Isomerization Reactions of Dideuteroethylene and *cis*-2-Butene Photosensitized by $Zn(^3P_1)$

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Unimolecular isomerizations of monoolefins have extensively been used for the study of the photosensitizations in which the energies transferred from photosensitizers to reactants are less than the dissociation energies of any hydrocarbon bond.[1-4] More than twenty years ago, for instance, Steacie and his collaborators showed that excited zinc atoms were capable of sensitizing the reaction of ethylene.[5] Since then, however, no paper has appeared on zinc-photosensitization except a short note.[6]

A zinc lamp emits two resonance lines, one at 3076 Å, the other at 2139 Å. The latter is easily filtered out with a glass filter such as UV29 supplied by the Toshiba Denki Co. The lifetime of $Zn(^3P_1)$ has been reported to be 2×10^{-5} sec.[7] The energy transferred from $Zn(^3P_1)$ is 93.0 kcal, which is in between the values with $Cd(^3P_1)$ and $Hg(^3P_1)$.

Using the detecting method previously reported,[2] we examined the reaction of *trans*-dideuteroethylene photosensitized by $Zn(^3P_1)$ over the temperature range from 320 to 350°C in the expectation that the reactions could be explained by a mechanism similar to that of the photosensitization by $Cd(^3P_1)$.[3] However, unexpected results were obtained. The main reaction observed was *cis-trans* isomerization, the quantum yield of which increased with an increase in the pressure of the reactant, reaching more than twenty at the pressure of 40 mmHg. On the other hand, the isomerization to 1,1-dideuteroethylene, which is one of the main reactions in the Cd-photosensitization at low pressures,[3] was observed to occur very slowly.

With *cis*-2-butene as a reactant, slow *cis-trans* isomerizations were observed to occur both with and without the irradiation of the zinc resonance line at 3076 Å. The reaction with the irradiation was much slower than that of ethylene. When a small amount of acetylene was added to this system, however, the dark reaction was inhibited and the reaction photosensitized by $Zn(^3P_1)$ was much enhanced. The results are shown in Fig. 1.

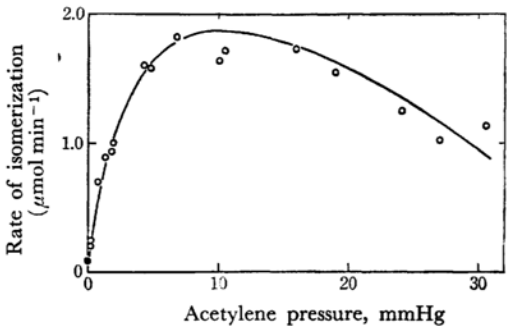

Fig. 1. Rate of the isomerization from *cis* to *trans*-2-butene photosensitized by $Zn(^3P_1)$ as a function of the pressure of acetylene added. (Initial pressure of *cis*-2-butene is 10 mmHg. Irradiation time is 2 min)

These results obviously show that excited zinc atoms react with ethylene or acetylene to produce catalyzers for the *cis-trans* isomerization of olefins. These catalyzers must be short-lived, because the isomerizations do not proceed after the termination of the irradiation. The mechanism of these reactions and the nature of the catalyzer are now being investigated.

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