The Temperature- and Viscosity-dependent Photostationary *E*/*Z* Ratio in Triplet-sensitized Photoisomerization of Cyclo-octene[1]

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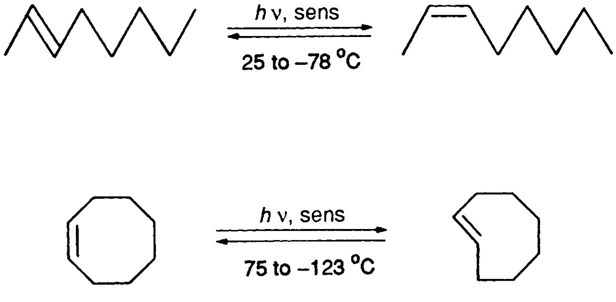
In the triplet-sensitized photoisomerization with benzene, toluene, or *p*-xylene, the photostationary *E*/*Z* ratio of cyclo-octene, $(E/Z)_{pss}$, dramatically increases with lowered irradiation temperature (+75 to −123 °C) or with increased solvent viscosity, whereas the $(E/Z)_{pss}$ ratio of oct-2-ene stayed unchanged over the temperature range +25 to −78 °C. Theoretical examinations indicate that the temperature-dependent (*E*/*Z*) value is not a simple function of solvent viscosity but also depends upon the solvent structure. The Stern–Volmer studies further revealed that the variable quenching rate constants for *Z* and *E* isomers are responsible for the temperature- and viscosity-dependent photostationary state.

The geometrical photoisomerization of aliphatic and aromatic alkenes is one of the most extensively investigated areas of organic photochemistry from both the theoretical and experimental points of view.[2–7] The *Z*–*E* isomerization of these alkenes can be effected through direct excitation and triplet photosensitization. However, the chemical consequences of the photoexcitation are substantially different between aliphatic and aromatic alkenes, mostly due to the difference in shape of the potential-energy surfaces for the singlet and triplet excited states. Because they possess rather flat, but still uneven, excited-state potential-energy surfaces, aromatic alkenes such as stilbene have long been known to give temperature- and viscosity-dependent quantum yields of photoisomerization and/or photostationary state *E*/*Z* ratios,[8–15] for which the small energy barrier encountered upon twisting the C=C bond is responsible.[3,5] In contrast, non-conjugated aliphatic alkenes, with much simplified U-shaped excited-state surfaces,[2] have never been presumed to exhibit such temperature-and/or viscosity-dependent photobehaviour.[4,6]

(*E*)-Cyclo-octene is known to suffer substantial torsional deformation around the C=C bond,[16–27] which was believed to be responsible for its unusual physical properties and chemical reactivity. In comparison with the *Z* isomer, (*E*)-cyclo-octene not only possesses a much higher strain energy[28–30] or dipole moment[16] and lower ionization potential[31,32] or singlet/triplet energies,[33] but also displays much enhanced and specific reactivity toward a variety of substrates in thermal[34–39] and photochemical reactions.[40–42]

We have previously reported that, in the triplet-sensitized photoisomerization of cyclo-octene with aromatic sensitizers, the photostationary *E*/*Z* ratios, $(E/Z)_{pss}$, are much smaller than unity[42a] and vary fairly drastically with the sensitizer employed.[42c] Thus, the $(E/Z)_{pss}$ ratio increases with increasing triplet energy (E_T) of the sensitizer. From the Stern–Volmer studies, these sensitizer E_T-dependent $(E/Z)_{pss}$ ratios were shown to be rationalized in terms of the quenching ratios varying with the sensitizer E_T, for which the endothermicity of the triplet-energy transfer process and the substantial difference in E_T are jointly responsible. In the subsequent experiments to determine the $(E/Z)_{pss}$ ratios more precisely under various conditions, we noticed that the ratios sometimes differed slightly from the previous values. The small deviation in $(E/Z)_{pss}$ was deduced to be due to the change in room temperature, (15 to 30 °C).



Scheme 1.

In this paper, we wish to report that, contrary to the well-accepted general understanding, the photostationary state *E*/*Z* ratio of cyclo-octene is drastically affected both by irradiation temperature and by solvent viscosity. Since there is no precedent for such a temperature- and/or viscosity-dependent $(E/Z)_{pss}$ ratio at least with less-strained acyclic simple alkenes, the origin of this unique dependence is elucidated by kinetic studies and its theoretical and synthetic implications are also discussed.

Experimental

Materials.—Commercially available (*Z*)-cyclo-octene, (*Z*)- and (*E*)-oct-2-enes, and aromatic photosensitizers were purified by fractional distillation. (*E*)-Cyclo-octene was prepared in the photochemical *Z*–*E* isomerization of the (*Z*)-isomer sensitized by dimethyl isophthalate and the subsequent isolation through its specific formation of a silver nitrate complex.[42d]

Hydrocarbon solvents and internal standards were stirred over concentrated sulphuric acid until the acid layer no longer turned yellow, washed with water, dried over potassium carbonate, and then fractionally distilled. Acetonitrile was

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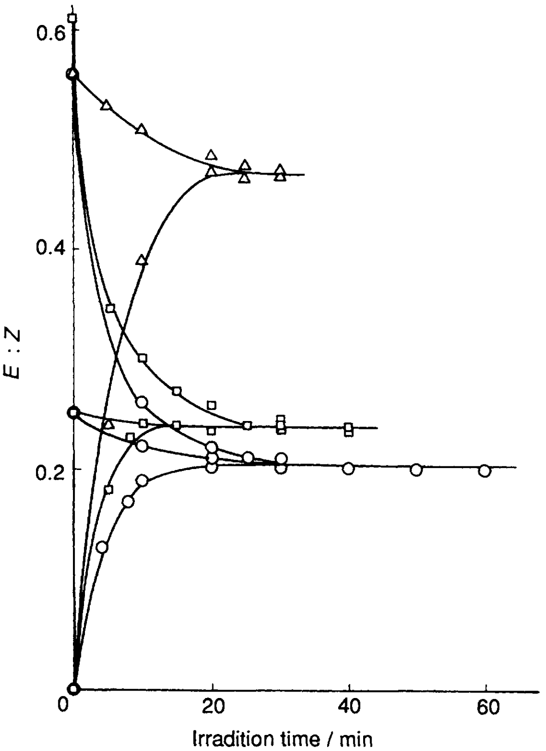

Figure 1. (*E*)- to (*Z*)-Cyclo-octene ratio as a function of irradiation time in benzene-sensitized photoisomerization of cyclo-octene of various initial isomer compositions in pentane at +25 (○), 0 (□), and −78 °C (△).

distilled twice from phosphorus pentaoxide. Ethylene glycol was fractionally distilled *in vacuo*.

Analysis.—Gas chromatographic analyses of the cyclo-octene photolysates were performed over a 3 m column of 10% β,β′-oxydipropiononitrile at 50 °C. For the oct-2-ene photolysates and when sensitizer has a retention time close to that of (*Z*)- or (*E*)-cyclo-octene, a 3 m column of 20% polyethylene glycol-300 at 65 °C was used. The injection port was maintained at 100 °C. Under the conditions employed, no appreciable thermal isomerization of (*E*)-cyclo-octene was detected, and the *Z*- and *E*-isomers of both alkenes were separated completely. The *E*/*Z* ratio was calculated from the integrated area of the respective peak.

Photolysis.—All experiments, except for that at −123 °C, were carried out in a thermostatted water (+75 to 0 ± 0.1 °C), methanol (−35 to −78 ± 0.5 °C), or ethanol (−90 to −108 ± 0.5 °C) bath. An Oxford cryostat DN1704 with a temperature controller VTC4 was used in the experiments at −123 °C. Solutions of cyclo-octene or oct-2-ene (2 mmol dm^{-3}) of given isomer compositions, containing a photosensitizer (0.1 mol dm^{-3}) and cyclo-octane or cycloheptane (0.5 mmol dm^{-3}) as an internal standard, were irradiated at 254 nm in quartz tubes under a nitrogen atmosphere by means of a 30 W mercury resonance lamp (Eikosha) fitted with a Vycor filter. The low concentration in cyclo-octene (2 mmol dm^{-3}) was employed throughout in order to avoid possible operation of the singlet mechanism at higher concentrations.[42c] The change in isomer composition following irradiation was monitored by periodic analysis of aliquots removed from the irradiated solution. In the photolyses in polar acetonitrile or ethylene glycol solution, the irradiated sample was poured into ten fold excess water and the mixture was extracted with pentane, which was then subjected to the gas chromatographic analysis. Kinetic studies were performed by using a 'merry-go-round' apparatus in a thermostatted water bath at 25 ± 0.1 °C.

Results

Temperature Effects.—At a variety of irradiation temperatures, +75 to −123 °C, the photostationary state *E*/*Z* ratios, $(E/Z)_{\text{pss}}$, were determined with cyclo-octene by approaching from both sides of the ultimate values. As was the case with the irradiation at room temperature,[42c] the major course of the photosensitization was the *Z*–*E* isomerization at every temperature examined. Typical changes of the *E*/*Z* ratio upon benzene sensitization in pentane are plotted against the irradiation time in Figure 1. The benzene sensitization of cyclo-octene was repeated in hydrocarbon solvents at various temperatures to give different $(E/Z)_{\text{pss}}$ ratios. Also examined were the photosensitizations with toluene and *p*-xylene in pentane at temperatures of +25 to −100 °C. These results are listed in Table 1, along with the sensitizer E_T values.[43]

For comparison purposes, the benzene photosensitizations of oct-2-ene were also carried out under similar photochemical conditions to give the practically invariant $(E/Z)_{\text{pss}}$ ratios over the temperature range of +25 to −78 °C, as shown in Table 1.

Solvent Effects.—Since lowering temperature inevitably makes a solvent more viscous, the effects of solvent viscosity, and also polarity, were checked to some extent at constant temperature. The benzene-, toluene-, and xylene-sensitizations of cyclo-octene were, therefore, carried out at 25 °C in typical non-polar, polar, and viscous solvents, *i.e.* hydrocarbons, acetonitrile, and ethylene glycol. Again, with all sensitizers and solvents examined, the major photoreaction was the geometrical isomerization. In ethylene glycol, however, the photoisomerization was extremely slow and the ultimate photostationary state did not appear to be reached even after prolonged irradiation. The results are listed in Table 2.

Stern–Volmer Studies.—In order to elucidate the apparent viscosity-dependent $(E/Z)_{\text{pss}}$ values shown in Table 2, the Stern–Volmer studies of the benzene-sensitized photoisomerization of cyclo-octene were carried out in solvents of different viscosity. Pentane or cyclohexane solutions containing benzene (0.1 mol dm^{-3}) as a sensitizer and pure (*Z*)- or (*E*)-cyclo-octene of given concentrations (0.2–10 mmol dm^{-3}) were irradiated at 25 °C in a 'merry-go-round' apparatus to afford varying amounts of isomeric cyclo-octene.

According to the conventional triplet-sensitization mechanism (Scheme 2) and the Stern–Volmer equation derived, the reciprocal of isomerization yield (Φ_{rel}^{-1}) was plotted as a function of reciprocal concentration of (*Z*)- or (*E*)-cyclo-octene to give a good straight line for each isomer both in pentane and in cyclohexane as shown in Figure 2.

Discussion

Assuming a twisted cyclo-octene in the triplet state (^{3}p) as a common intermediate, the photoisomerization of (*Z*)- and (*E*)-cyclo-octene sensitized by an aromatic sensitizer (S_0) is described by equations (1)–(6).

$$S_0 \xrightarrow{h\nu} {}^1S \xrightarrow{\Phi_{\text{isc}}} {}^3S \qquad (1)$$

$$^3S \xrightarrow{k_d} S_0 \qquad (2)$$

$$Z + {}^3S \xrightarrow{k_{qc}} {}^3p + S_0 \qquad (3)$$

Table 1. Photostationary E/Z ratio upon triplet-sensitized photoisomerization of oct-2-ene and cyclo-octene in some hydrocarbon solvents at +75 to −123 °C.[a]

Sensitizer	Triplet energy[b]/ kcal mol^{-1}	Solvent	T^c/°C									
			75	50	25	0	−35	−78	−90	−100	−108	−123
(Oct-2-ene)												
Benzene	84.3	Pentane	*d*	*d*	1.04	1.04	*d*	1.03	*d*	*d*	*d*	*d*
(Cyclo-octene)												
Benzene	84.3	Pentane	*d*	*d*	0.20	0.24	0.30	0.48	0.56	0.58	0.62	0.66
		Hexane	*d*	0.22	0.25	0.29	*d*	0.54	*d*	*d*	*d*	*d*
		Cyclohexane	0.21	0.23	0.26	*d*	*d*	*d*	*d*	*d*	*d*	*d*
		Methylcyclohexane	*d*	0.22	0.25	0.29	*d*	0.58	*d*	*d*	*d*	*d*
Toluene	82.8	Pentane	*d*	*d*	0.16	0.18	0.22	0.33	0.37	0.44	*d*	*d*
p-Xylene	80.3	Pentane	*d*	*d*	0.089	0.098	0.12	0.17	0.18	0.22	*d*	*d*

[a] Photostationary E/Z ratio determined by approaching from both sides of the ultimate value. [b] Ref. 43; 1 cal = 4.184 J. [c] Accuracy ±0.1–0.5 °C. [d] Not determined.

Table 2. Photostationary E/Z ratio upon sensitized photoisomerization of cyclo-octene in various solvents at 25 °C.[a]

Solvent	Viscosity/ mPa s	Sensitizer		
		Benzene	Toluene	*p*-Xylene
Pentane	0.219	0.20	0.16	0.089
Hexane	0.298	0.25	0.19	0.096
Cyclohexane	0.895	0.26	0.22	0.12
Methylcyclohexane	0.676	0.25	0.21	0.11
Acetonitrile	0.342	*b*	0.18	*b*
Ethylene glycol	15.43	>0.37[c]	*b*	*b*

[a] Photostationary E/Z ratio determined by approaching from both sides of the ultimate value, unless noted otherwise. [b] Not determined. [c] Photostationary state not attained even after prolonged irradiation of the Z-isomer.

$$E + {}^3S \xrightarrow{k_{qt}} {}^3p + S_0 \qquad (4)$$

$$ {}^3p \xrightarrow{k_{dc}} Z \qquad (5)$$

$$ {}^3p \xrightarrow{k_{dt}} E \qquad (6)$$

Scheme 2.

Superscripts refer to the multiplicities of the excited states.

In the photostationary state, the (E)- to (Z)-cyclo-octene ratio, $(E/Z)_{pss}$, is expressed as a product of the quenching rate ratio, k_{qZ}/k_{qE}, and the decay rate ratio, k_{dE}/k_{dZ}, as shown below.

$$(E/Z)_{pss} = (k_{qE}/k_{qE})(k_{dE}/k_{dZ}) \qquad (7)$$

It is interesting that, in sharp contrast with the oct-2-ene case, the photostationary state ratio obtained for cyclo-octene is evidently temperature-dependent over a wide range of temperatures (Table 1). Since the logarithm of the $(E/Z)_{pss}$ value is expressed as a linear combination of the logarithms of four rate constants [equation (7)], the Arrhenius equation is applied to each constant to give equation (8), which enables us to examine the temperature dependence of the $(E/Z)_{pss}$ ratio.

$$\ln (E/Z)_{pss} = \ln [(A_{qZ}/A_{qE})/(A_{dE}/A_{dZ})] - [(E_{qZ} - E_{qE}) + (E_{dE} - E_{dZ})]/RT \qquad (8)$$

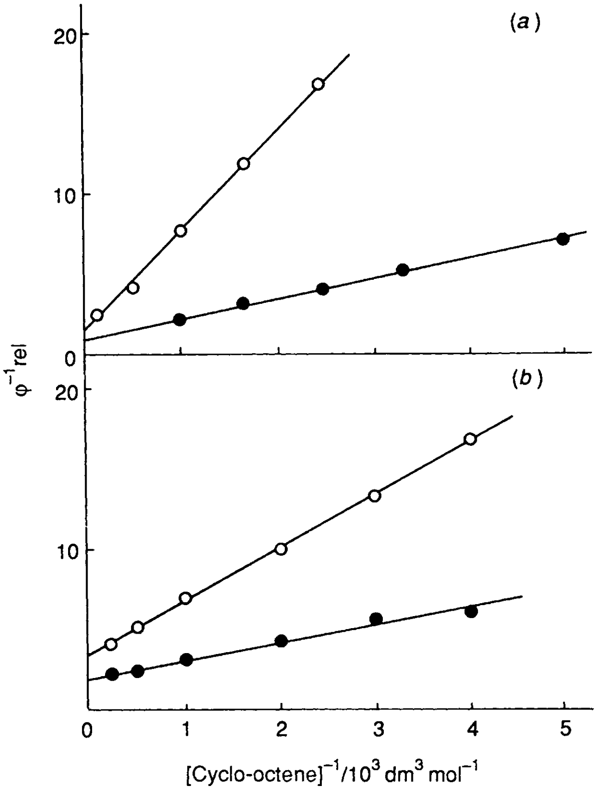

Figure 2. Stern–Volmer plots for Z-to-E (○) and E-to-Z (●) photoisomerization of cyclo-octene sensitized by benzene in pentane (*a*) and in cyclohexane (*b*) at 25 °C.

The plot of $\ln (E/Z)_{pss}$ *vs.* the inverse temperature gives a good straight line ($\gamma > 0.99$) to −100 °C for each sensitizer and solvent examined, as shown in Figure 3. Although a simple extension of the regression line for the benzene sensitization in pentane may anticipate the $(E/Z)_{pss}$ ratio of unit at *ca.* −125 °C, the ratio deviates gradually from the line at temperatures below −100 °C. From the slope and the intercept of the plot are calculated the differential activation energies, $(E_{qE} - E_{qZ}) - (E_{dE} - E_{dZ})$, and the natural logarithms of the relative frequency factors, $\ln [(A_{qE}/A_{qZ})/(A_{dE}/A_{dZ})]$, for the overall photoisomerization process. The results are listed in Table 3.

The differential activation energy and, in particular, the relative frequency factor are critical functions of the sensitizer

Table 3. Differential activation energies, $(E_{qE} - E_{dE}) - (E_{qZ} - E_{dZ})$, and relative frequency factors, $(A_{qE}/A_{dE})/(A_{qZ}/A_{dZ})$, for the overall photoisomerization of cyclo-octene sensitized by aromatics in hydrocarbon solvents.

Sensitizer	Solvent	$(E_{qE} - E_{dE}) - (E_{qZ} - E_{dZ})$[a]	$(A_{qE}/A_{dE})/(A_{qZ}/A_{dZ})$
Benzene	Pentane	0.92	23
	Hexane	0.87	17
	Cyclohexane	0.86	16
	Methylcyclohexane	0.95	20
Toluene	Pentane	0.83	25
p-Xylene	Pentane	0.73	39

[a] In kcal mol^{-1}, 1 cal = 4.184 J.

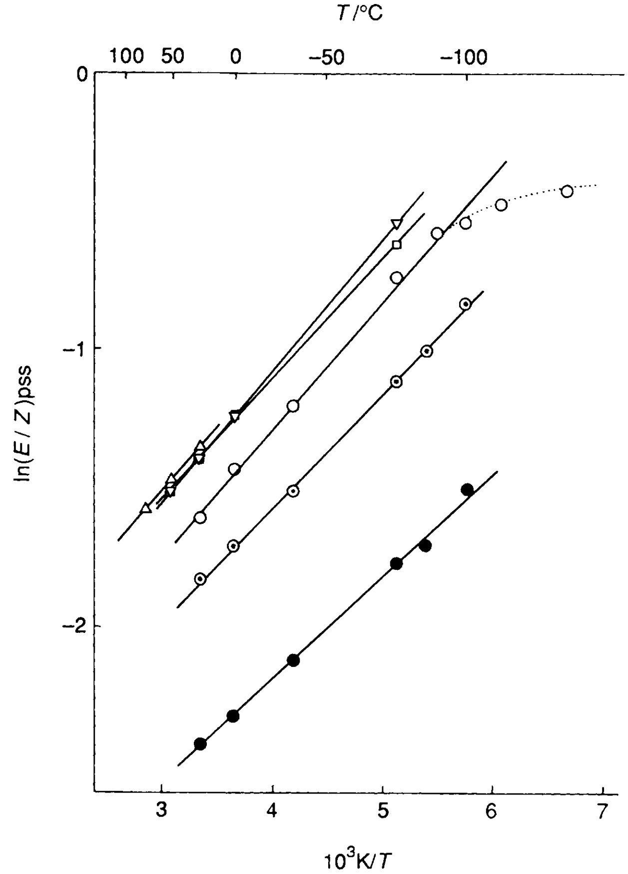

Figure 3. Temperature dependence of photostationary *E*/*Z* ratio of cyclo-octene sensitized by benzene in pentane (○), hexane (□), cyclohexane (△), and methylcyclohexane (▽), and by toluene (⊙) or *p*-xylene (●) in pentane.

and, to a lesser extent, of the solvent. According to the reaction sequence (1)–(6), the decay processes (5) and (6) are independent of the sensitizer E_T and, therefore, the activation parameters for the decay process, *i.e.* $E_{dE} - E_{dZ}$ and A_{dE}/A_{dZ}, must be invariant for the sensitizations in pentane irrespective of the sensitizer employed. Hence, any difference in activation energy or frequency factor, obtained in the same solvent, should be attributed to the quenching processes (3) and (4). This is not unexpected, since the quenching rate constants for the *Z*- and *E*-isomers are known to differ substantially in the triplet photosensitizations.[42c] Within this framework, the temperature independence of $(E/Z)_{pss}$ values for oct-2-ene is reasonably understood, since the less-strained acyclic alkenes, including oct-2-ene, give $(E/Z)_{pss}$ values of approximately unity and both the quenching and decay ratios are believed to be very close to unity.[44,45]

The viscosity of solvent also affects the $(E/Z)_{pss}$ value substantially. As can be seen from Table 2, with all sensitizers employed, the $(E/Z)_{pss}$ value increases with increasing solvent viscosity, while the solvent polarity does not significantly affect the ratio.

Empirically, the temperature dependence of solvent viscosity is expressed by the Andrade equation (9) where *B* and *C* are

$$\ln \eta = \ln B + C/T \qquad (9)$$

the constants obtained experimentally for each solvent. Combination of equations (8) and (9) leads to equation (10), in which the $(E/Z)_{pss}$ ratio is expressed as a function of viscosity.

$$\begin{aligned}\ln (E/Z)_{pss} = {} & \ln [(A_{qZ}/A_{qE})/(A_{dE}/A_{dZ})] + \\ & \ln B[(E_{qZ} - E_{qE}) + (E_{dE} - E_{dZ})]/C \\ & - \ln \eta \times [(E_{qZ} - E_{qE}) + (E_{dE} - E_{dZ})]/C \qquad (10)\end{aligned}$$

Although the data in Table 2 were plotted according to equation (10), the resulting plot did not appear to show a linear relationship, indicating that the change in $(E/Z)_{pss}$ is not a simple function of viscosity but may be rationalized by the combination of viscosity and some other solvent properties.

Equation (10) was applied also to the temperature-dependent $(E/Z)_{pss}$ values shown in Table 1. As can be seen from Figure 4, the plots of $\ln (E/Z)_{pss}$ against $\ln \eta$ give good straight lines for all solvents. Interestingly the slope and the intercept appear to depend upon the solvent category. Thus, the acyclic and cyclic solvents afforded distinctly different slope and intercept, which are, however, quite comparable to each other within the category.

Since the temperature- and solvent-dependent $(E/Z)_{pss}$ values of cyclo-octene upon triplet photosensitization are shown to arise from the changes in, not only solvent viscosity, but also solvent structure, we carried out Stern–Volmer studies in two representative solvents. A steady-state treatment of the sequence (1)–(6) leads to the Stern–Volmer equations (11) and (12) for the reciprocal quantum yields of *Z* to *E* and of *E* to *Z* photoisomerizations.

$$\Phi^{-1}_{Z\to E} = \Phi_{isc}\frac{k_{dZ} + k_{dE}}{k_{dE}}\left(1 + \frac{k_d}{k_{qZ}[Z]}\right) \qquad (11)$$

$$\Phi^{-1}_{E\to Z} = \Phi_{isc}\frac{k_{dZ} + k_{dE}}{k_{dZ}}\left(1 + \frac{k_d}{k_{qE}[E]}\right) \qquad (12)$$

The Stern–Volmer constant ($k_q\tau$) for each isomer is given by dividing the intercept by the slope and the decay ratio (k_{dE}/k_{dZ}) as a ratio of the intercepts of equations (11) and (12).

The Stern–Volmer studies of benzene sensitization of cyclo-octene in pentane and cyclohexane at 25 °C gave good straight lines in both solvents, as shown in Figure 2. The kinetic parameters derived are listed in Table 4. Importantly, the quenching ratio ($k_{qZ}/k_{dE} = 0.56$) in cyclohexane is far greater

Table 4. Kinetic parameters for triplet photoisomerization of cyclo-octene sensitized by benzene at 25 °C.

Solvent	Viscosity/ mPa s	$k_{qZ}\tau$/ dm^3 mol^{-1}	$k_{qE}\tau$/ dm^3 mol^{-1}	Quenching ratio k_{qZ}/k_{qE}	Decay ratio k_{dE}/k_{dZ}	$(E/Z)_{pss}$ calc.[a]	obs.
Pentane	0.219	280	760	0.37	0.5	0.19	0.20
Cyclohexane	0.895	1 030	1 850	0.56	0.5	0.28	0.26

[a] Calculated by $(k_{qZ}/k_{qE})(k_{dE}/k_{dZ})$.

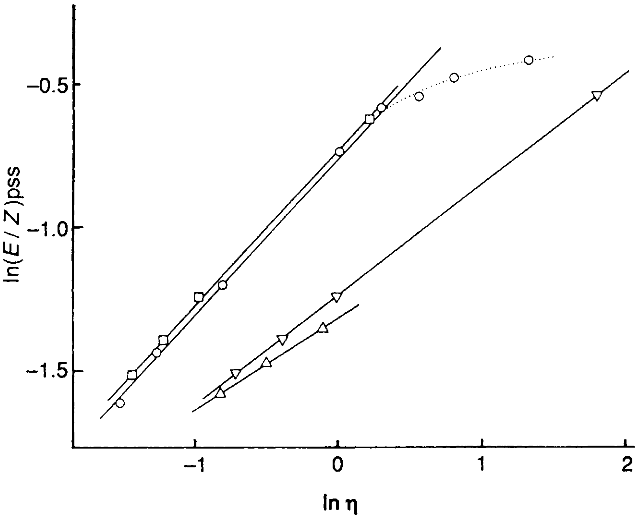

Figure 4. Viscosity dependence of photostationary E/Z ratio of cyclo-octene sensitized by benzene in pentane (○), hexane (□), cyclohexane (△), and methylcyclohexane (▽).

than that (0.37) in pentane, whereas the decay ratio k_{dE}/k_{dZ} is comparable in both solvents. The $(E/Z)_{pss}$ values, calculated as products of the quenching ratio k_{qZ}/k_{qE} and the decay ratio k_{dE}/k_{dZ}, are in good agreement with the observed values (Table 4). Therefore, the temperature- and viscosity-dependent $(E/Z)_{pss}$ value of cyclo-octene is attributable solely to the variable quenching ratio. The sensitivity of the quenching ratio to temperature and solvent viscosity/structure is inferred to originate from the large difference in E_T between Z- and E-isomers which does not exist in the less strained acyclic alkene, oct-2-ene.

In this context, it is probable that the smaller cycloalkenes also exhibit similar temperature- and viscosity-dependent behaviour of the $(E/Z)_{pss}$ value, although their E-isomers are highly strained and the temperature-dependent photochemistry has not been explored in detail.[46,47] Synthetically, the dependence found in this study may be used as a convenient tool for enhancing chemical yield in the one-step synthesis of highly strained alkene from its geometrical isomer through photosensitized isomerization.

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