Frequency Effect of Ultrasound on Debromination of Stilbenedibromides with Zinc Powder

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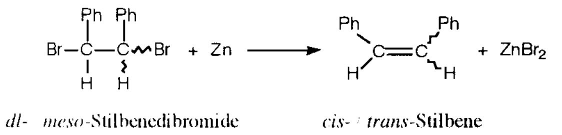
Stereoselectivity in the debromination of *dl*-stilbenedibromide with zinc powder remakably depended on the frequency of ultrasounds, while that of the *meso*-form did not.

Chemical application of ultrasounds has received much attention, since ultrasounds with frequencies between 20 and 100 kHz influence chemical reactions through an effect known as the cavitation phenomenon.[1-5] It is also well known that most of chemical effects of ultrasounds is caused by ultrahigh temperature, pressure and jet-stream generated by the cavitation. On the other hand, ultrasounds with much higher frequencies such as MHz ranges, although used for chemical analysis particularly for remote sensing in flow systems, are unsuitable for changing chemical reactivity since an extremely large amount of ultrasonic energy is required for the cavitation and consequently no cavitation can actually occur in most case in MHz ranges.[1, 2, 6] Therefore, frequency effects of ultrasounds involving MHz ranges on chemical reactions have been rarely studied so far. Recently, Deckerheer *et al.*[7] have reported that reaction rates of the Weissler reaction and the Br_2-catalyzed isomerization of maleic acid into fumaric acid are different in the kHz and MHz ranges, but the difference in the rates might be merely due to difference in not the frequency but the cavitation intensity.

From the above point of view, we aimed to explore a more significant effect of the high frequency on a chemical reactivity, *i.e.* stereoselectivity in the debromination of stilbenedibromides with zinc powder[8-10] (Scheme 1) in the present work.



Scheme 1. The debromination of stilbenedibromides with zinc powder.

A cylindrical vessel (Diameter, 3 cm) equipped with an alumel-chromel thermocouple was used for the debromination of stilbenedibromides (0.15 mmol) with zinc powder (Kanto Chemical Co., Inc., < 300 mesh, 15 mmol) in CH_3OH (30 cm^3). The zinc powder was activated by pretreatment with 4% HCl.[11] *dl*-Stilbenedibromide (Mp : found, 109-110 °C; literature, 110-111 °C) was prepared by a procedure in the literature[9] and other reagents were used as received. Irradiation of ultrasound was conducted by inserting ultrasound oscillators (Tokin Co., NMP for 500 kHz and 1.5 MHz; Shimadzu Co., USP 400 for 20 kHz) into the reaction vessel. The output power of ultrasounds was determined by adiabatic measurement of temperature raise of sonicated water.[12] Cavitation intensity index was monitored by a cavitation meter (Arock Industrial Co., Ltd., Model KS-8201R) which indicates the total acoustic energy of sounds generated when cavities crush without physical unit. Reaction temperature during the sonication was kept constant at 30, 40 or 50 °C by using a cooling bath, and the zinc powder was mechanically stirred to suspend by a rotating magnet bar (800 rpm). After completion of the reaction (Reaction time, 60 min), the zinc powder unreacted was filtered off and a mixture of *cis*- and *trans*-stilbene formed was analyzed by ultraviolet absorption spectroscopy.[13] The debromination gave stilbenes in 100% yields in each experiment. No stereoisomerization of *cis*- and *trans*-stilbenes took place by the sonication at any frequencies.

Figure 1 shows an influence of ultrasonic power on selectivity for *cis*-stilbene formed in the debromination of *dl*-stilbenedibromide under sonication at various frequencies. The selectivity is decreased with an increase in the power (at > ca. 4 W cm^{-2}) and reachs 0% at 14 W cm^{-2} under sonication at 20 kHz. Contrary to the result at 20 kHz, the selectivity is increased with an increase in the power at 1.5 MHz. The selectivity is almost independent of the power at 500 kHz.

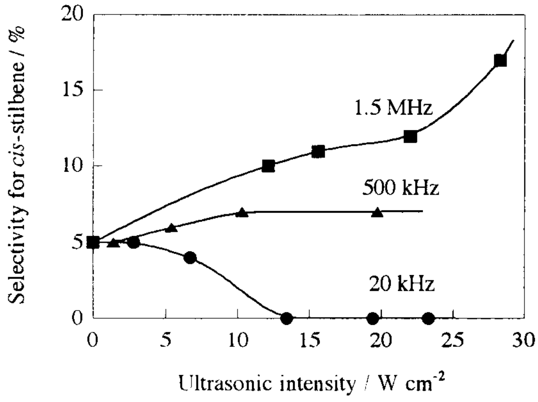


Figure 1. Influence of ultrasonic power on the stereoselectivity for *cis*-stilbene in the debromination of *dl*-stilbenedibromide under sonication at some various frequencies.

Coincidently with the decrease in the selectivity at 20 kHz, cavitation intensity index monitered in the reaction mixture without zinc powder increases steeply with an increase in the ultrasonic power at > 4 W cm^{-2}, as shown in Figure 2. The power of 4 W cm^{-2} is a so-called cavitation threshold value in this experimental system. On the other hand, the cavitation intensity indexes were extremely small and zero values in the wide range of the power at 500 kHz and 1.5 MHz, respectively. From facts shown in Figures 1 and 2, it can be stated that the ultrasonic effect on the stereoselectivity at a low frequency such as 20 kHz is rationalized as being due to cavitation, while that at a high frequency such as 1.5 MHz is caused by an ultrasonic phenome-non other than the cavitation, for instance, ultrasonic energy relaxation or absorption with chemical species involved in the reaction.

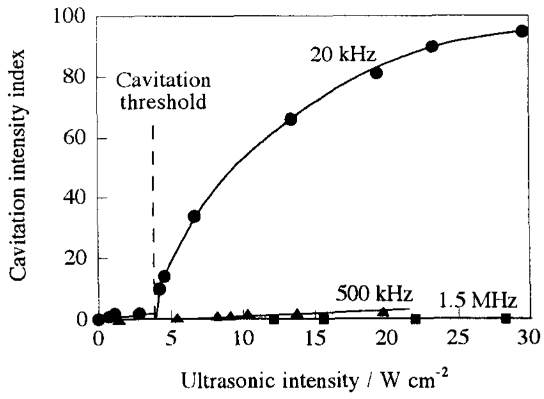


Figure 2. Relationship between cavitation intensity index and ultrasonic power at various frequencies.

It is known that the ultrasonic energy relaxation with *vic*-dibromides is greatly affected by temperature.[14] From this viewpoint, the stereoselectivity was also examined at various reaction temperatures. As shown in Figure 3, a significant temperature dependence on the stereoselectivity was observed at 1.5 MHz, while that was not at 20 kHz and under no sonication merely with mechanical stirring. This fact indicates a possibility that the ultrasonic effect on the stereoselectivity at 1.5 MHz may be due to the relaxation.

The stereoselectivity did not change to be ca. 5%, when the reaction was performed under no sonication using zinc powder pretreated by an ultrasound at either 20 kHz or 1.5 MHz. This fact indicates that the stereoselectivity control above mentioned is not due to surface treatment / activation of the zinc powder by ultrasounds. In addition, the reaction of *meso*-stilbenedibromide gave *trans*-stilbene in 100% of stereoselectivity, regardless of sonication at any frequency and power. This result also suggests that the reduction takes placevia a complicated non-stereospecific process which involves intermediate species to be stereochemically isomerized by ultrasounds with either low or high frequencies.

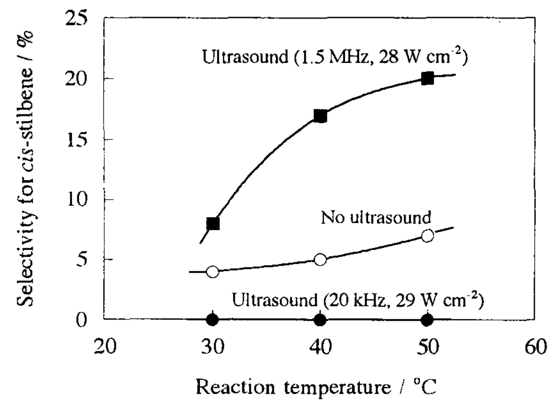


Figure 3. Influence of reaction temperature on the stereoselectivity for *cis*-stilbene without and with sonication at 20 kHz and 1.5 MHz.

A further investigation from mechanistic aspects is in progress.

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