

PRESSURE EFFECTS ON THE PHOTOCYCLOADDITION OF 2-ADAMANTANONE WITH FUMARONITRILE

NICHOLAS J. TURRO[†], WEN-SHENG CHUNG and MASAMI OKAMOTO[‡]

Department of Chemistry, Columbia University, New York, NY 10027 (U.S.A.)

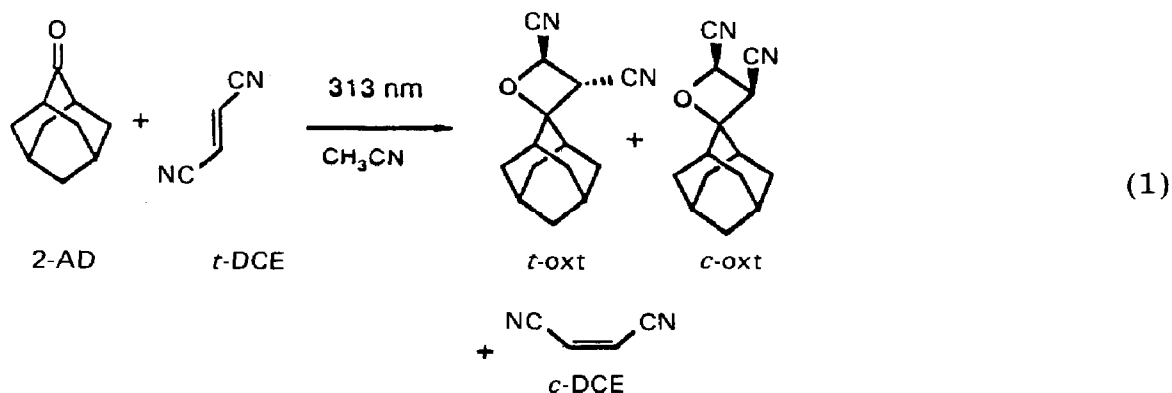
(Received May 5, 1988)

Summary

The photochemical [2+2] cycloaddition of 2-adamantanone (AD) with *trans*-dicyanoethylene (*t*-DCE) was studied in acetonitrile as a function of pressure, and the activation volumes for both singlet and triplet reactions were determined. The competing reactions between excited singlet and triplet states of AD were found to be pressure dependent. At high pressure, the intersystem crossing rate, k_{st} , from singlet to triplet increased, and as a result the singlet lifetime of AD was shortened and the triplet reaction which leads to *cis*-*trans* isomerization of the starting olefin became favored as pressure was increased. The Stern-Volmer slopes were found to correlate linearly with solvent viscosity; however, the triplet reaction (k_q^t/k_t) correlated linearly only with the solvent dielectric constant.

1. Introduction

Irradiation of acetonitrile solutions of 2-adamantanone (AD) and *trans*-dicyanoethylene (*t*-DCE) leads to the formation of oxetanes (for reviews of oxetane formation see refs. 1 - 4) and to the *cis*-*trans* isomerization of the olefin as shown in eqn. (1).

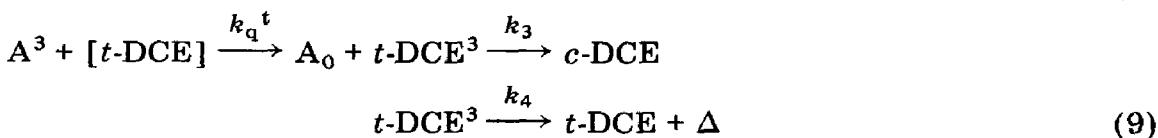
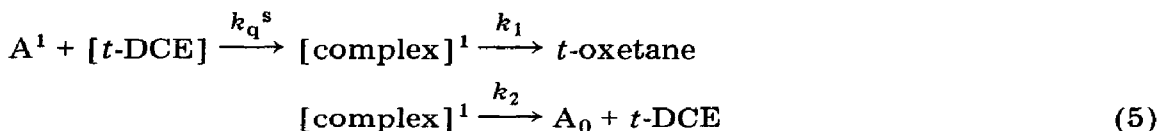


[†] Author to whom correspondence should be addressed.

[‡] Current address: Technical College, Kyoto Institute of Technology, Kyoto 606, Japan.

Kinetic analysis reveals that the oxetane formation occurs by attack of the singlet AD $^1n,\pi^*$ state on the ground state olefin [5]. The photocycloaddition reaction [6], although inefficient, is quite stereospecific: at low conversion, only *trans*-oxetane is formed. The *cis*-oxetane appears only after isomerization of the starting olefin to *cis*-dicyanoethylene (*c*-DCE) has occurred. It has also been shown that *cis*-*trans* isomerization occurs exclusively via ketone triplet sensitization [5, 7 - 9].

Scheme 1 shows the accepted mechanism [5, 8, 9] for the photoreaction of AD with *t*-DCE.



$$\frac{\Phi_{t\text{-oxt}}}{\Phi_{c\text{-DCE}}} = \frac{k_q^s(k_t + k_q^t[t\text{-DCE}])}{k_{st}k_q^t} \frac{k_1(k_3 + k_4)}{(k_1 + k_2)k_3}$$

$$= a\{(k_q^s/k_{st})[t\text{-DCE}] + k_q^s k_t / (k_{st} k_q^t)\} \quad (10)$$

where $a = k_1(k_3 + k_4)/k_3(k_1 + k_2)$, $k_t = k_p + k_d^t$ and $k_s = k_f + k_d^s$

Scheme I.

At high concentrations of *t*-DCE the singlet state is trapped efficiently and there will be little intersystem crossing to the AD triplet state; hence, only a small amount of sensitized isomerization of the *t*-DCE occurs. Intermediates, such as an exciplex [10, 11], a charge transfer complex [5, 12] or a diradical [13] have been suggested to explain the observation that even at concentrations of *t*-DCE such that nearly all of the AD singlets are quenched by *t*-DCE the quantum yield of oxetane formation is still much smaller than unity [2].

Since the cycloaddition presumably involves the approach and interaction of two roughly parallel π -electron systems, bond formation can occur in a stereospecific fashion. From these considerations, the photocycloaddition of alkyl ketones was proposed to occur through a concerted, or quasi-concerted, attack of the nucleophilic π^* system of the n, π^* singlet state of the ketone on the empty π^* orbital of *t*-DCE [14, 15].

Although pressure has long been known to be a valuable tool in the elucidation of reaction mechanisms [16], little work has been published concerning photochemical processes at high pressure [17]. We report here the results of an investigation of the influence of pressure on the photochemical processes in the reaction of AD singlet and triplet with *t*-DCE.

2. Experimental details

2.1. Reagents

Spectroscopic grade acetonitrile (Eastman Kodak) was used without further purification. AD (Aldrich) and 1-adamantanol (Aldrich) were used as received. Fumaronitrile (Aldrich) was decolorized with activated carbon (Fisher Scientific) and recrystallized from benzene until no residual absorption above 240 nm was observed.

2.2. Fluorescence quenching

Solutions of 0.05 M AD and 0.05 - 0.2 M fumaronitrile in acetonitrile were prepared. The standard fluorescence intensities were checked between different runs and were plotted against time. The complete fluorescence spectra were taken, then studies were conducted using the emission intensity at the λ_{\max} of fluorescence. Fluorescence spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer or a SPEX DM1B Fluorolog double spectrometer with excitation at 313 nm. A circulated water supply maintained the sample chamber temperature at 25.0 ± 0.5 °C during the irradiation. The high pressure instrument has been described previously [18].

At least five determinations of sample fluorescence peak height (after subtraction of the emission from solvent) *vs.* standard were taken at each quencher concentration. The variation was found to be less than 5%. The absorbance of all solvents was checked periodically with a Perkin-Elmer UV-visible spectrophotometer to determine if any competitive absorption due to the quencher was occurring. In no case did the quencher cause the absorption of solution to increase.

Since the shape of the fluorescence spectrum did not vary with pressure, the ratio of the fluorescence intensities at the maximum peak (422 nm, at 0.1 MPa and 298 K) is regarded as the ratio of the respective quantum yields. (The spectrum, after being corrected by a standard NBS tungsten-halogen lamp (Optronic Lab. Inc.) provided by SPEX company, was found to have a λ_{\max} at 440 ± 2 nm for AD (0.05 M in acetonitrile).)

2.3. Gas chromatography product analysis

Solutions of 0.05 M AD in acetonitrile were prepared with or without a measured amount of quencher in 10 ml volumetric flasks. 1-Adamantanol (2.5 mM) was used as an internal standard. Either 0.1 ml or 4 ml of sample was irradiated at 313 nm by a Xe-Hg 1000 W lamp with a filter solution (1.4 mM K_2CrO_4 in a 9.4 mM aqueous solution of K_2CO_3) and was maintained at low conversions (<10%). Gas chromatographic analyses were carried out on a Varian series 3700 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3390 A reporting integrator and an HP-1 cross-linked methyl silicone gum phase column (12 m \times 0.2 mm \times 0.33 mm).

2.4. Photolysis of AD and *t*-DCE

Irradiation of AD (1.5 g) and *t*-DCE (2.2 g) in acetonitrile (50 ml) provides a mixture of *trans*- and *cis*-oxetanes ($\geq 95\%$ based on unrecovered AD). The structures of the oxetanes are fully characterized from their 1H -NMR, ^{13}C -NMR, gas chromatography-mass spectrometry (GC-MS) and by comparison with data from the literature.

3. Results and discussion

3.1. Quenching of AD fluorescence by *t*-DCE [5, 8]

The Stern-Volmer (S-V) treatment of fluorescence quenching follows eqn. (11), where I° is the unquenched emission intensity and I is the intensity at various *t*-DCE concentrations.

$$\frac{I^\circ}{I} = 1 + k_q^s \tau_f [t\text{-DCE}] \quad (11)$$

A plot of I°/I against *t*-DCE concentration was found to be linear as predicted by eqn. (11) (see Fig. 1). The S-V slopes decreased with application of pressure from $39 \pm 2 \text{ M}^{-1}$ (0.1 MPa) to $32 \pm 2 \text{ M}^{-1}$ (203 MPa). Previous studies reported that $k_q^s \tau_f = 40 \text{ M}^{-1}$ and that $\tau_f = 8.0 \text{ ns}$ for AD at atmospheric pressure [19]. The relative singlet lifetime τ_f of AD at high pressures was measured by monitoring the fluorescence spectra and UV absorption [20]; therefore, k_q^s values can be obtained from S-V slopes with the reported value of τ_f . The observed relative singlet lifetimes τ_f and k_q^s are summarized in Table 1.

3.2. GC product analysis

A plot of the ratio of quantum yields for oxetane and isomerization, $\Phi_{t\text{-ox}t}/\Phi_{c\text{-DCE}}$, vs. $[t\text{-DCE}]$ yields a slope equal to ak_q^s/k_{st} and an intercept, $ak_q^s k_t/k_{st} k_q^t$ (see Fig. 2). On the assumption that the partition function, a (refer to Scheme I), is not changed by pressure, the experimental results of product distribution analysis are summarized in Table 2. The bimolecular quenching rate k_q^s , which leads to exciplex formation, is found to decrease

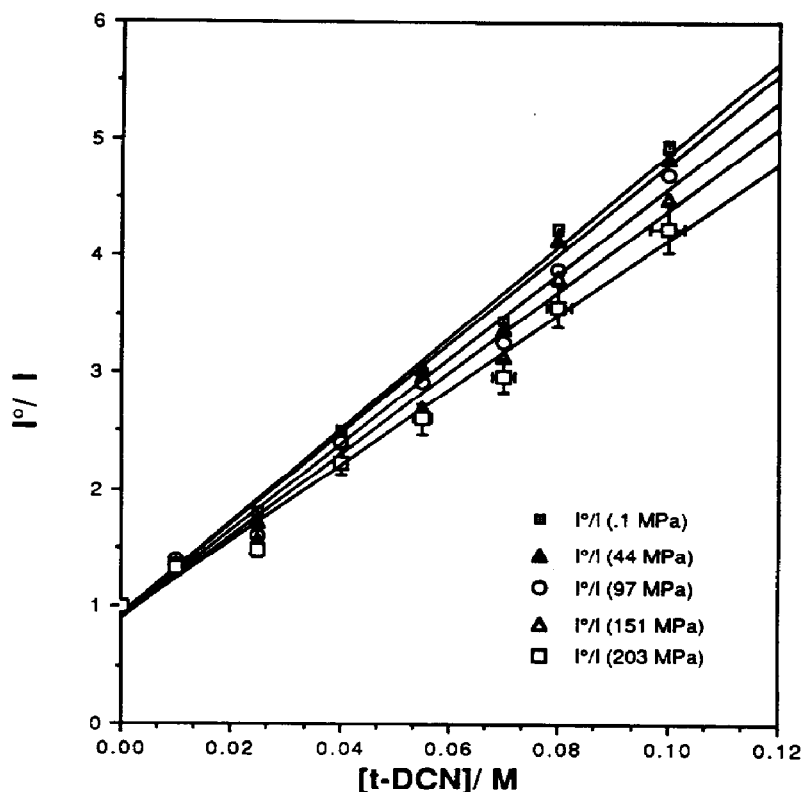


Fig. 1. Stern–Volmer plot of fluorescence quenching of AD by *t*-DCE in CH_3CN at 25 °C as a function of pressure (without correction for compressibility).

TABLE 1

Results^a of fluorescence quenching of AD by *t*-DCE in CH_3CN at 25 °C

<i>P</i> (MPa)	ϵ_{max} ^b	Φ_f ^c	τ_{rel} ^d	<i>S</i> – <i>V</i> slopes ^e	k_q^s	k_{st}^f	k_{diff}^g
0.1	1.00	1.00	1.00	1.00	1.00	1.00	1.00
44	1.06	1.02	0.97	0.98	1.01	1.01	0.86
97	1.12	1.06	0.95	0.93	0.98	1.09	0.72
151	1.21	1.07	0.88	0.89	1.01	1.22	0.61
203	1.26	1.10	0.87	0.82	0.94	1.27	0.51
ΔV^\ddagger ($\text{cm}^3 \text{mol}^{-1}$)				1.0 ± 0.1		-3.2 ± 0.6	8.2 ± 0.1

^aValues at high pressure are all relative to standard values at 0.1 MPa.

^bError about 3%, without correction for compressibility.

^c $\lambda_{\text{ex}} = 313 \text{ nm}$, monitored at $I_{\text{max}}^\circ = 422 \text{ nm}$, error about 2%, without correction for solvent compressibility.

^dDerived from ref. 20. See text.

^eError about 5%.

^fRelative k_q^s divided by relative slope (k_q^s/k_{st}) from Table 2; error about $\pm 18\%$.

^gDiffusion rates were calculated by Stokes–Einstein equation, $k_d = 8RT/2000\eta$, where η data were from ref. 21.

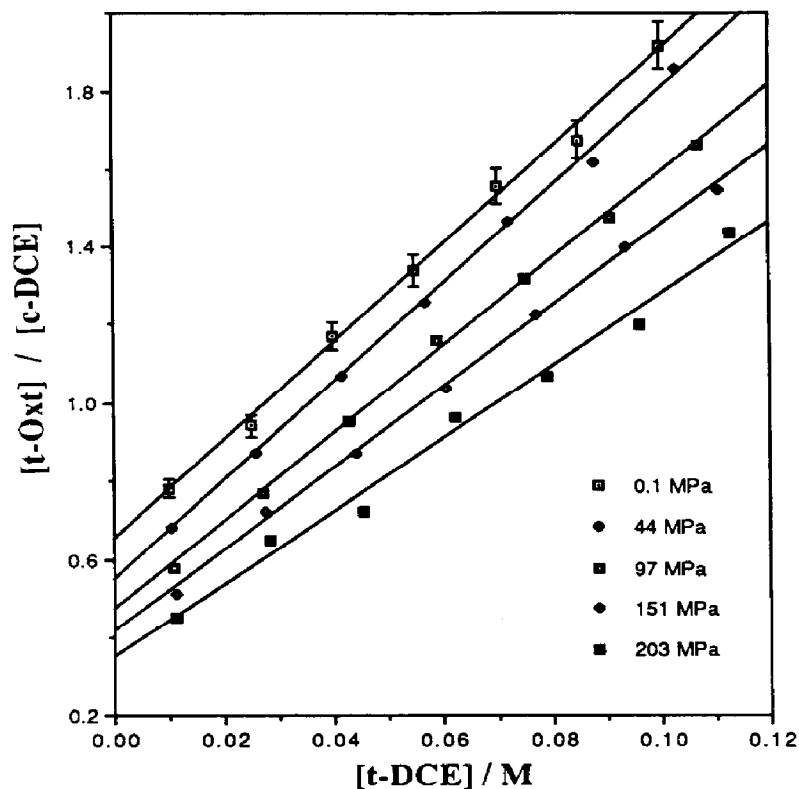


Fig. 2. $\Phi_{t\text{-Oxt}}/\Phi_{c\text{-DCE}}$ as a function of the t -DCE concentration and pressure at 25 °C.

TABLE 2

Results of GC product analysis of the ratio of quantum yields for the formation of oxetane to c -DCE

Pressure (MPa)	Relative slope ^a (k_q^s/k_{st})	Relative intercept ^a $k_q^s k_t / (k_{st} k_q^t)$	Relative slope/ Relative intercept ^b k_q^t/k_t
0.1	1.00	1.00	1.00
44	1.00	0.85	1.18
97	0.90	0.72	1.25
151	0.83	0.63	1.32
203	0.74	0.54	1.37
$\Delta\Delta V^\ddagger$ ($\text{cm}^3 \text{mol}^{-1}$)	$+3.7 \pm 0.3$		-7.4 ± 1.1

^aErrors about $\pm 10\%$.

^bErrors about $\pm 15\%$.

slightly (about 5%) over the pressure range studied. At first, this seems surprising, since reactions for bond formation are invariably promoted by application of pressure [22 - 25]. For such a near-diffusion-controlled

process, one would expect that as the solvent viscosity increases the rate should decrease. However, the rate of singlet state quenching k_q^s is usually considered to be a product of k_{diff} and the partition function $k_r/(k_r + k_{-q})$ from the encounter complex [26 - 28], where k_{-q} is the rate constant for diffusion of the encounter pair out of the solvent cavity, and k_r is the rate constant for the quenching reaction. As pressure increases the diffusion rate k_{diff} slows down, but, concurrently, pressure may favor the formation of a charge transfer complex, *i.e.* with higher $k_r/(k_r + k_{-q})$ ratio. A similar conclusion was reached in the study of the temperature dependence of fluorescence quenching of AD and acetone by a series of olefins [5]. The quenching of AD by *cis*-1,3-pentadiene decreases slightly with decreasing temperature (about 10%). To date, there are only several known cases in which an increase in pressure decreases the cycloaddition quantum yield: the cycloaddition of ethylene to maleic anhydride [29], which is due to a simultaneous quenching process, and the dimerization of 9-methylanthracene [26], which is due to a diffusion-controlled mechanism.

We consider that the pressure dependence may have its origins in several factors including viscosity η [27, 28, 30, 31], dielectric constant ϵ [21, 27, 32] and activation volume of the transition state. The S-V slopes $k_q^s \tau_f$ and GC analysis slopes k_q^s/k_{st} correlate linearly with the viscosity changes with pressure for acetonitrile, whereas the relative k_q^t/k_t correlates linearly only with the change in the dielectric constant with pressure for acetonitrile (see Figs. 3 and 4). These results suggest that, at high pressure, the intersystem crossing rate k_{st} of the singlet excited state to the triplet state increases, leading to the shortening of the singlet excited state lifetime of AD. As a result, the triplet-sensitized *cis-trans* isomerization of starting alkene becomes a relatively favored process.

In the current investigation the quadratic function $\ln k = a + bp + cp^2$ was employed [22 - 25] to get the volume of activation at zero pressure from the equation

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = - \frac{\Delta V^\ddagger}{RT} \quad (12)$$

From measurement of $\ln(k_q^s/k_{st})$ and $\ln(k_q^t/k_t)$ as a function of pressure from 0.1 to 203 MPa, the activation volumes for AD with *t*-DCE are found to be $+3.7 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ and $-7.4 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$ respectively. That is, the singlet reaction gives a positive activation volume, $\Delta V_q^{s,\ddagger} - \Delta V_{st}^\ddagger$, of $+3.7 \text{ cm}^3 \text{ mol}^{-1}$, and the triplet reaction gives a negative activation volume, $\Delta V_q^{t,\ddagger} - \Delta V_t^\ddagger$, of $-7.4 \text{ cm}^3 \text{ mol}^{-1}$. The activation volume difference for triplet reaction is a combination of two processes and further investigation of the unimolecular decay processes involving the phosphorescence from the triplet state is required. $\Delta V_q^{t,\ddagger}$ may be negative, since ΔV_t^\ddagger is expected to be very small.

The observed fluorescence quenching yields, Φ_f , of AD in acetonitrile are listed in Table 1. Since $I^\circ/I = \Phi_f^\circ/\Phi_f$, $I_{422 \text{ nm}}^\circ$ can be used instead of the

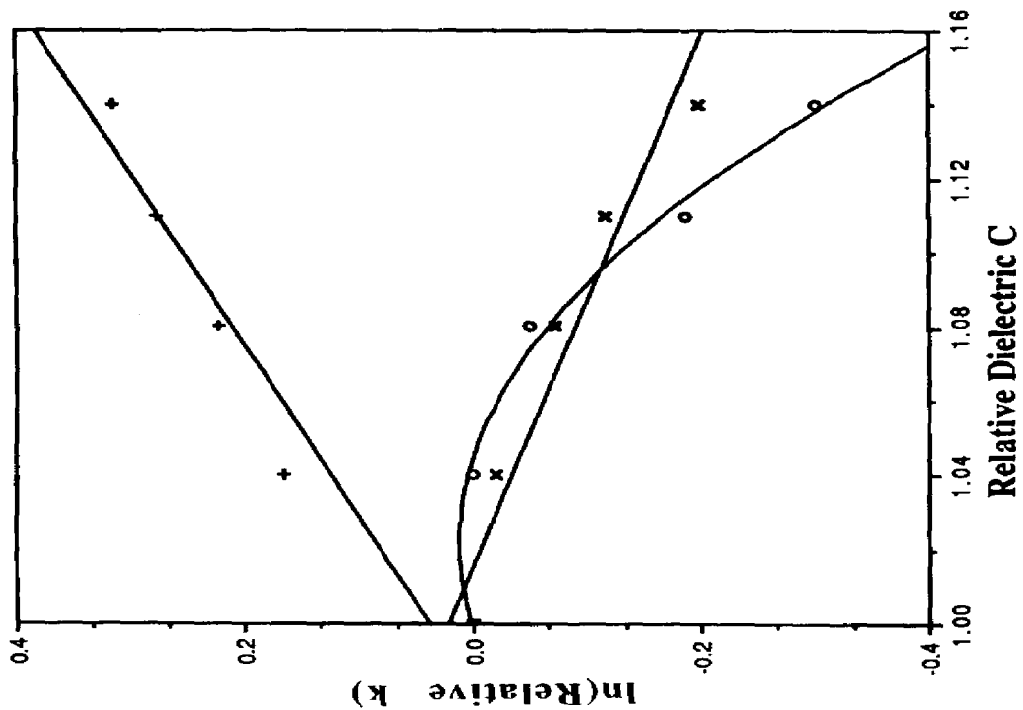


Fig. 3. Plot of $\ln(\text{Relative } k)$ against relative solvent viscosity at 25 °C: ○, $\ln(R. k_q^s/k_{st})$; ×, $\ln(R. S-V \text{ slopes})$; +, $\ln(R. k_q^t/k_t)$.

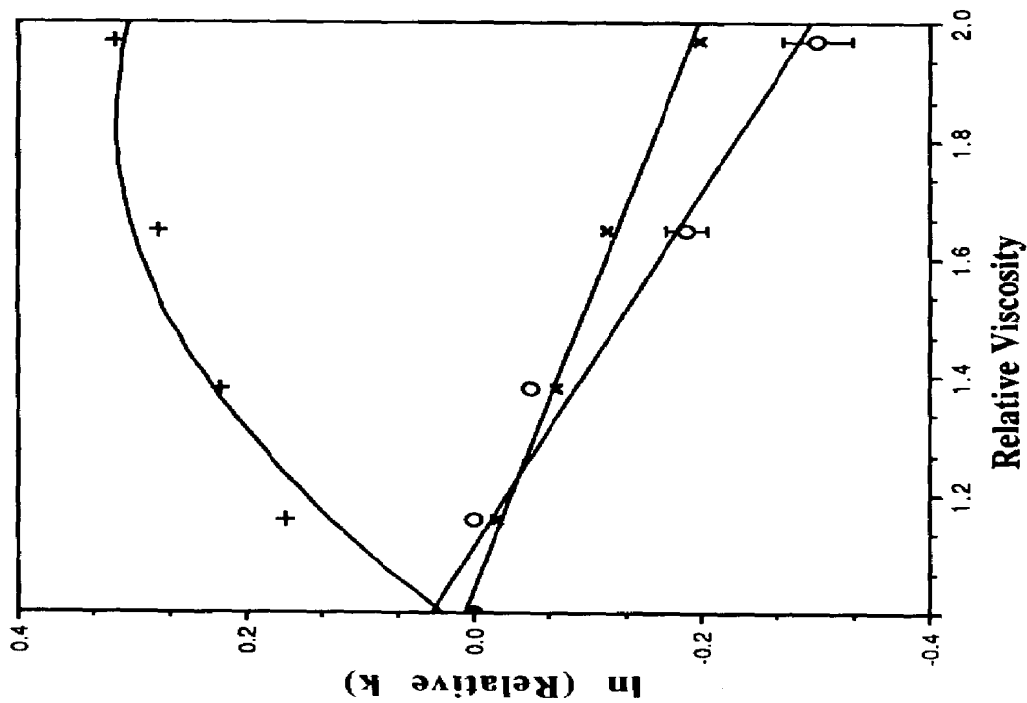


Fig. 4. Plot of $\ln(\text{Relative } k)$ against relative solvent dielectric constant at 25 °C: ○, $\ln(R. k_q^s/k_{st})$; ×, $\ln(R. S-V \text{ slopes})$; +, $\ln(R. k_q^t/k_t)$.

more rigorously correct quantum yield $\Phi_f^\circ (=k_f/(k_f + k_{st} + k_d^s))$ [33]. The observed increase in fluorescence efficiencies and decrease in τ_f of AD at high pressure can be explained in terms of the following mechanisms. Increased pressure may increase the rates of the primary decay routes of the AD singlet, which are intersystem crossing (k_{st}) to the lowest triplet, internal conversion (k_d^s) to the ground state and the intrinsic rate of fluorescence (k_f) from the n,π^* singlet state of AD. The intersystem crossing rate, k_{st} , listed in Table 1 increased by about 27% over the range of pressure applied (more accurate lifetime measurements by the single-photon-counting technique are needed to confirm the pressure dependence of the intersystem rate k_{st}). This increase in k_{st} leads to the observed shortening of the singlet lifetime at higher pressure compared with that at ambient pressure; therefore the singlet reaction which leads to oxetane formation is relatively unfavored compared with the triplet reaction of cis-trans isomerization. Alternatively, the observed increase in the absorptivity and fluorescence efficiencies could result from an increased rate of fluorescence. These pressure-accelerated radiative (k_f) and non-radiative (k_{st}) rate constants are consistent with all of the results presented here, and are confirmed by the observation that both S-V slopes (from fluorescence quenching) and relative slopes of product ratio (from GC analysis) show a very similar pressure dependence (Fig. 3). In the study of the pressure effect on the luminescence of 3-hydroxyflavone and indole. Salman and Drickamer found a correlation between k_f and solvent dielectric constant. In acetonitrile at 450 MPa, k_f increased by 21% - 26% and ϵ by 35% [27, 31]. Hara *et al.* [34] also have proposed similar mechanisms in a high pressure study of the UV properties and fluorescence of solid AD to explain the increase in fluorescence efficiencies caused by pressure, and a pressure-dependent UV absorption spectrum.

Three accepted pathways for [2+2] cycloadditions are (1) the two-step reaction via a diradical (2) the two-step reaction via a zwitterionic intermediate and (3) the one-step mechanism in which the formation of the two new σ bonds is concerted, but not necessarily synchronous [35]. For a diradical pathway a modest solvent dependence and ΔV^\ddagger of about -15 to -20 $\text{cm}^3 \text{mol}^{-1}$ are anticipated [36 - 38]. Polar [2+2] cycloadditions show large and negative activation volumes which are of the same order of magnitude as those for Diels-Alder reactions [36 - 38]. Previous pressure studies on the concerted Diels-Alder reaction have shown that the activation volumes are large and negative and are generally not very sensitive to solvent polarity [22 - 25]. However, in this work, both S-V slopes (from fluorescence analysis) and relative slopes of product ratio (from GC analysis) are shown to be depressed by increasing the pressure (*i.e.* with positive ΔV^\ddagger), a result consistent with increasing solvent viscosity with pressure. In turn, this conclusion is consistent with the diffusion-controlled photocycloaddition of AD with *t*-DCE. To investigate the true volume profile for oxetane formation, measurements on reactions that are slower than diffusion-controlled quenching is necessary.

4. Conclusions

The photochemical [2+2] cycloaddition of AD with *t*-DCE is pressure dependent, with the triplet product, *c*-DCE, being favored over the singlet oxetane product. (Since the pressure dependence of the volume of activation can be correlated with the compressibility of the solvent [27, 32], the concentrations of *t*-DCE at high pressures were corrected for the compressibility of acetonitrile.) At high pressure, quenching of the singlet state of AD becomes less efficient owing to the increasing rate of a competing process, intersystem crossing from the singlet state to the triplet state. The results from both fluorescence quenching and relative quantum yield studies are consistent with an increase in solvent viscosity with pressure and a diffusion-controlled singlet reaction.

Acknowledgments

We thank Professor W. J. le Noble at SUNY Stony Brook for his helpful discussions and comments on this work, and Dr. Kevin Welsh for his assistance in preparing the manuscript. The authors also thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research.

References

- 1 D. R. Arnold, *Adv. Photochem.*, **6** (1968) 301.
- 2 J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, **21** (1970) 499.
- 3 W. M. Horspool (ed.), *Synthetic Organic Photochemistry*, Plenum, 1984, Chapter 8, p. 425.
- 4 G. Jones, in A. Padwa (ed.), *Organic Photochemistry*, Vol. V, Dekker, 1981, Chapter I.
- 5 N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes and J. C. Dalton, *J. Am. Chem. Soc.*, **99** (1977) 3023.
- 6 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA, 1978, Chapter 11.
- 7 N. J. Turro and G. L. Farrington, *J. Am. Chem. Soc.*, **102** (1980) 6056 - 6063.
- 8 G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam and J. C. Liu, *J. Am. Chem. Soc.*, **97** (1975) 7110.
- 9 J. C. Dalton, P. A. Wriede and N. J. Turro, *J. Am. Chem. Soc.*, **92** (1970) 1318.
- 10 R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13** (1980) 45 - 50.
- 11 N. J. Turro, P. A. Wriede and J. C. Dalton, *J. Am. Chem. Soc.*, **90** (1968) 3274.
- 12 J. A. Barltrop and H. A. J. Carless, *J. Am. Chem. Soc.*, **94** (1972) 1951.
- 13 N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, **92** (1970) 320.
- 14 N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk and D. M. Pond, *J. Am. Chem. Soc.*, **92** (1970) 6978.
- 15 N. D. Epiotis, *J. Am. Chem. Soc.*, **94** (1972) 1946.
- 16 N. S. Issacs, *Liquid Phase High Pressure Chemistry*, Wiley, 1981, Chapter 6.
- 17 W. J. le Noble and K. Tamura, *Tetrahedron Lett.*, (1977) 495 - 498, and references cited therein.
R. C. Neuman and C. T. Berge, *Tetrahedron Lett.*, (1978) 1709.

- M. Okamoto and H. Teranishi, *J. Am. Chem. Soc.*, *108* (1986) 6378.
N. J. Turro, M. Okamoto, I. R. Gould, R. A. Moss, W. Lawrynowicz and L. M. Hadel, *J. Am. Chem. Soc.*, *109* (1987) 4973.
- 18 N. J. Turro and T. Okubo, *J. Am. Chem. Soc.*, *103* (1981) 7224.
 - 19 J. C. Dalton, D. M. Pond and N. J. Turro, *J. Am. Chem. Soc.*, *92* (1970) 2173.
 - 20 J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.*, *93* (1971) 3569.
 - 21 M. L. Fetterolf and H. W. Offen, *J. Phys. Chem.*, *89* (1985) 3320.
 - 22 H. Kelm (ed.), *High Pressure Chemistry*, Reidel, 1978, pp. 281 - 309.
 - 23 T. Asano and W. J. le Noble, *Chem. Rev.*, *78* (1978) 407 - 489.
 - 24 B. S. El'yanov and E. M. Vasylytskaya, *Rev. Phys. Chem. Jpn.*, *50* (1980) 169 - 183.
 - 25 R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, *92* (1970) 2918, 7149.
 - 26 F. Tanaka and J. Osugi, *Rev. Phys. Chem. Jpn.*, *42* (1972) 85 - 93.
 - 27 W. D. Turley and H. W. Offen, *J. Phys. Chem.*, *88* (1984) 3605 - 3607.
 - 28 T. R. Evans, *J. Am. Chem. Soc.*, *93* (1971) 2081.
 - 29 M. F. Mirbach, M. J. Mirbach and A. Saus, *Chem. Rev.*, *82* (1982) 59 - 76, and references cited therein.
 - 30 L. A. Brey, G. B. Schuster and H. G. Drickamer, *J. Chem. Phys.*, *67* (1977) 5763.
 - 31 O. A. Salman and H. G. Drickamer, *J. Chem. Phys.*, *77* (1982) 3329.
 - 32 K. R. Srinivasan and R. L. Kay, *J. Solution Chem.*, *6* (1977) 357.
 - 33 H.-D. Brauer, R. Schmidt and H. Kelm, in H. Kelm (ed.), *High Pressure Chemistry*, Reidel, 1978, pp. 521 - 567.
 - 34 K. Hara, G. B. Schuster and H. G. Drickama, *Chem. Phys. Lett.*, *47* (1977) 462.
 - 35 G. Swieton, J. von Jouanne and H. Kelm, *J. Chem. Soc., Perkin Trans. II*, (1983) 37.
 - 36 J. von Jouanne, H. Kelm and R. Huisgen, *J. Am. Chem. Soc.*, *101* (1979) 151.
 - 37 M. Sasako, H. Tsuzuki and J. Osugi, *J. Chem. Soc., Perkin Trans. II*, (1980) 1596.
 - 38 N. S. Issacs and E. Rannala, *J. Chem. Soc., Perkin Trans. II*, (1975) 1555.

Note added in proof

Picosecond laser fluorescence spectroscopy has shown that the lifetimes of S_1 of AD decrease by only 10% over the pressure range 0.1 - 250 MPa.