

ZINC-PHOTOSENSITIZED ISOMERIZATION OF 2-BUTENES

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Summary

The reactions of the *cis*- and *trans*-2-butenes photosensitized by $Zn(^3P_1)$ have been studied. The main reaction was *cis*-*trans* isomerization. The photostationary [trans]/[cis] ratio was 1.5/1.0 and did not vary with pressure. This ratio is different from those obtained in the mercury- and cadmium-photosensitized reactions. The isomerization of 2-butenes photosensitized by $Zn(^3P_1)$ could not be explained in terms of the simple mechanism proposed for the mercury- and cadmium-photosensitized reaction of 2-butenes. Possible mechanisms are discussed.

1. Introduction

The photosensitized isomerization of 2-butenes in the gas phase has been investigated with mercury [1 - 3], cadmium [2, 4, 5], SO_2 [1, 6], benzene [7 - 10] and other organic compounds [8, 11, 12] as sensitizers. It is generally accepted that the isomerization occurs via an excited triplet state of butene which is formed by an energy transfer from the triplet states of these sensitizers.

Since the excitation energy of $Zn(^3P_1)$ lies between those of $Cd(^3P_1)$ and $Hg(^3P_1)$, it would be interesting to compare the reactions photosensitized by these three atoms. However, only a brief report by Hirokami and Sato [13] had appeared on the zinc-photosensitized isomerization of 2-butenes before we undertook this study. They pointed out that slow *cis*-*trans* isomerization occurred both with and without the irradiation of the zinc resonance line at 307.6 nm. They found that the dark reaction was inhibited and that the reaction photosensitized by $Zn(^3P_1)$ was greatly enhanced by the addition of a small amount of acetylene. They only reported results for the butene-acetylene system [13].

In a preliminary report on the zinc-photosensitized *cis*-*trans* isomerization of 2-butenes we compared the results with those of cadmium- and mercury-photosensitized isomerizations [14]. The photostationary [cis]/[trans] ratio was found to be about 1/1.5 in the zinc-photosensitized

reaction, which is different from the ratios observed in the cadmium- and mercury-photosensitized isomerizations. We therefore undertook a detailed study of the zinc-photosensitized isomerization of the 2-butenes.

2. Experimental details

The zinc-photosensitized reaction of 2-butenes was carried out in a cylindrical quartz cell 4 cm in diameter and 5 cm long with quartz windows. A spiral Pyrex zinc discharge lamp filled with 2000 Pa argon was used as the source of the 307.6 nm resonance line. The cell and the lamp were inserted in an electric furnace kept at a temperature in the range $305 - 395 \pm 2$ °C to get a sufficient vapor pressure of zinc. The intensity of the 307.6 nm radiation transmitted through the cell was measured by means of a Hitachi model 139 spectrophotometer.

The zinc metal used was high purity zinc (99.9999%) manufactured by the Osaka Asahi Metal Co. Research-grade *cis*-2-butene (Nihon Tokushu Gasu K.K., 99.5%) and *trans*-2-butene (Takachiho-Shoji Co., 99.5%) were used after degassing at liquid nitrogen temperature. The major impurities detected by gas chromatography were *trans*-*cis* isomers, the amounts being below 0.2%.

Product analysis was carried out by fractionation at -196 °C, gas burette measurements and gas chromatography. The first portion, which was non-condensable at -196 °C, was collected by a Toepler pump. This portion consisted of hydrogen alone. The products in the second portion, which were condensable at -196 °C, were analysed by gas chromatography, using a 6 m column of VZ-7 (Gasukuro Kogyo Co. Ltd.) at 0 °C.

For zinc photosensitization, it is necessary to raise the reaction temperature as mentioned above. To check the possibility of thermal reaction of 2-butene, 500 Pa 2-butene was kept at 360 °C for 5 h in the reaction cell, which contained a few small pieces of zinc metal. Neither isomerization nor decomposition products could be detected, showing that neither the thermal reaction of 2-butene in the gas phase nor the reaction between 2-butene and zinc vapor occur at 360 °C. However, when the cell was kept at 360 °C for longer than 10 h, when the cell was used repeatedly without cleaning or when zinc powder was used instead of pieces of zinc metal, some products were observed. In the first two cases, spongy deposits of zinc were found on the wall of the cell. Therefore zinc powder and the deposits are thought to catalyse the isomerization and the decomposition of 2-butene. These thermal reactions were avoided by cleaning the cell with nitric acid and water and using freshly cut pieces of zinc metal in every experimental run, and thus we could follow the photosensitized reaction.

3. Results

The products obtained in the zinc-photosensitized reaction of 2-butenes were *cis*-*trans* isomers and small amounts of hydrogen, ethylene (or ethane),

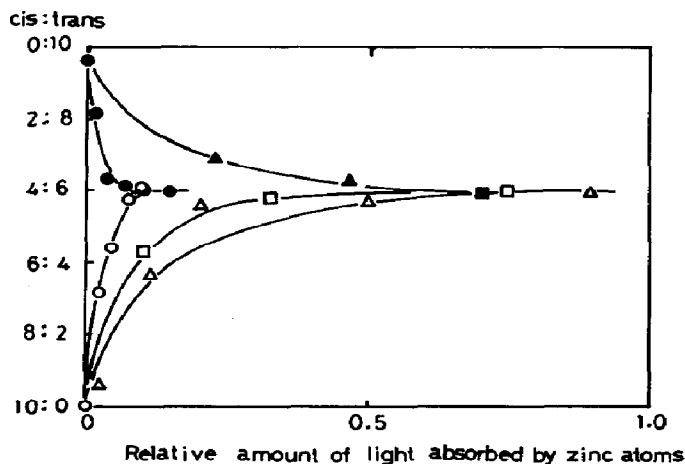


Fig. 1. $[\text{trans}]/[\text{cis}]$ ratio as a function of the relative amount of light absorbed by zinc atoms. Initial pressure: \circ , \bullet 500 Pa; \square , \blacksquare 3750 Pa; \triangle , \blacktriangle 7060 Pa.

propylene and 1-butene. The rate of decomposition was about 1/50 of that of isomerization.

The time dependence of the $[\text{cis}]/[\text{trans}]$ ratio is shown in Fig. 1, where both pure *cis*- and *trans*-2-butenes were used as a starting material. It was found that the light intensity from the lamp, and hence the intensity of the light absorbed by zinc atoms, was not always constant during a series of measurements. Therefore we plotted the ratio against the relative amount of light absorbed by zinc atoms instead of against the reaction time; the amount was estimated from the area under the curves of the intensity of the transmitted light *vs.* time. Figure 1 shows that after prolonged irradiation the $[\text{cis}]/[\text{trans}]$ ratio approaches a constant value (4:6) which is independent of the initial pressure of 2-butene. The same photostationary $[\text{cis}]/[\text{trans}]$ ratio was obtained when 1:1 and 2:1 mixtures of *trans*- and *cis*-2-butenes were used as starting materials (Fig. 2). In these cases, the ratio reached a constant value much earlier; the influence of photochemical and thermal decomposition products on the ratio is thought to be much smaller.

The decomposition products were scarcely detectable when the reaction time was shorter than 10 h, but thereafter we began to detect decomposition products and these increased with the reaction time. The total amount of the decomposition products was about 10% of that of 2-butenes when the reaction time was 20 h. The reduction in the total amount of 2-butenes during the 10 h irradiation was negligibly small.

In Fig. 3, yields of *trans*- and *cis*-butenes in the zinc-photosensitized isomerization of *cis*- and *trans*-2-butenes are plotted against the reaction time. Points at the time zero show the amounts of isomers which are contained as impurities. The yields increase linearly with reaction time. The initial rates of *cis*-to-*trans* and *trans*-to-*cis* isomerizations of 2-butenes which were estimated from the slopes of the straight lines shown in Fig. 3 are listed

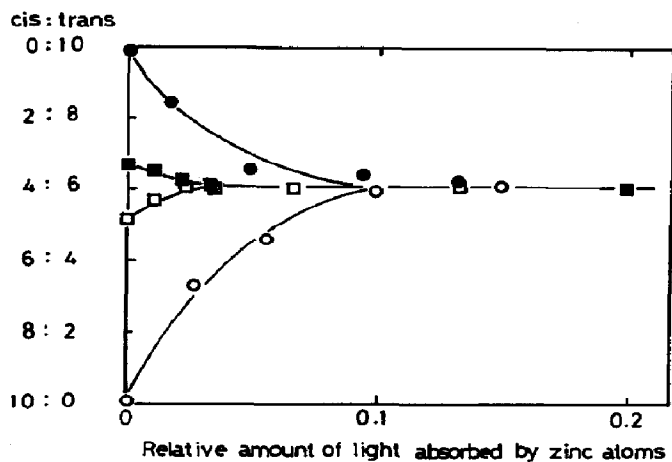


Fig. 2. [trans]/[cis] ratio as a function of the relative amount of light absorbed by zinc atoms. Initial pressure, 500 Pa. ○, *cis*-2-butene; ●, *trans*-2-butene; □, 1:1 mixture of *trans*- and *cis*-2-butenes; ■, 2:1 mixture of *trans*- and *cis*-2-butenes.

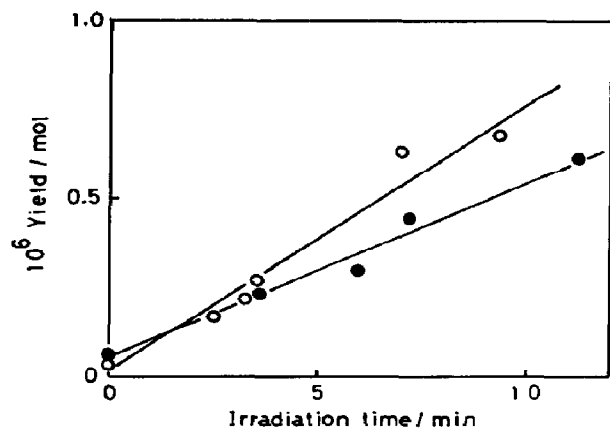


Fig. 3. Yield of isomerization products as a function of irradiation time. Initial pressure of 2-butenes, 3750 Pa. ○, *cis* → *trans*; ●, *trans* → *cis*.

in Table 1. The initial rates were found to increase linearly with light intensity and to be independent of butene pressure.

In order to estimate the quenching rate of the 307.6 nm resonance line of zinc by *cis*- and *trans*-2-butenes, the emission intensity at 307.6 nm was measured as a function of butene pressure. Figure 4 shows the Stern–Volmer plots for the quenching of the resonance line by *cis*- and *trans*-2-butenes. I^0 and I are the intensities of the resonance line in the absence and in the presence of butenes respectively. From the slopes of the straight lines, the quenching rate constants were estimated by the method described previously [15], and are listed in Table 1.

TABLE 1

Initial rate of *cis*-*trans* isomerization and quenching rate constant of the 307.6 nm zinc resonance line by *cis*- and *trans*-2-butenes

Gas	$10^6 R^0$ (mol min ⁻¹)	$10^{11} k_Q$ (cm ³ molecule ⁻¹ s ⁻¹)
<i>cis</i> -2-Butene	0.075 ± 0.004	85.8 ± 2.0
<i>trans</i> -2-Butene	0.049 ± 0.003	89.4 ± 2.0
Ratio	1.53	1.04

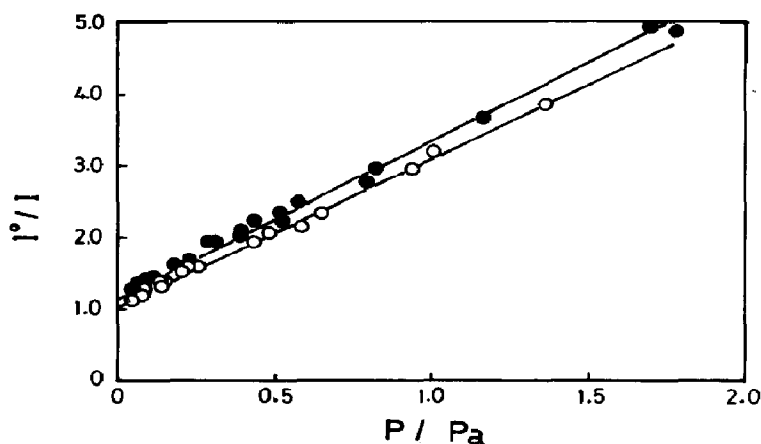


Fig. 4. Stern-Volmer plots for quenching of resonance line at 307.6 nm by *trans*- and *cis*-2-butenes. ●, *trans*-2-butene; ○, *cis*-2-butene.

4. Discussion

In Table 2, the photostationary [trans]/[cis] ratios for the isomerization of 2-butenes by various sensitizers are given. The ratio in the cadmium- and mercury-photosensitized isomerizations is about unity, but the ratio for other sensitizers, including zinc, is considerably larger than unity.

The photosensitized isomerization of 2-butenes was discussed in terms of the following reactions.

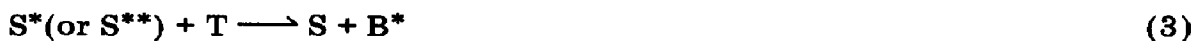
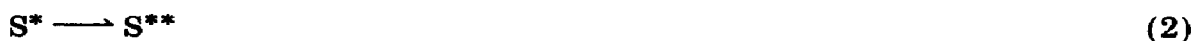


TABLE 2

Photosensitized isomerization of 2-butenes

Sensitizer	E_T (kJ mol ⁻¹)	$[T]_\infty/[C]_\infty$	T (K)	P_{butene} (Pa)	Reference
Hg(³ P ₁)	470	1.13	295	10850	1
		1.03 ^a	298	2670	2
		1.00 ± 0.02 ^a	295	4000 - 7030	3
Cd(³ P ₁)	365	1.07 ± 0.02	548 - 623	1330	2
		1.00 ± 0.07	590	160 - 1800	4
		1.56 ± 0.10	578	500	This work
Zn(³ P ₁)	387	1.50 ± 0.09	633	500 - 7060	This work
		1.44 ± 0.10	668	500	This work
		1.27	305	1480	1
SO ₂	307	1.9 ± 0.1	298	17.5 - 133	6
		1.38	320	2660	7, 8
Benzene	356	0.95 ± 0.10	298	665 - 2666	9
		0.92 ± 0.02	295	133	10
		1.70	320	2660	8
Toluene	347	1.70	320	2660	8
Pyridine	356	1.35	320	2660	8
Pyrazine	318	1.60 ^a			11
Benzaldehyde	301	2.07 ^a	333	1320 - 33300	12

^aRatio of the quantum yields for *cis* → *trans* and *trans* → *cis* isomerization.

Here, S is a sensitizer and S* and S** are the excited states of the sensitizer which are formed directly by light absorption and formed from S* by inter-system crossing respectively. T and C are *trans*- and *cis*-2-butenes and B* is the triplet state of 2-butene. α is the fraction of *trans* isomer formed from B*.

By assuming a steady state for S* (and S**) and B*, the $[trans]/[cis]$ ratio obtained after prolonged irradiation can be expressed by the equation

$$\frac{[T]_\infty}{[C]_\infty} = \frac{\alpha}{1 - \alpha} \frac{k_4}{k_3} \quad (6)$$

The fact that the ratio is about unity in the cadmium- and mercury-photosensitized isomerizations shows that $k_3 = k_4$ and $\alpha = 0.5$ [1 - 4], while it has been pointed out that the photostationary ratio greater than unity for the isomerization sensitized by organic sensitizers and SO₂ results from different quenching rates of the isomers ($k_3 \neq k_4$) [6 - 10].

Table 1 shows, however, that in the zinc-photosensitized reaction the quenching rate of *trans*-2-butene is almost the same as that of the *cis* isomer. It is improbable that α for zinc is different from the values for cadmium and mercury. It seems to be difficult to interpret the results of the zinc-photosensitized reaction in terms of the above mechanism.

The vertical singlet-triplet transition energies of *cis*- and *trans*-2-butenes are 406.3 and 409.2 kJ mol⁻¹ [16]. Since the excitation energy of Hg(³P₁) is 470 kJ mol⁻¹, vertical energy transfer from Hg(³P₁) to butenes is possible

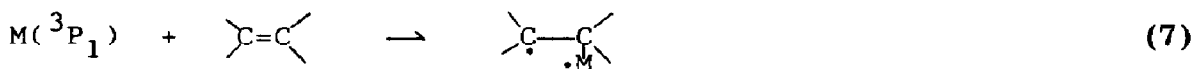
and triplet butenes are produced in the mercury-photosensitized reaction as mentioned above. In contrast, the excitation energies of Cd(3P_1) and Zn(3P_1) are 365 and 387 kJ mol $^{-1}$ and these are smaller than the vertical singlet-triplet transition energies of butenes. Therefore, in the cadmium- and zinc-photosensitized reactions of 2-butenes, the transfer of triplet energy from these sensitizers to both the 2-butene isomers is endothermic and probably "non-vertical" [17]. For energy transfer in these photosensitizations a mechanism different from that in the mercury-photosensitized reaction must be considered.

Here, we have assumed that the reactions in the cadmium- and zinc-photosensitizations may proceed through transient triplet addition complexes formed between Cd(3P_1) or Zn(3P_1) and the butene π system. Presumably these complexes undergo one of the following two reactions.

(1) They may collapse into biradicals, which allows rotation of the methyl groups about the central C—C bond with the ultimate dissociation of the complexes into the butene isomers and Cd(1S_0) or Zn(1S_0). In this case, a photostationary ratio different from that found in the mercury-photosensitized reaction may be obtained.

(2) They may decay to triplet state of *cis*- or *trans*-2-butenes in the most stable configuration and Cd(1S_0) or Zn(1S_0); the triplet butenes undergo isomerization. In this case, the same photostationary ratio as that in the mercury photosensitized reaction must be obtained.

The change in enthalpy for the reaction



is given by the equation

$$-\Delta H^\circ = E_T(M) - D_\pi + D_{C-M} \quad (8)$$

$E_T(M)$ is the excitation energy of M(3P_1), D_π is the π -bond energy of 2-butene and D_{C-M} is the bond energy of C—M. The change in enthalpy for zinc and cadmium were calculated and are listed in Table 3, together with relevant data.

TABLE 3
Change in enthalpy of reaction (7)

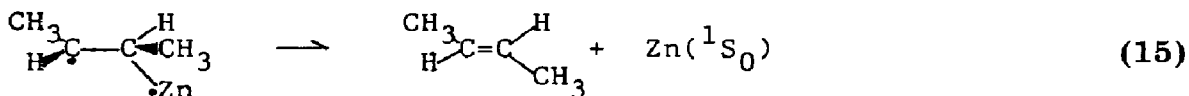
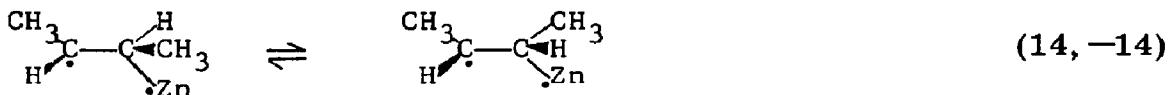
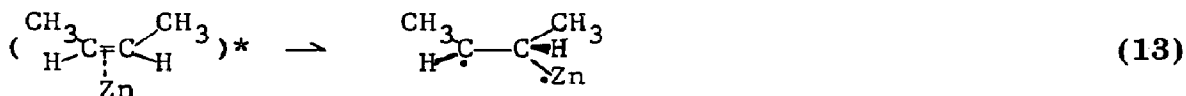
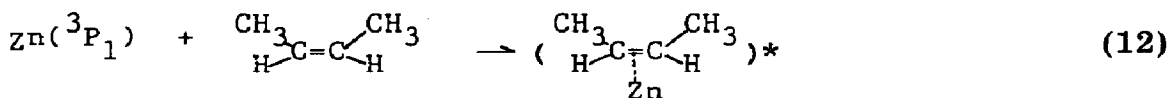
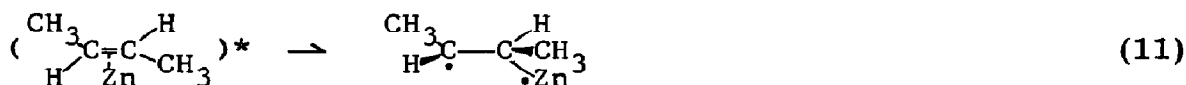
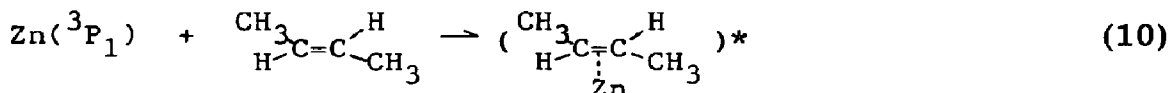
M	$E_T(M)$ (kJ mol $^{-1}$)	D_π^a (kJ mol $^{-1}$)	D_{C-M}^b (kJ mol $^{-1}$)	$-\Delta H^\circ$ (kJ mol $^{-1}$)
Zn	387	241.8	175.7	320.9
Cd	365	241.8	139.3	262.5

^aFrom ref. 18.

^bFrom ref. 19.

As mentioned above, in the cadmium-photosensitized reaction of 2-butene the photostationary [trans]/[cis] ratio was found to be unity, showing that case (2) holds in this instance. Table 3 shows that reaction (7) is much more exothermic for zinc than for cadmium. Therefore it seems that the isomerization in the zinc-photosensitized reaction proceeds through a biradical (case (1)). This is probably responsible for the different photostationary ratio obtained in the zinc-photosensitized reaction of 2-butenes.

We tentatively propose the following mechanism to explain the results obtained in the zinc-photosensitized reaction.



The species formed in reactions (10) and (12) are transient triplet addition complexes formed between $\text{Zn}(^3\text{P}_1)$ and the π system of *trans*- and *cis*-2-butenes.

This mechanism is similar to those proposed for the isomerization of 2-butenes catalysed by a number of atoms and radicals [20].

A steady state treatment gives the following equations.

$$\frac{[\text{T}]_\infty}{[\text{C}]_\infty} = \frac{k_{12}}{k_{10}} \frac{k_{14}}{k_{-14}} \frac{k_{15}}{k_{16}} \quad (17)$$

$$\frac{R_{C \rightarrow T}^{\circ}}{R_{T \rightarrow C}^{\circ}} = \frac{k_{14}}{k_{-14}} \frac{k_{15}}{k_{16}} \quad (18)$$

$$\frac{k_Q(C)}{k_Q(T)} = \frac{k_{12}}{k_{10}} \quad (19)$$

The photostationary ratio will be larger than unity when one of the following conditions holds: (1) $k_{10} < k_{12}$; (2) $k_{14} > k_{-14}$; (3) $k_{15} > k_{16}$. As mentioned above, the quenching rate constants of *trans*- and *cis*-2-butenes are nearly equal, that is $k_{10} \approx k_{12}$. This indicates that either condition (2) or condition (3) holds (or that they both do). This is consistent with the fact that the ratio $R_{C \rightarrow T}^{\circ}/R_{T \rightarrow C}^{\circ}$ of the initial rates is almost the same as the photostationary ratio $[T]_{\infty}/[C]_{\infty}$.

From the similarity between the structures of the biradicals produced by the addition of an excited zinc atom to *cis*- and *trans*-2-butenes, it can be assumed that k_{15} is nearly equal to k_{16} . Thus the step which determines that the photostationary ratio is larger than unity seems to be the isomerization of the biradicals.

TABLE 4

Photostationary [trans]/[cis] ratio and equilibrium constant

T (K)	$[T]_{\infty}/[C]_{\infty}$	$K_{T/C}^a$
578	1.56 ± 0.10	1.57
633	1.50 ± 0.09	1.51
668	1.44 ± 0.10	1.48

^aThe equilibrium constant for thermal isomerization of *cis*-2-butene to *trans*-2-butene was calculated using the equation [21]

$$K_{T/C} = 0.01947 \left(\frac{10^3}{T} \right)^2 + 0.08663 \left(\frac{10^3}{T} \right) - 0.006692$$

Table 4 shows that the photostationary ratio at 578, 633 and 668 K is almost the same as the equilibrium constant between *cis*-butene and *trans*-2-butene at these temperatures, indicating that the above mechanism is reasonable for the zinc-photosensitized reaction.

Although the excitation energy of zinc lies between those of cadmium and mercury, it is interesting that only the zinc-photosensitized reaction gives a different photostationary ratio. We could explain the results in terms of the tentatively proposed mechanism. However, a number of details in the mechanism seem to remain open to question. Further experiments and different approaches are needed to confirm that this mechanism is correct.

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