., Perkin Trans. II*, (1983) 1147.
- 4 J. G. Calvert and J. N. Pitts, Jr. (eds.), *Photochemistry*, Wiley, New York, 1966, p. 783.
- 5 W. H. Melhuish, *J. Phys. Chem.*, 65 (1961) 229.
- 6 D. Valentine, N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, 86 (1964) 5202.

- 7 S. G. Cohen, G. A. Davis and W. D. K. Clark, *J. Am. Chem. Soc.*, **94** (1972) 869.
- 8 L. M. Stephenson, D. G. Whitten, G. F. Vesley and G. S. Hammond, *J. Am. Chem. Soc.*, **88** (1966) 3665.
- 9 G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85** (1963) 477.
- 10 J. G. Calvert and J. N. Pitts, Jr. (eds.), *Photochemistry*, Wiley, New York, 1966, p. 304.
N. J. Turro (ed.), *Modern Molecular Photochemistry*, Benjamin, New York, 1978, p. 191.
- 11 F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro and J. C. Dalton, *J. Am. Chem. Soc.*, **92** (1970) 1793.
R. G. Brown and D. Phillips, *J. Am. Chem. Soc.*, **96** (1974) 4784.
D. A. Labianca, G. N. Taylor and G. S. Hammond, *J. Am. Chem. Soc.*, **94** (1972) 3679.
A. A. Lamola, *Tech. Org. Chem.*, **14** (1969) 96.
- 12 J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2** (1970) 133.