M^{-1} s⁻¹. Part of the difference may reflect the difference in extinction coefficients.

The combination of CH_3O_2 radicals could give CH_2O + $CH_3OH + O_2$ either directly via a cyclic intermediate,²⁰ or indirectly via the intermediate formation of CH₃O radicals.²¹ We could not observe either CH₃O or CH₂O formation and, therefore, could not distinguish between the two possibilities. In our experiments, direct formation of formaldehyde, for example, would produce <0.3% absorption at 3050 Å and was therefore not measureable. On subjecting a static sample to 15 flashes and then examining it on a Cary spectrophotometer, the expected amount of CH₂O was observed.

Acknowledgment. This research was sponsored by the U.S. Energy Research and Development Administration under contract with the Union Carbide Corporation.

References and Notes

- C. J. Hochanadel, J. A. Ghormley, and P. J. Ogren, J. Chem. Phys., (1)56, 4426 (1972).
 T. T. Paukert and H. S. Johnston, *J. Chem. Phys.*, 56, 2824 (1972).
 G. Herzberg and J. Shoosmith, *Can. J. Phys.*, 34, 523 (1956).

- (4) D. A. Parkes, D. M. Paul, C. P. Quinn, and R. C. Robson, Chem. Phys. Lett., 23, 425 (1973).
- F. C. James and J. P. Simons, Int. J. Chem. Kinet., VI, 887 (1974).
 A. M. Bass and A. H. Laufer, Int. J. Chem. Kinet., V, 1053 (1973).
- (7) H. E. Van den Bergh and A. B. Callear, Trans. Faraday Soc., 67, 2017 (1971).
- A. H. Laufer and A. M. Bass, Int. J. Chem. Kinet., VII, 639 (1975). (8) N. Basco, D. G. L. James, and F. C. James, Int. J. Chem. Kinet., (9) IV, 129 (1972).
- (10) (a) R. Renaud and L. C. Leitch, Can. J. Chem., 32, 545 (1954); (b) (10) (a) A. Heinada and B. C. Johnston, J. Am. Chem. Soc., 91, 1276 (1969).
 (11) C. J. Hochanadel, J. A. Ghormley, and J. W. Boyle, J. Chem. Phys.,
- 48, 2416 (1968); Rev. Sci. Instrum., 39, 1144 (1968).
- 40, 2410 (1906); *Hev. Sci. Instrum.*, 39, 1144 (1968).
 (12) A. M. Bass and A. H. Laufer, *J. Photochem.*, 2, 465 (1973–1974).
 (13) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1967, p 453.
 (14) H. E. Van den Bergh, A. B. Callear, and R. J. Norstrom, *Chem. Phys.* (14) H. E. Van den Bergh, A. B. Callear, and R. J. Norstrom, *Chem. Phys.* (14) H. E. Van den Bergh, A. B. Callear, and R. J. Norstrom, *Chem. Phys.* (15) (1607).
- Lett., 4, 101 (1969).
- (15) N. Basco, D. G. L. James, and R. D. Suart, Int. J. Chem. Kinet., II, 215 (1970).
- (16) M. Pohlonen, L. Leinonen, H. Lemmetyinen, and J. Koskikallio, Finn. Chem. Lett., 207 (1974).

- (17) B. Hickel, J. Phys. Chem., **79**, 1054 (1975).
 (18) J. K. Thomas, J. Phys. Chem., **71**, 1919 (1967).
 (19) G. C. Stevens, R. M. Clarke, and E. J. Hart, J. Phys. Chem., **76**, 3863 (1972).
- (1972).
 (20) G. A. Russell, J. Am. Chem. Soc., 79, 3871 (1957).
 (21) W. C. Sleppy and J. G. Calvert, J. Am. Chem. Soc., 81, 769 (1959).

Direct and Sensitized Cis-Trans Photoisomerization of Cyclooctene. Effects of Spin Multiplicity and Vibrational Activation of Excited States on the Photostationary Trans/Cis Ratio¹

Yoshihisa Inoue,* Setsuo Takamuku, and Hiroshi Sakurai

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan (Received May 24, 1976)

The direct and sensitized cis-trans photoisomerizations of cyclooctene were investigated in the liquid phase along with photosensitization in the vapor phase. Upon direct photoisomerization at 1849 Å, an anomalously high photostationary state ratio as obtained for strained cycloalkene, i.e., trans/cis = 0.96, was observed after prolonged irradiation. A number of carbonyl and aromatic additives with triplet energy $(E_T) > 72$ kcal/mol were effective for sensitizing the cis-trans isomerization and the sensitizers with $E_T > 79$ kcal/mol gave a definite photostationary trans/cis ratio of 0.049. On vapor-phase photosensitization, some of these same sensitizers and others with $E_{\rm T} > 80$ kcal/mol gave higher ultimate trans/cis ratios, which increased up to 0.20 with increasing triplet energy of the sensitizer employed. The effects of spin multiplicity and vibrational activation of the excited states on the photostationary state are discussed and the potential curves for the ground state and the excited singlet and triplet states of cyclooctene which account for the above results are proposed.

Introduction

Photochemical cis-trans isomerization when sterically allowed is a universal photoreaction of alkenes and has been studied in considerable detail.² With simple alkenes where direct excitation is difficult because of weak absorption in the UV region above 2300 Å,3 triplet sensitization and the use of acyclic alkenes as substrates have been adopted in most photoisomerization studies to produce an alkene triplet state. The triplet state of an acyclic alkene thus generated, and probably the singlet state as well, is assumed to decay to the cis or trans isomer with equal probability, since the potential energy curves for the electronically excited singlet and triplet states of ethylene,⁴ in which energy minima of the both excited states occur when the methylene groups are orthogonal, can be used as models for those of acyclic alkenes. As demonstrated in the vapor-phase photosensitized cis-trans isomerization of 2-butene,⁵ in open-chain alkenes any vibrational excitation in the triplet state is believed to have

no significant influence on the photostationary trans/cis ratio in accord with the above accepted view on the potential surface of the excited states. However, less is known of the cis-trans photoisomerization of cycloalkenes with steric restrictions,⁶ and the geometry and the energetics of the excited states of these molecules have not been discussed.

In the present paper, we report a study on the direct and sensitized cis-trans photoisomerization of cyclooctene in the vapor and liquid phases and discuss the drastic effects of spin multiplicity of the excited states involved and of vibrational activation in the triplet state on the photostationary trans/cis ratio, which have not been observed in the photoisomerization of acyclic alkenes.

Experimental Section

Materials. Commercially available cis-cyclooctene was purified by fractional distillation through a spinning-band column and preparative gas chromatography to a purity

| TABLE I: | Liquid-Phase | Photosensitized | Cis-Trans |
|-------------|---------------|--------------------|-----------|
| Isomerizati | ion of Cycloo | ctene ^a | |

| | Sensitizer | Concn, M | $E_{\mathrm{T}},$ kcal/mol | $(trans/cis)_{pss}{}^b$ |
|----|-----------------------|-------------|----------------------------|-------------------------|
| 1 | Benzene | 0.4 | 84.4 | 0.048 |
| | | 0.04 | | 0.047 |
| 4 | Toluene | 0.4 | 82.8 | 0.052 |
| 7 | <i>p</i> -Xylene | 0.4 | 80.4 | 0.047 |
| | | 0.04 | | 0.046 |
| 8 | Durene | 0.25 | 80.0 | 0.041 |
| 9 | Benzamide | 0.005 | 79.3 | 0.050 |
| 10 | Benzonitrile | 0.4 | 76.5 | 0.031 |
| 11 | <i>m</i> -Tolunitrile | 0.4 | 75.1 | 0.024 |
| 12 | Propiophenone | 0.4 | 74.5 | 0.033 |
| 13 | Acetophenone | 0.4 | 73.7 | 0.032 |
| | - | 0.04 | | 0.030 |
| 14 | 4-Methylacetophenone | 0.4 | 72.9 | 0.017 |
| 15 | 1-Tetralone | 0.4 | 72.2 | 0.009 |
| 16 | Phenylacetylene | 0.4 | 72.0 | 0 |
| 17 | Benzaldehyde | 0.4 | 72.0 | 0 |
| 18 | Benzophenone | 0.25 | 68.6 | 0.005 |
| 19 | Fluorene | 0.035 | 68.0 | 0 |

^a The concentration of cyclooctene was 0.08 M. ^b Photostationary state *trans*- to *cis*-cyclooctene ratio.

of 99.5%. The product contained a small amount (0.5%)of cyclooctane but was free from the trans isomer. *trans*-Cyclooctene was prepared by a three-step process starting from its cis isomer. The procedure consisted of performic acid oxidation of *cis*-cyclooctene to *trans*-cyclooctane-1,2-diol,⁷ followed by condensation with benzaldehyde to give the acetal, and subsequent treatment with *n*-butyllithium.⁸ Fractional distillation under a reduced pressure of the product gave the experimental sample of *trans*-cyclooctene (99.6% trans, 0.38% cis). The sensitizers employed in the vapor- and liquid-phase photosensitizations were purified by fractional distillation or recrystallization. *n*-Pentane was washed with concentrated sulfuric acid and then fractionally distilled.

Analysis. Gas chromatographic analyses of the reaction mixtures were performed using a 3-m column of 20% β , β -oxydipropionitrile at 50 °C or, when a sensitizer has a retention time close to that of *cis*- or *trans*-cyclooctene, a 6-m column of 15% polyethylene glycol-6000 at 70 °C. The cis-trans isomers of cyclooctene were separated completely under these conditions. As an internal standard, *n*-octane or cyclooctane was employed for the direct photolysis and the liquid-phase photosensitization.

Direct Photolysis in Liquid Phase. Direct photolyses at 1849 Å (as the effective resonance line of mercury) were run at 17 °C using a 30-W U-shaped low-pressure mercury lamp with an immersion reactor. A pentane solution containing 0.01 M cis- or trans-cyclooctene and 0.002 M *n*-octane as an internal standard was flushed with nitrogen gas and then irradiated. The product distribution following the direct irradiation was determined by gas chromatographic analysis of aliquots removed from the irradiation mixture.

Liquid-Phase Photosensitization. All experiments of liquid-phase photosensitization were carried out at 17 °C in a quartz or Pyrex tube, 1 cm in diameter, using a 500-W high-pressure mercury lamp. Pyrex tubing was used only for the ketone sensitizers. Pentane solutions of 0.08 M cyclooctene of a given isomer composition containing various sensitizers and 0.002 M cyclooctane or *n*-octane as an internal standard were flushed with nitrogen gas and then irradiated. The sensitizers are shown in Table I along with their concentrations employed. The isomer compositions following the UV irradiation were determined by periodic analysis of aliquots on gas chromatography. The photostationary states were obtained after prolonged ir-



Figure 1. Combined yield (a) and percent of *trans*-cyclooctenes recovered on direct photoisomerization: (**●**) initial composition, 99.6% trans: 0.4% cis; (**●**) 47:53; (**O**) 0:100.

radiation: ca. 3-5 h for the aromatics and 1-1.5 h for the ketone sensitizers.

Vapor-Phase Photosensitization. The apparatus and the procedures employed in the vapor-phase photosensitizations were described previously.⁹ A mercury-free vacuum system and cylindrical quartz cells, 5 cm long and 5 cm in diameter, were used. The light source was a spiral array of a 30-W low-pressure mercury lamp fitted with a Toshiba UV-25 filter which removes the 1849-Å resonance line of mercury. The vapor-phase photosensitization of a given mixture (3 Torr) of cis- and trans-cyclooctene was run in the presence of the sensitizers, the pressure of which was fixed at 3 Torr with benzene, fluorobenzene, benzotrifluoride, toluene, o-, m-, and p-xylene, and phenylacetylene, or at 1 Torr with benzonitrile. The photostationary state was obtained for each sensitizer by repeated approach from both sides of the final composition. Control runs revealed that no detectable reactions occurred in the absence of either the UV irradiation or the sensitizers.

Results

The direct photolysis at 1849 Å of a pentane solution containing 0.01 M cis- or trans-cyclooctene gave cis-trans isomerization as a major photoreaction. Moderate disappearance of cyclooctenes was observed; after 5 h of irradiation, almost half of the substrate initially used disappeared.¹⁰ The combined yield of cyclooctenes recovered and percent of trans-cyclooctene are plotted as a function of irradiation time in Figure 1. After prolonged. irradiation, the pentane solution containing each pure isomer came to a photostationary state, the trans- to cis-cyclooctene ratio of which was 49:51. In order to ensure that the decomposition products did not affect the photostationary ratio, the direct irradiation of a 53:47 mixture of cis- and trans-cyclooctene was examined under similar conditions to give the same photostationary state mixture immediately (within 30 min).

The triplet-sensitized photoisomerization of cyclooctene (0.08 M) in pentane solution was carried out in the presence of a variety of carbonyl and aromatic sensitizers (0.4 M in most cases). Regardless of the sensitizers em-



Triplet Energy of Sensitizer, kcal/mol

Figure 2. Variations of the photostationary ‡rans/cis ratio with triplet energy of sensitizers, which are shown in Tables I and II, on vapor-phase (O) and liquid-phase (●) photosensitizations.

ployed, slow disappearance (2-5%/h) of the substrate was observed. The photostationary state was determined for each sensitizer by approach from both sides of the final value. The trans/cis ratios at the photostationary state obtained for these sensitizers after prolonged irradiation are presented in Table I and Figure 2. As demonstrated there, a number of sensitizers with triplet energy $(E_T)^{11}$ above 72 kcal/mol are effective for the reversible cis \Rightarrow trans photoisomerization; the photostationary ratios were almost constant for the sensitizers with $E_T > 74$ kcal/mol.¹² Photosensitization of cyclooctene (0.08 M) by benzene, *p*-xylene, and acetophenone with lower sensitizer concentration (0.04 M) also gave the same photostationary ratios.

Limited experiments revealed that, although the additives with $E_{\rm T} \leq 72$ kcal/mol, i.e., phenylacetylene ($E_{\rm T}$ = 72.0 kcal/mol), benzaldehyde (72.0), and benzophenone (68.7), failed to sensitize the cis \rightarrow trans isomerization, these additives effected irreversible trans \rightarrow cis isomerization; fluorene (68.0) was no longer completely effective for the photoisomerization.

Photosensitized isomerization of cyclooctene in the vapor phase was also performed in order to examine the effect of vibrational activation in the triplet state on the photostationary state. Since the sensitizers available in the vapor phase are limited by the vapor pressure, nine aromatic compounds were chosen as effective sensitizers.¹³ The vapor-phase photolysis of cyclooctene (3 Torr) at 2537 Å in the presence of sensitizers (3 Torr in most cases) gave the cis-trans isomer as a major photoproduct, although prolonged irradiation led to the formation of considerable amounts of 1,7-octadiene and bicyclo[4.2.0]octane as reported previously.⁹ The variations of the photostationary ratio with sensitizer triplet energy are shown in Table II and Figure 2. The photostationary trans/cis ratio obtained in the vapor-phase photosensitization intimately depended on the triplet energy of the sensitizer used; the ratio was almost zero (more exactly trans/cis = 0.0007) at $E_{\rm T}$ = 72.0 kcal/mol (phenylacetylene) and then increased gradually with increasing sensitizer triplet energy in sharp contrast with the result of the liquid-phase photosensitization where the ratios were independent of the sensitizers with $E_{\rm T}$ > 79 kcal/mol.

Discussion

Upon direct irradiation at 1849 Å, a ground state molecule of cyclooctene is promoted spectroscopically to an electronically excited planar singlet state and then suffers fast rotational relaxation to a twisted, not necessarily orthogonal, singlet cyclooctene. Since it is believed

TABLE II: Vapor-Phase Photosensitized Cis-TransIsomerization of Cyclooctene^a

| | Sensitizer | Pressure, Torr | $E_{\mathrm{T}}, \mathrm{kcal}/\mathrm{mol}$ | $(trans/cis)_{pss}^{b}$ |
|----|------------------|-------------------|--|-------------------------|
| 1 | Benzene | 3.0 | 84.4 | 0.198 |
| 2 | Fluorobenzene | 3.0 | 84.4 | 0.168 |
| 3 | Benzotrifluoride | 3.0 | 83.4 | 0.156 |
| 4 | Toluene | 3.0 | 82.8 | 0.153 |
| 5 | o-Xvlene | 3.0 | 82.1 | 0.111 |
| 6 | <i>m</i> -Xylene | 3.0 | 81.0 | 0.108 |
| 7 | n-Xylene | 3.0 | 80.4 | 0.094 |
| 10 | Benzonitrile | 1.0 | 76.5 | 0.026 |
| 16 | Phenylacetylene | 3.0 | 72.0 | 0.0007 |
| | | | | |

^a The pressure of cyclooctene was 3 Torr. ^b Photostationary state *trans*- to *cis*-cyclooctene ratio.

that the large separation in energy causes excited singlet-to-triplet intersystem crossing to be very slow in such a monoolefin, the precursor of the direct cis-trans photoisomerization is inferred to be an excited singlet state of cyclooctene. The considerable disappearance of the substrate on direct photolysis suggests the existence of obscure reactions which give rise to some polymers and, if any, other uncharacterized products.¹⁰ On the assumption of a common twisted singlet intermediate, the cis-trans photoisomerization by direct irradiation can be described by the following simple sequence:

| $e \xrightarrow{\mu\nu} p$ | (1) |
|----------------------------|-----|
| - | (-) |

hν

 $t \stackrel{h\nu_1}{\longrightarrow} p$ (2)

 $^{1}\mathbf{p} \rightarrow \mathbf{c}$ (3c)

$$\rightarrow$$
 t (3t)

 \rightarrow other products (4)

where c and t represent *cis*- and *trans*-cyclooctenes in their ground states and ${}^{1}p$ represents the twisted singlet cyclooctene.

A steady-state treatment of the above sequence leads to the following expression for the trans/cis ratio at the photostationary state (pss):

$$([t]/[c])_{pss} = (\epsilon_c/\epsilon_t)(k_{at}/k_{ac})$$
(5)

where ϵ_c and ϵ_t represent the extinction coefficients of *cis*and *trans*-cyclooctenes at 1849 Å. The reported extinction coefficient for *trans*-cyclooctene is 5500 M⁻¹ cm⁻¹ at 1849 Å,¹⁴ while the coefficient of *cis*-cyclooctene was measured as 6000 M⁻¹ cm⁻¹.¹⁵ From these values, the excitation ratio ϵ_c/ϵ_t is calculated as 1.09, and then we can evaluate the decay ratio using eq 5 and the observed photostationary ratio: $k_{3t}/k_{3c} = 0.88$. It is worth noting that, in spite of the strain energy in the trans form (9.3 kcal/mol),¹⁶ an anomalously high decay ratio of 0.88 is obtained upon direct photoisomerization.

Extremely low trans/cis photostationary ratios were observed on liquid-phase sensitized photoisomerization; the additives with $E_{\rm T} > 72$ kcal/mol were effective for the $cis \rightleftharpoons trans photoisomerization$. As shown in Figure 2, a definite photostationary ratio of 0.049 was observed for the sensitizers with $E_{\rm T}>79$ kcal/mol, while the sensitizers in the triplet energy range 72-77 kcal/mol give rise to somewhat lower photostationary ratios. When the sensitizer is a carbonyl compound, special regard should be paid to the intermediate of the cis-trans isomerization since, as is shown in the Schenck mechanism,^{2,17} the 1,4 biradical formed by the addition of a ketone triplet to an acyclic alkene falls apart regenerating the alkene with geometrical isomerization. However, in the case of ketone sensitization of cyclooctene, such a 1,4 biradical, if formed, is considered to decompose preferentially to the cis isomer

because of the strain energy in the trans form.¹⁶ Actually benzophenone, which has fairly low $E_{\rm T}$ and is known to form a 1,4 biradical with alkenes,¹⁸ photosensitized the irreversible trans \rightarrow cis isomerization of cyclooctene, probably suggesting the predominant formation of the cis isomer from the 1,4 biradical. It seems, therefore, likely that regarding the ketone sensitizers with $E_{\rm T} > 72$ kcal/ mol, the mechanism involving triplet energy transfer to cyclooctene is operative, although the Schenck mechanism is applicable only for benzophenone sensitization.

Since the benzene-sensitized photostationary ratios for several acyclic alkenes in solution are unity and the triplet energy transfer from benzene triplet to alkenes is sufficiently exothermic,¹⁹ it has been recognized that, when benzene is the sensitizer, the common intermediate for the sensitized cis-trans isomerization is the twisted alkene triplet whose decay ratio is unity.^{2,20} In the present system, assuming that the rates of triplet energy transfer from the excited benzene to cis- and trans-cyclooctenes are the same in accord with the above accepted view on the benzene photosensitization, the extremely low trans/cis ratio at the photostationary state is attributable to a low decay ratio (k_t/k_c) from a common twisted, vibrationally relaxed cyclooctene triplet ³p. Toluene and *p*-xylene sensitized photoisomerizations gave the same, or nearly so, photostationary ratios as those obtained by benzene sensitization, suggesting that these sensitizers with $E_{\rm T} > 80$ kcal/mol also excite both isomers of cyclooctene with an equal rate.

The calculated potential curves for the excited states of ethylene,⁴ which suggest the same decay ratio for singlet and triplet excited states, are evidently unsuitable for the present system. The extremely low $cis \rightarrow trans$ isomerization efficiency for the photosensitization of cyclooctene may be attributable to a torsional conversion barrier from the vibrationally relaxed triplet state ³p into the trans form. Taking into account the strain energy¹⁶ and the torsional angle²¹ of trans-cyclooctene in its ground state, the fundamental potential energy curves calculated with ethylene⁴ are qualitatively modified to obtain hypothetical potential curves of the ground state (N) and the excited singlet (V) and triplet (T) states of cyclooctene. Since electronically the double bond of cyclooctene is close to that of ethylene and the strain in the trans form, which arises from the steric restrictions of methylene chain, is considered not to be so great compared with the electronic energy, the potential curves for cyclooctene may not be far removed in energy from those for ethylene. Therefore, the crossing of potential curves of the N and T states occurs to give an ethylene-like energy well, although the torsional angle which give the potential minimum of the T state and the maximum of the N state as well, should not be necessarily perpendicular. As shown in Figure 3, a greater activation energy (E_t) is postulated for the decay of ³p to the trans isomer in order to account for the low decay ratio in the liquid phase photosensitization. The following Arrhenius equations are obtained for the rate constants of the decay from ³p to the ground-state *trans*- and *cis*-cyclooctenes.

$$k_{\rm t} = A \, \exp(-E_{\rm t}/RT) \tag{6}$$

$$k_{\rm c} = A' \exp(-E_{\rm c}/RT) \tag{7}$$

Assuming the same preexponential factor, i.e., A = A', the logarithm of the decay ratio is represented by the following equation

$$\ln (k_{\rm t}/k_{\rm c}) = -\Delta E_{\rm a}/RT \tag{8}$$

where $\Delta E_{a} = E_{t} - E_{c}$. Since the experiment was carried



Figure 3. Schematic potential curves for the ground-state (N) and excited singlet (V) and triplet (T) states of cyclooctene.

out at 290 K and the decay ratio (k_t/k_c) observed equals 0.049, then we can evaluate the difference of the activation energies: $E_t - E_c = 1.74$ kcal/mol.²²

The photosensitized cis-trans isomerization in the vapor phase can be used as a test of the speculated potential surface described above, since the triplet state of cyclooctene generated in the vapor-phase photosensitization is considered to have some excess vibrational energy in the absence of fast collisional deactivation by solvent molecules. As shown in Figure 2, the trans/cis photostationary ratios observed in vapor-phase photosensitization are higher than those obtained in liquid-phase photosensitization employing the same sensitizers, and the ratio increases with increasing triplet energy of the sensitizer used, whereas the ratio observed in the liquid phase is independent of the sensitizer with $E_{\rm T} > 79$ kcal/mol. One might assume the deviation from unity of the excitation ratio on the vapor-phase photosensitization in order to account for the higher trans/cis photostationary ratios and their dependence on the sensitizer triplet energy, although the excitation ratio is regarded as unity in the liquid-phase photosensitization employing sensitizers with $E_{\rm T} > 79$ kcal/mol. This seems unlikely because the rates of energy transfer from benzene triplet to both cis and trans isomers of simple disubstituted alkenes have been reported to be so close in the vapor phase^{5,23} that the higher trans/cis ratios observed in the present work are attributable to the higher decay ratios (k_t/k_c) . The higher trans/cis photostationary ratios and their $E_{\rm T}$ dependence should therefore be interpreted in terms of the excess vibrational energy in the triplet state of cyclooctene. The cyclooctene triplet generated in the vapor-phase photosensitization has some excess vibrational energy, the amount of which increases with rising triplet energy of the sensitizers. According to eq 8, the excess vibrational energy, which is energetically equivalent to thermal activation in the triplet state, enhances the decay ratio (k_t/k_c) . Then, the enhanced decay ratio via vibrational activation qualitatively rationalizes the higher photostationary trans/cis ratios and their dependence on the triplet energy in the vapor-phase photosensitization. In this context, the high internal energy of the relaxed singlet state ¹p in itself may account for the anomalously high decay ratio observed on the direct photoisomerization. However, we feel prompted to propose that, since the excited singlet state of alkenes is believed not to undergo intersystem crossing to its triplet state but to suffer rapid internal conversion to its ground state, the twisted ground-state cyclooctene thus formed is deactivated collisionally to give the relaxed cis or trans isomer with almost equal probability, if the correlation between the potential curves for the V and N states is as shown in Figure 3.

References and Notes

- (1) Preliminary report: Y. Inoue, S. Takamuku, and H. Sakurai, J. Chem.
- Soc., Chem. Commun., 423 (1976). J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973), and (2)references cited therein.
- references cited therein. L. C. Jones, Jr., and L. W. Taylor, Anal. Chem., **27**, 228 (1955). A. J. Merer and R. S. Mulliken, Chem. Rev., **69**, 639 (1969). R. B. Cundall, Prog. React. Kinet, **2**, 165 (1964); R. B. Cundall and T. F. Palmer, Trans. Faraday Soc., **56**, 1211 (1960); R. B. Cundall, F. J. Fletcher, and D. G. Milne, J. Chem. Phys., **39**, 3536 (1963); S. Sato, K. Kikuchi, and M. Tanaka, *ibid.*, **39**, 239 (1963); M. Tanaka, T. Terumi, and S. Sato, *Bull. Chem. Soc. Jpn.*, **38**, 1645 (1965); S. Tsunashima and S. Sato, *ibid.*, **41**, 284 (1968); E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., J. Chem. Phys., **48**, 4547 (1968); M. Termonia and G. R. De Mare, Chem. Phys. Lett., **25**, 402 (1974). The xviene-sensitized photoisomerization of *cis*-cyclooctene has been (4) (5)
- (6)The xylene-sensitized photoisomerization of cis-cyclooctene has been reported as a synthetic method for preparing trans-cyclocotene; J. S. Swenton, J. Org. Chem., 34, 3217 (1969). This study of Swenton, however, did not provide any quantitative information but demonstrated the extremely low efficiency of the cis \rightarrow trans photoisomerization of cyclooctene; xylene photosensitization of *cis*-cyclooctene (600 ml) in cyclohexane gave only 2.1–2.4 g (\sim 0.5%) of the trans isomer after 36 h of Irradiation.
- A. C. Cope, S. W. Fenton, and C. F. Spencer, J. Am. Chem. Soc., (7)
- 74, 5884 (1952).
 J. N. Hines, M. J. Pergram, G. H. Whitram, and M. Wright, J. Chem. Soc., Chem. Commun., 1593 (1968).
 Y. Inoue, K. Moritsugu, S. Takamuku, and H. Sakurai, J. Chem. Soc., Perkin Trans. 2, 569 (1976).
 A further study for the products which may be produced from the study. (8)
- A further study for the products which may be produced from the unrecovered cyclooctene was made; formation of methylene-cycloheptane and bicyclo[5.1.0]octane was detected on gas (10)chromatography. In the early stages of photolysis (within 1 h) the combined yield of these two products amounted to almost half of the unrecovered cyclooctene.
- (11) D. F. Evans, J. Chem. Soc., 2753 (1959); Y. Kanda and R. Shimada, Spectrochim. Acta, 17, 279 (1961); K. Takel and Y. Kanda, *ibid.*, 18, 1201 (1962); S. L. Murov, "Handbook of Photochemistry", Marcell Decker, New York, N.Y., 1973.

- (12) In another experiment, the photosensitization of cyclooctene by methylbenzoate ($E_{\rm T}$ = 78.7 kcal/mol) gave a higher trans/cis photostationary ratio of 0.25. It is, however, doubtful whether, as is the case with the other sensitizers, the triplet-triplet energy transfer process is operative. Limited quenching experiments with piperylene suggest that this photoisomerization involves the benzoate singlet rather than the triplet state. The detailed mechanism and the nature of the intermediate involved are under investigation and may be the subject of a separate paper.
- S. Hirokami and S. Sato, Can. J. Chem., 45, 3181 (1967)
- (14) M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968); O. Schnepp, E. F. Pearson, and E. Sharman, *ibid.*, **52**, 6424 (1970); M. G. Mason and O. Schnepp, *ibid.*, **59**, 1092 (1973). The extinction coefficient of *cis*-cyclooctene was measured with a
- Hitachi 356 spectrophotometer. (16)
- R. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, J. Am. Chem. Soc., 92, 2377 (1970).
 G. S. Schenck and R. Steinmetz, Bull. Soc. Chim. Belg., 71, 781
- (17)(1962).
- (18) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, Tetrahedron Lett., 3657 (1964); N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964); G. Porter and P. Suppan, *Trans. Faraday Soc.*, **62**, 3375 (1966); C. Rivas and E. Payo, *J. Org. Chem.*, **32**, 2918 (1967). The lowest triplet energy of benzene is 84.4 kcal/mol,¹¹ while the
- spectroscopic E_T of ethylene has been located near 82 kcal/mol (D. F. Evans, J. Chem. Soc., 1735 (1960)), and alkyl substituted
- ethylenes are considered to have somewhat lower triplet energies.
 (20) M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966); H. Morrison, J. Pajak, and P. Peiffer, *J. Am. Chem. Soc.*, 93, 3978 (1971).
- G. Buemi, G. Farini, and F. Zuccarello, J. Mol. Struct., 5, 101 (1970);
 N. L. Allinger and J. T. Sprague, J. Am. Chem. Soc., 94, 5734 (1972);
 P. Ganis, U. Lepore, and E. Martuscelli, J. Phys. Chem., 74, 2439 (1970); P. C. Manor, D. P. Shoemaker, and A. S. Parkes, J. Am. Chem. (21)Soc., 92, 5260 (1970).
- Although this value may be confirmed by a similar Arrhenius treatment of the photostationary ratio at the elevated temperature, attempted (22)p-xylene photosensitization of cyclooctene in cyclohexane at 80 failed to get a higher photostationary trans/cis ratio because of significant thermal isomerization in the dark of trans-cyclooctene at that temperature.
- S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. (23)E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969); G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, 71, 3104 (1967).