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Catalytic Oxidation of Sulfur Dioxide by Oxygen in an Aqueous Solution of Sulfuric Acid in the presence of Bivalent Manganese Ions under Ultrasound Irradiation

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Ultrasound irradiation is shown to cause oxidation of sulfur dioxide by oxygen, in an aqueous solution of H_2SO_4 containing Mn^{2+} ions as a catalyst, with an energetic yield typical for chain reactions.

The study of sulfur dioxide oxidation under various conditions is of great importance in connection with the problems of industrial waste purification.

Many redox reactions induced by ultrasound irradiation in aqueous solutions, including catalytic ones, have already been investigated. These reactions often resemble those that are initiated by ionizing irradiation, although there are a number of considerable differences.[1,2] It was interesting to examine whether the SO_2 oxidation reaction in the system of SO_2–$MnSO_4$–H_2SO_4–H_2O–O_2 proceeds under ultrasound irradiation as it does under ionizing irradiation, the influence of the latter on this system having been thoroughly studied.[3,4]

Radiation-induced SO_2 oxidation in aqueous solutions containing H_2SO_4 is known to follow a chain mechanism.[3] In the presence of Mn^{2+} the extremely large growth of the yield of this reaction has been shown to take place because of an increase in the chain length. Indirect proof is given that Mn^{3+} ions, formed from Mn^{2+} ions by radiation oxidation, are able to form complex ions with oxygen and thus can act as an oxygen transfer agent.[4]

The purpose of the present work is to examine the possibility of ultrasound-induced SO_2 oxidation in aqueous solution in the presence of Mn^{2+} ions as a catalyst.

The experimental equipment is shown in Fig. 1. A 1 mol dm^{-3} aqueous solution of H_2SO_4 containing $MnSO_4$ was pumped with a peristaltic pump (6) successively through the absorber (4) (from top to bottom), through the cooler (5) and then through the glass ultrasonic reactor (1) with a thin polyethylene film bottom which is perfectly transparent to ultrasound. In this reactor the solution was exposed to ultrasound irradiation. The reactor was immersed in an ultrasonic bath (2) filled with water, with an ultrasound transducer (3) on the bottom. A mixture of N_2 and SO_2 was introduced into the absorber from bottom to top through the gas inlet (10). The working atmosphere within the ultrasound reactor was maintained by a slight flow of gas (O_2 or Ar) through the gas inlet (9) on its side. Sonication was accompanied by the formation of a fountain and a dense fog. The SO_2 concentration in the solution was measured at a wavelength of 280 nm using a UV detector 'Uvicord' (LKB) (7) through which the solution was pumped from the reactor by the extra closed loop. The detector output signal (proportional to the SO_2 concentration) was recorded with a strip-chart recorder (8).

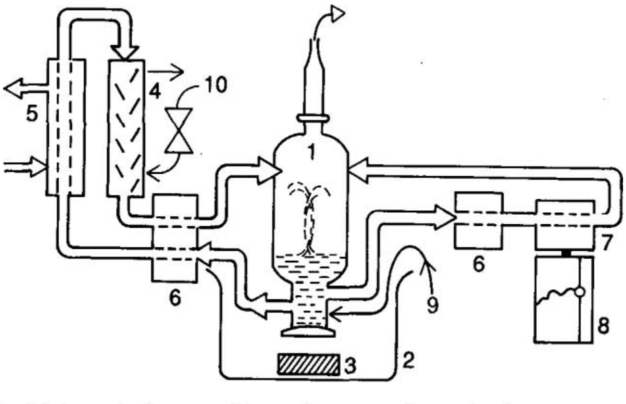

Fig. 1 Schematic diagram of the equipment used to study ultrasonic SO_2 oxidation (see text)

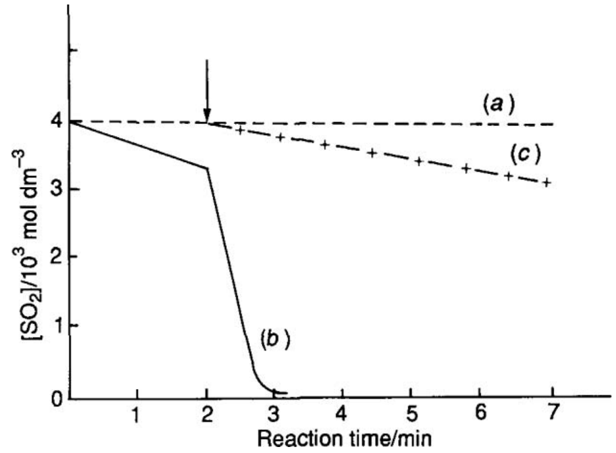

Fig. 2 Kinetic curves for ultrasonic SO_2 oxidation. Curves show SO_2 consumption under sonication in O_2 atmosphere (*a*) without catalyst and under sonication is the presence of 10^{-1} mol dm^{-3} Mn^{2+} ions in (*b*) O_2 atmosphere and (*c*) Ar atmosphere. The start of sonication is indicated by an arrow

The ultrasound frequency was 700 kHz, the acoustic power was 40 W, the maximal ultrasound intensity was 13 W cm^{-2}, the ultrasound reactor volume was 500 ml, the volume of liquid in the reactor was 55 ml, the total volume of liquid was 70 ml, liquid flow rate was 100 ml min^{-1}, absorber height was 40 cm (a glass rectification column was used as the absorber).

The experiment was carried out as follows: while pumping the solution continuously the gas mixture containing SO_2 was passed through the absorber until the SO_2 concentration in the solution reached the necessary value, then the gas flow was stopped, the ultrasound irradiation was started and the time dependence of the SO_2 concentration was registered. A Fricke dosimeter system (0.005 mol dm^{-3} $FeSO_4$, 0.002 mol dm^{-3} NaCl and 0.4 mol dm^{-3} H_2SO_4 in distilled water) was sonicated in the oxygen atmosphere under the same conditions as the system studied. The Fe^{3+} yield was measured spectrophotometrically at 305 nm.

The time dependences of the SO_2 concentration are shown in Fig. 2(*a*–*c*). These are the kinetic curves of SO_2 consumption under sonication in O_2 atmosphere without the catalyst [Fig. 2(*a*)], under sonication in the presence of 10^{-1} mol dm^{-3} Mn^{2+} ions in O_2 atmosphere [Fig. 2(*b*)] and Ar atmosphere [Fig. 2(*c*)]. It can be seen that without the catalyst the reaction practically does not run either with or without sonication. In the presence of the catalyst in an O_2 atmosphere, comparatively slow spontaneous SO_2 oxidation is observed. The ultrasound irradiation accelerates the oxidation reaction considerably. Because the ultrasound-induced oxidation rate does not depend on the SO_2 concentration (the kinetic curve is linear), the order of the reaction with respect to SO_2 concentration is zero [Fig. 2(*b*)]. The transformation of SO_2 under Ar atmosphere is slower than that under O_2 (it is possible that oxidation is caused by an O_2 impurity in Ar of approximately 0.2%).

Ultrasound irradiation is a kind of mechanical action. Most of the peculiar ultrasound effects observed in liquids are due to

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the cavitation phenomenon, *i.e.* the formation of little gas bubbles oscillating at ultrasound frequency, these are often referred to as cavitation bubbles. It is known from literature data[2] that most of the chemical effects of ultrasound irradiation in aqueous solutions originate from thermal processes within the cavitation bubbles. Non-volatile solutes react with active species (mainly H and OH radicals) which are formed within the bubbles and then escape into the bulk solution, Volatile solutes (including SO_2) can also be affected directly by the high temperatures within the bubbles. The ultrasound-induced SO_2 oxidation rate does not depend on the SO_2 concentration under the conditions of our experiment. It is thus possible to conclude that the second pathway does not play a considerable role in the reaction studied under the given conditions. Indeed, if direct thermal oxidation of SO_2 by oxygen within the bubbles were of importance the oxidation rate should rise with SO_2 concentration increase in the bulk, becauses the greater the concentration in the bulk, the greater is that in the gas phase within the cavitation bubbles. Therefore, the reaction is promoted by the products of the thermal water decay: the active radicals H and OH. The same active species cause γ-irradiation-induced Fe^{2+} oxidation. Hence, it is possible to estimate the energetic yield of SO_2 oxidation using the SO_2 oxidation rate estimated from the slope of the kinetic curve in Fig. 2(*b*) and the γ-equivalent ultrasound dose rate measured with the Fricke dosimeter (*i.e.*, the γ-irradiation dose rate that causes Fe^{2+} oxidation at the same rate as ultrasound irradiation under the conditions of the experiment). The γ-equivalent ultrasound dose rate was measured to be $900\,\mathrm{Gy\,h^{-1}}$,† assuming $G(Fe^{3+}) = 15.5$ ion/100 eV.[5] The oxidation rate under ultrasound irradiation in oxygen atmosphere in the presence of $10^{-1}\,\mathrm{mol\,dm^{-3}}$ Mn^{2+} was $8 \times 10^{-5}\,\mathrm{mol\,dm^{-3}\,h^{-1}}$. Calculated from these data, the oxidation energetic yield $G(SO_2) = 3 \times 10^3$ molecules/100 eV. Such a high energetic yield is typical for chain reactions. We propose that the oxidation chain (by analogy with radiation-induced oxidation) starts with oxidation of bivalent manganese ions by H and OH radicals, escaping into the bulk solution from cavitation bubbles. The high oxidation state manganese compounds thus formed act as an oxygen transfer agent. These manganese compounds are probably much more active catalysts of SO_2 oxidation than the Mn^{2+} ions themselves. The reaction slows down considerably as soon as ultrasound irradiation ceases, therefore, these manganese compounds are unstable under the conditions of the reaction. So, the role of the ultrasound radiation is probably to maintain a certain steady concentration of catalytically active manganese compounds.

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† $1\,\mathrm{Gy} = 1\,\mathrm{J\,kg^{-1}}$.

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