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ZINC-PHOTOSENSITIZED CIS-TRANS ISOMERIZATION OF 2-BUTENES

Shunzo YAMAMOTO,* Naoki NOBUSADA, Yoshimi SUEISHI, and Norio NISHIMURA
Department of Chemistry, School of Science, Okayama University, 3-1-1, Tsushima-naka, Okayama 700

The zinc-photosensitized isomerization of cis- and trans-2-butenes has been studied. The photostationary cis/trans ratio was found to be about 1/1.5 and to be independent of the 2-butene pressure.

In spite of several comprehensive studies of the reactions photosensitized by excited mercury[1)] and cadmium[2)] atoms, there have been few studies on the zinc-photosensitized reactions. Since the excitation energy of Zn($^3P_1$) lies between those of Cd($^3P_1$) and Hg($^3P_1$), a comparison of the reactions photosensitized by these three atoms would give further information about the detailed mechanism of the reactions. We have studied the isomerization of 2-butenes photosensitized by Zn($^3P_1$), since this reaction is often taken as a standard in mercury- and cadmium-photosensitized reactions.

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. The cell and the lamp were inserted in an electric furnace kept at 360 ± 2 °C to get a sufficient vapor pressure of zinc. The 307.6 nm resonance line was emitted from the lamp. The intensity of the light transmitted through the cell was measured by means of a Hitachi spectrophotometer, Model 139. Products were analyzed 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 of 2-butene was kept at 360 °C for five hours 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 ten hours, or when the cell was used repeatedly without cleaning, some products were observed. In these cases, spongy deposits of zinc were found on the wall of the cell. Therefore, the spongy deposits are thought to catalyze the isomerization and the decomposition of 2-butene. Since these thermal reactions were avoided by cleaning the cell with nitric acid and using freshly cut pieces of zinc metal in every experimental run, we could follow the photosensitized reaction.

Photosensitized isomerization of 2-butenes in the gas phase has been investigated with mercury,[3-6] cadmium,[5] SO_2,[4,7] benzene,[8-10] and other organic compounds[9] as sensitizers. It is generally accepted that the isomerization occur via an excited triplet state of butene which is formed by an energy transfer from the triplet states of these sensitizers. On the zinc-photosensitized isomerization of 2-butene, however, only a brief report by Hirokami and Sato appeared.[11] They pointed out that slow cis-trans isomerization occured both with and without the irradiation of the zinc resonance line at 307.6 nm, and that the dark reaction was inhibited, and the reaction photosensitized by $Zn(^3P_1)$ was much enhanced, by the addition of a small amount of acetylene. Thus they reported only the results of isomerization for the butene-acetylene system. However, we could observe the zinc-photosensitized isomerization in pure butene system as mentioned above.

Time dependence of the cis-to-trans ratio is shown in Fig. 1, when both cis- and trans-2-butenes were used as starting materials. It was found that the light intensity from the lamp and hence the intensity of the light absorbed by zinc were 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 the reaction time; the amount was estimated from the area under curves of the intensity of the transmitted light vs. time.

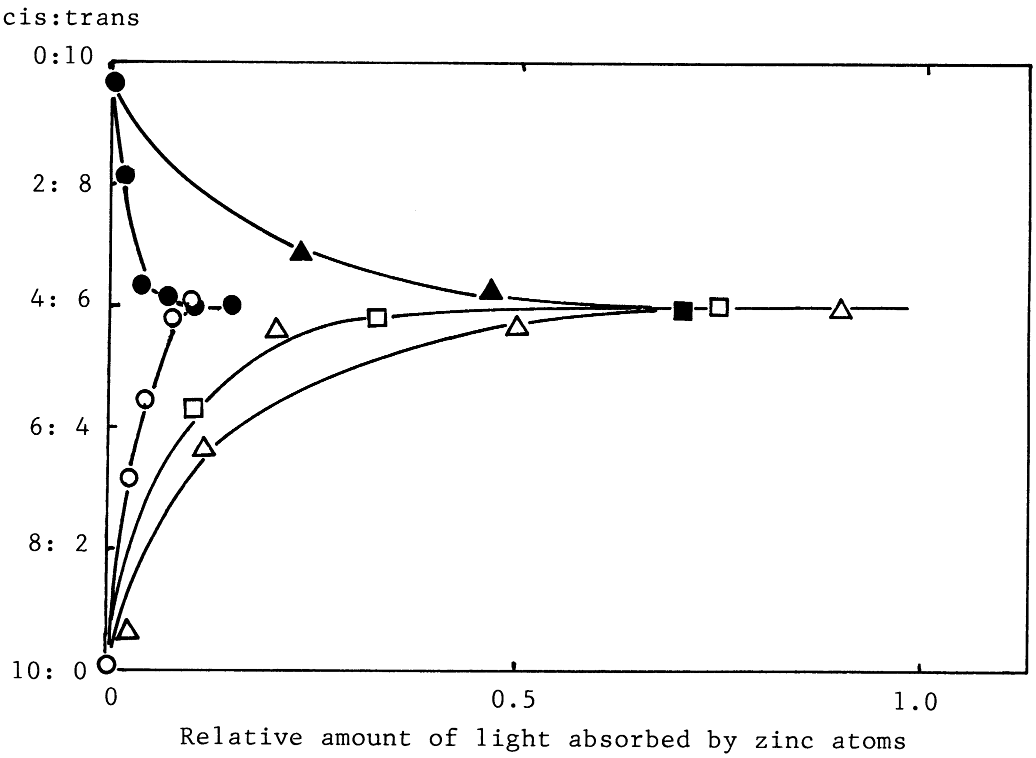

Fig. 1. The ratio of trans- to cis-2-butene as a function of the relative amount of light absorbed by zinc atoms. (Initial pressure: ○,● 500 Pa; □,■ 3750 Pa; △,▲ 7060 Pa)

The decomposition products were scarcely detected when the reacrion time was shorter than ten hours, and after that they began to be detected and increased with the reaction time. The total amount of the decomposition products was about ten percent of that of 2-butenes when the reaction time was twenty hours.

By analogy with the mechanism presented for the photosensitization by Cd($^3P_1$), the isomerization photosensitized by Zn($^3P_1$) can be discussed in terms of the following reactions:

$$\mathrm{Zn}(^1S_0) + h\nu(307.6\ \mathrm{nm}) \longrightarrow \mathrm{Zn}^*(^3P_1) \tag{1}$$

$$\mathrm{Zn}^* \longrightarrow \mathrm{Zn} + h\nu \tag{2}$$

$$\mathrm{Zn}^* + \mathrm{T} \longrightarrow \mathrm{Zn} + \mathrm{B}^* \tag{3}$$

$$\mathrm{Zn}^* + \mathrm{C} \longrightarrow \mathrm{Zn} + \mathrm{B}^* \tag{4}$$

$$\mathrm{B}^* + \mathrm{M} \longrightarrow \alpha\mathrm{T} + (1-\alpha)\mathrm{C} + \mathrm{M} \tag{5}$$

Here, T and C are trans- and cis-2-butenes, B* is the triplet state of 2-butene, and α is the fraction of trans isomer formed from B*. By assuming the steady-state for Zn* and B*, the trans/cis ratio obtained after prolonged irradiation ($[\mathrm{T}]_\infty/[\mathrm{C}]_\infty$) can be derived as follows,

$$\frac{[\mathrm{T}]_\infty}{[\mathrm{C}]_\infty} = \frac{\alpha}{1-\alpha}\,\frac{k_4}{k_3} \tag{6}$$

This equation shows that the photostationary trans/cis ratio is independent of butene pressure, this being in agreement with the observation shown in Fig. 1.

Table 1. Photosensitized isomerization of 2-butenes

Photosensitizer	E_T/kJ mol^{-1}	$[\mathrm{T}]_\infty/[\mathrm{C}]_\infty$	T/K	P/Pa	Ref.
Hg($^3P_1$)	470	1.13	295	10850	4
		1.03[a]	298	2670	5
		1.00 ± 0.02[a]	295	4000-7030	6
Cd($^3P_1$)	365	1.07 ± 0.02	548-623	1330	5
Zn($^3P_1$)	387	1.50 ± 0.09	578-633	500-7060	This work
SO_2	307	1.27			4
		1.9 ± 0.1			7
Benzene	356	1.38			8,9
		0.95 ± 0.10			10
Toluene	347	1.70			9
Pyridine	356	1.35			9

[a] Ratio of the quantum yields for cis→trans and trans→cis isomerization

In Table 1, the photostationary trans/cis ratio for the isomerization photosensitized by various sensitizers is shown. The ratio, $[\mathrm{T}]_\infty/[\mathrm{C}]_\infty$, in the cadmium- and mercury-photosensitized isomerization is about unity, but the ratio for other sensitizers including zinc is larger than unity.

The fact that the ratio is about unity in the cadmium-photosensitized reaction shows that k_3 equals to k_4 and $\alpha = 0.5$.[5)] However, in the zinc-photosensitized reaction, the ratio is considerably larger than unity. This observation seems to come from either of the following cases: (1) trans- and cis-2-butenes have different quenching cross sections for $Zn(^3P_1)(k_3 \neq k_4)$, (2) the ratio of trans- to cis-2-butene formed from the excited butene molecule is not unity($\alpha \neq 0.5$). Cundall pointed out that the photostationary ratio larger than unity for the reaction photosensitized by organic sensitizers results entirely from different quenching cross-section of the isomers in their interaction with the sensitizer molecules.[9)] As Table 1 shows, the ratio does not seem to be correlated energy of sensitizers, and the ratio is independent of reaction temperature and pressure. To check the possibilities (1) and (2) for the zinc-photosensitization, the initial rates of the isomerization from both isomers and the quenching efficiencies of zinc resonance line for both isomers are necessary to be measured.

A more detailed discussion will be made in future.

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