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On the Thermal Decomposition of Shock-heated SO_2

Ko Saito,* Teiji Yokubo, Tetsuo Higashihara, and Ichiro Murakami
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashi Senda-machi, Hiroshima 730

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Synopsis. The SO_2 pyrolysis was measured behind reflected shock waves under low SO_2 concentrations. A typical induction zone was observed in the decomposition process. It was found that the overall rate constants after the induction zone were in good agreement with the values for the primary reaction obtained by the following investigators: Just and Rimpel, Kiefer, and Grillo *et al.* This implies that, even in highly diluted mixtures at low pressures, the kinetics of the SO_2 decomposition is complicated.

The thermal decomposition of SO_2 behind shock waves has been investigated by many workers.$^{1-8)}$ However, a problem regarding the second-order rate constant, k_1, for the primary reaction: $SO_2+M\rightarrow SO+O+M$, remains, since the decomposition has been found to proceed in a complex manner when high concentration mixtures are used. Olschewski *et al.*$^{2)}$ measured the rate constant, k_1, for highly diluted mixtures (less than 0.1 mol % in Ar). Later, their results were revised slightly by Astholtz *et al.*$^{6)}$ of the same laboratory by using mixtures of SO_2–Ar ranging from 100 to 2000 ppm SO_2 ($5\times10^{-10}<[SO_2]<\sim10^{-8}$ mol cm^{-3}). Just and Rimpel$^{5)}$ measured k_1 by observing the O-atom production rate by means of atomic resonance absorption spectroscopy. Since they measured the rate for highly diluted mixtures (20—200 ppm SO_2 in Ar) and at low total pressures, corresponding to $\sim10^{-11}<[SO_2]<\sim10^{-10}$ mol cm^{-3}, they assumed that subsequent reactions play only a minor role in the process, and they obtained the k_1 values which were much higher than the values of Astholtz *et al.* (higher more than one order). The values of Just and Rimpel were, though, in rather good agreement with those obtained by Kiefer$^{4)}$ (3—30% SO_2 in Kr) and by Grillo *et al.*$^{7)}$ (0.13 and 0.26% SO_2 in Ar). It is considered that, under the experimental conditions in Kiefer's work ($[SO_2]>3\times10^{-8}$ mol cm^{-3}), the obtained data presumably relate to the complex reaction involving the bimolecular reaction of the reactant, not to the primary unimolecular process, although the rate constants were expressed simply as first order in $[SO_2]$, with a very high activation energy (close to the bond dissociation energy of OS–O). In the same sense, the experiments of Grillo *et al.* ($[SO_2]>1\times10^{-8}$ mol cm^{-3}) may also be considered to be connected with the complex reaction.

Thus, the experimental values of k_1 reported hitherto split into two groups, which differ from each other by a factor of about 20. There thus arises the question of whether or not the reaction is really simple in low-concentration mixtures, as in the Just and Rimpel work. There is another problem for the higher k_1 values as to the collision efficiency factor of 0.17 at about 3000 K,$^{5)}$ which is considerably higher than in the other similar reactions.

Levitt and Sheen$^{3)}$ observed the visible emission from shock-heated SO_2–Ar mixtures (5—10% SO_2) and obtained the overall rate of the SO_2 decomposition at around 3000 K on the basis of the proportionality between the emission intensity and the concentration of SO_2. This method is considered to give a good time and spatial resolution, without any large noises. In this study, therefore, we tried to measure the decomposition rate of SO_2 by monitoring the light emission from the shock-heated mixtures under the same conditions as those of Just and Rimpel.

Experimental

A shock tube 9.4 cm in inner diameter was used. The test section was evacuated to less than 1×10^{-6} Torr (1 Torr=133.322 Pa) before each run. The gas conditions behind the reflected shock were calculated by using the incident shock speed in the manner reported in a previous paper.$^{9)}$ The light emitted from the shock-heated gas was taken out of a quartz window through a slit 0.5 mm wide and was passed again through a second slit 0.5 mm wide placed at 15 cm apart from the window. Then the light was passed through a filter of 392.5±5 nm and was detected by means of a photomultiplier. The output signal was fed to a preamplifier and was recorded by a wave-memory with a sampling speed of 0.2 μs. Since, occasionally, the emission profile varies with a change in the optical arrangement and depends on the conditions of the inner wall of the tube,$^{10)}$ we carefully checked to see that the field of view in the tube was less than 1 mm and that the reflection diffused by the opposite wall was removed completely.

Commercial SO_2 (99.0% minimum purity) was used after trap-to-trap distillation. Ar (99.998%) was used as the diluent, without any further purification. Mixtures of 0.01 and 0.05 mol% of SO_2 in Ar were prepared by diluting a premixed 5 mol % mixture.

Results and Discussion

The experiments were performed under these conditions: temperature=3000—4700 K; total density=6.7×10^{-7}—3.3×10^{-6} mol cm^{-3}. Figure 1 shows typical emission records at different temperatures and $[SO_2]\simeq9\times10^{-11}$ mol cm^{-3}. The peak height was ascertained to be the thermal emission from the electronically excited state of SO_2.$^{11)}$ That is, a logarithmic plot of the peak intensity per unit of SO_2 concentration *vs.* 1/T agreed with the curve calculated theoretically, considering the temperature dependences of the partition functions of the ground and excited states.

The emission profiles obviously reveal the existence of an induction zone during the pyrolysis, as is shown in Fig. 1. The length of the induction zone decreases with an increase in the temperature, and at high temperatures it disappears from the profile (Fig. 1d).$^{12)}$ The first-order rate constants, $k_{1st}=-d(\ln I)/dt$, were obtained from the decay curves after the induction

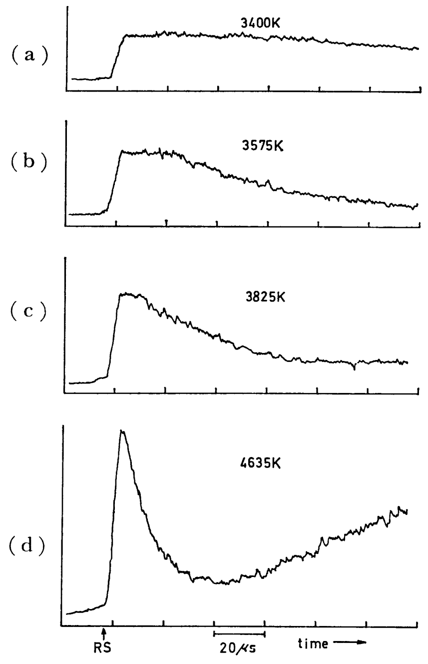

Fig. 1. Typical emission profiles at different temperatures.
Total densities are $(8.5\pm1)\times10^{-7}$ mol cm^{-3}. RS: reflected shock front.

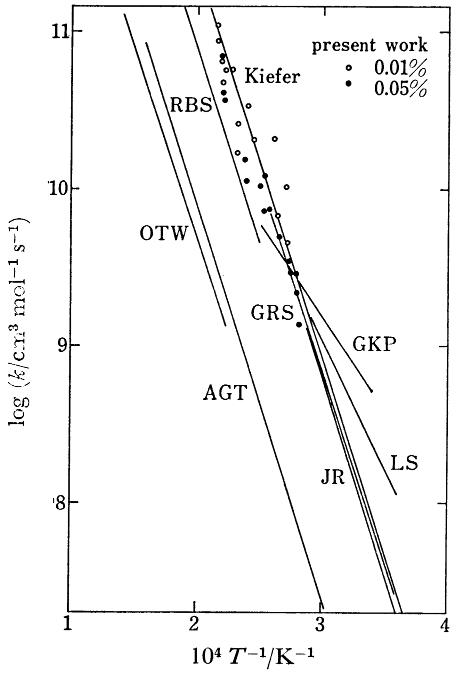

Fig. 2. Comparison of second-order rate constants.
GKP: Ref. 1, OTW: Ref. 2, LS: Ref. 3, Kiefer: Ref. 4, JR: Ref. 5, AGT: Ref. 6, GRS: Ref. 7, RBS: Ref. 8.

zone, where I is the emission intensity. Then, the values of the second-order rate constant were calculated as: $k_{2nd}=k_{1st}/[Ar]$. In this method, there arises no problem regarding the ambiguousness of the absolute SO_2 concentration in the mixture due to the adsorption of SO_2 on the walls of the reservoir and the shock tube. A plot of the second-order rate constant, k_{2nd}, is shown in Fig. 2, together with the previous data. It is obvious that our data points are near Kiefer's result and also the extended lines of the results of the Just and Rimpel and Grillo *et al.* The values of k_{2nd} correspond clearly to the complex decomposition rate of SO_2, since they were determined not from the initial decay, but from the decay behind the induction zone. The primary reaction rate is considered to reflect the initial decay rate at the earlier position in the induction zone; thus, it should give much smaller values than k_{2nd}. From the emission experiment, however, at least in our present work, no measurable decrease of the intensity was observed in the induction zone. From the present observations, it is likely that the primary reaction rate is as much as one order slower than the overall reaction rate behind the induction zone. In this respect, at the present time, Astholtz *et al.*'s data on the primary reaction rate constant are considered to be the most reliable. As has been described above, the data obtained by Kiefer and Grillo *et al.* obviously correspond to the complex reaction and, therefore, do not conflict with the present results. However, we cannot explain why the observation of the initial production rate of the O atom by Just and Rimpel gave such large values for k_1 under their experimental conditions.

Although, in this work we could not measure the value of k_1, it was confirmed that the decomposition of SO_2 proceeds in a complex manner, even in highly diluted mixtures and at low total pressures. Further investigations with more elaborate techniques will be needed to determine the true value of k_1.

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11) The emitting state at this wavelength was assumed to be the a $^3B_1$ state. According to the analysis by Levitt and Sheen (*Trans. Faraday Soc.*, **63**, 540 (1967)) the emission from the A^1B_2 state is slightly involved at this wavelength.

12) The increase in the intensity in the later part of the reaction period, appearing in Fig. 1d, is the emission due to the recombination of SO and O. The effect of this emission on the earlier part of the profile is considered to be negligible.