Application of Microwave Spectroscopy to Kinetic Study of the Reaction of Carbonyl Sulfide with Atomic Oxygen

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Microwave spectroscopy has been applied to the determination of the rate constant for $OCS+O \rightarrow SO+CO$. A short cell of a parallel-plate type was devised for the detection of the SO radicals produced in a fast flow reactor. Production of the SO radical was traced by measuring its spectral line intensity under the condition of $[OCS] \gg [O]$. The rate constant for the reaction was determined to be $(7.1 \pm 0.7) \times 10^9$ cm^3/mol·s at room temperature (24—25) °C, in good agreement with the values obtained by other methods.

Microwave spectroscopy has been so far mainly concerned with molecular structural studies. Recently some of its applications to the studies of reaction mechanisms have been reported, examples of which are the detection of transient species and the quantitative analysis of final products. In the former studies, about forty species of free radicals, unstable molecules and molecular ions have been detected, though major interest has been focused on their structures. The latter kind of studies have been encouraged by the establishment of an improved technique[1] for measuring the relative intensities of microwave absorption lines. The catalytic hydrogen-exchange reaction of propene with deuterium or deuterium oxide has been thoroughly investigated by analyzing the geometric isomers of deuterated propenes produced. Thus the adsorbed species of propene on various catalysts have been clarified more precisely than before.[2] Other catalytic reactions have been also investigated with remarkable success.[3]

The success of these applications is entirely due to the high specificity of microwave spectroscopy with respect to the detection of molecular species and its high sensitivity. These distinctive features led to the application of microwave spectroscopy to the kinetic studies of gas-phase fast reactions reported here. The reaction investigated was

$$OCS + O \xrightarrow{k} SO + CO. \qquad (1)$$

The initial step of the reaction of carbonyl sulfide with atomic oxygen has been investigated kinetically by means of ESR and MS spectroscopies.[4] Reliable values of the rate constant k reported in five seperate studies[5—9] enable the applicability of the microwave spectroscopic technique to be tested.

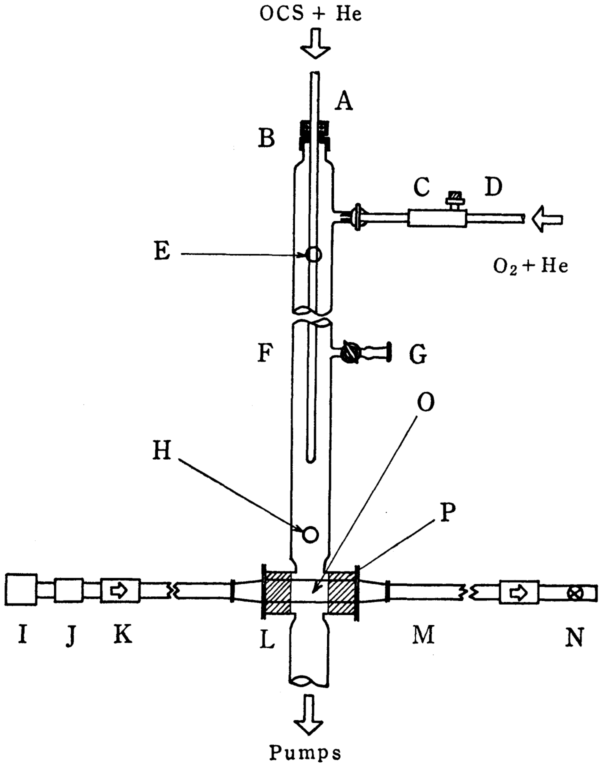

Fig. 1. Schematic diagram of experimental apparatus. A: Injector tube, B: O-ring sliding seal, C: microwave discharge cavity, D: quartz tube, E: McLeod gauge, F: flow tube, G: additional tap for thermal decomposition of $\underline{CH_2CH_2SO}$, H: capacitance manometer, I: klystron, J: power attenuator, K: ferrite isolator, L: absorption cell, M: X-band waveguide, N, crystal detector, O: Stark electrode, P: Teflon block.

Experimental

The reaction of carbonyl sulfide with atomic oxygen was studied at about 0.13 Torr at room temperature (24—25) °C, by the use of a fast flow reactor with a microwave spectroscopic detection system. The apparatus used is shown schematically in Fig. 1. The reactor consisted of a flow tube (36 mm inner diameter Pyrex) coated with H_3PO_4 for reducing atom recombination, a movable injector tube (10 mm outer diameter Pyrex) with nine evenly spaced small holes on its head, and a microwave discharge tube (9 mm inner diameter quartz) equipped with an Evenson-Broida type 2a cavity operating at 2450 MHz. A Baratron capacitance manometer (MKS Instruments, Inc.) and a McLeod gauge were placed at about 10 and 94 cm upstream from the microwave absorption cell, respectively.

The atomic oxygen was produced by passing a mixture of O_2 and He through a microwave discharge tube. About 2.5% of the O_2 molecules dissociated into O atoms. Carbonyl sulfide gas, diluted with He was fed into the partially dissociated O_2 flow via the injector. The duration of the reaction was controlled by the distance between the injector head and the cell. The injector was moved less than 50 cm in each run, which covered

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the reaction range of about 50 ms. Flow rates of the gases were controlled by means of stainless steel needle valves, monitored roughly with glass flow meters, and determined accurately by measuring the pressure rise in a bulb known volume after each run. The initial concentration of oxygen atoms, $[O]_0$, was titrated with NO_2[10] in the absence of OCS, by visual observation of the greenish yellow afterglow emitted by the recombination reaction of O with NO in the presence of an excess of O atoms over NO_2 molecules.

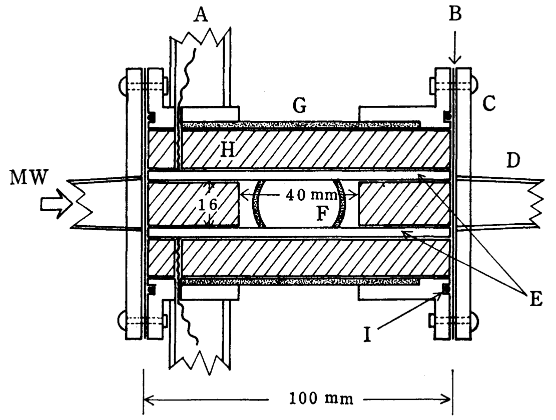

Fig. 2. Cross-sectional view of microwave absorption cell.
A: Stark input, B: mica window, C: blass flange, D: tapered transition unit, E: Stark electrodes, F: flow tube, G: Pyrex tube (55 mmϕ), H: Teflon block, I: O-ring.

The cross-sectional view of the microwave absorption cell is shown in Fig. 2, where the direction of the gas flow is perpendicular to the plane of the paper. A pair of gold-plated brass plates (3×30×100 mm), which served as Stark electrodes, were fixed 16 mm apart from each other in a Pyrex tube (55 mm outer diameter). Unessential spaces in the cell were filled up with Teflon blocks in order to obtain a smooth gas flow. The effective absorption length of the cell was 40 mm. The cell was completely vacuum-tight with O-rings and mica windows for microwave. A pair of ferrite isolators were incorporated to prevent multiple reflection of the microwave in the cell.[1] They were placed 80 cm apart from the cell (see Fig. 1) to avoid the influence of their magnetic field leakage upon the paramagnetic species SO. The microwave spectrometer used was a conventional one with 110 kHz sinusoidal Stark modulation.[11]

The SO appearance was monitored by observing a microwave absorption line at 13044 MHz, the transition $J,K=1,2\leftarrow 1,1$.[12] The signal was recorded very slowly (1 MHz/min) with a time constant of 3 s in order to obtain almost true line shape. Three or four sweep runs were averaged for each signal. As the sinusoidal Stark modulation was used, the observed signal was the first derivative of the Lorenzian absorption line. The absolute intensity is proportional to $H\cdot(\Delta\nu)^2$, where H and $\Delta\nu$ denote the peak-to-peak amplitude and the width of the derivative,[13] respectively. In the determination of the rate constant k for Reaction 1, however, only the relative amplitude of the signal was sufficient to obtain relative concentration of SO, since the widths were practically constant over the reaction range. The signal intensity, H, was calibrated into the absolute concentration only to examine the stoichiometry of Reaction 1. The calibration was performed by using another source of SO, that is, the thermal decomposition of ethylene episulfoxide $(\underbrace{\mathrm{CH_2CH_2SO}})$ in He at 600 °C,[14] and by titrating with NO_2:[15] $SO+NO_2\rightarrow SO_2+NO$.

The sample gases, helium (airco, 99.9995%), oxygen (Toyo Sanso, 99.99%) and carbonyl sulfide (Matheson, 97.5%), were taken directly from their respective cylinders. Matheson NO_2 was purified by mixing it with O_2 and passing it over evaporated P_2O_5 films. This was followed by vigorous pumping of the white frozen solid at 77 K, in order to remove the impurities of H_2O and NO. Ethylene episulfoxide was prepared by the reaction of ethylen episulfide with *m*-chloroperbenzoic-acid in CH_2Cl_2[16] at −10 °C, and was purified by distillation under reduced pressure.

Results and Discussion

Performance of the Spectrometer. The quantitative steady-state experiment, such as the present one, indispensably requires a detection system which is stabilized over a long period of time and whose response is proportional to the concentration of species to be detected. This aspect was examined using a flow of OCS highly diluted with He at about 0.05 Torr. The signal amplitude of the OCS ($J=1\leftarrow 0$, 12163 MHz), having a signal-to-noise ratio of about 50, was monitored over 4 h. Maximum fluctuation of the amplitude was about 3%, while that of the total pressure was only 0.5%. Figure 3 shows plots of the signal amplitudes and widths as a function of OCS concentration. The linearity of the spectrometer is clearly shown in the figure, where the signal amplitude is directly proportional to the concentration while the signal width remains constant. Figure 3 also indicates the sensitivity of the spectrometer. On the basis of the noise intensity of 0.3 unit in the above results, the OCS signal with the signal-to-noise ratio of 2 corresponds to 2×10^{-12} mol/cm^3. The minimum detectable concentration of SO was proved to be 1×10^{-12} mol/cm^3.

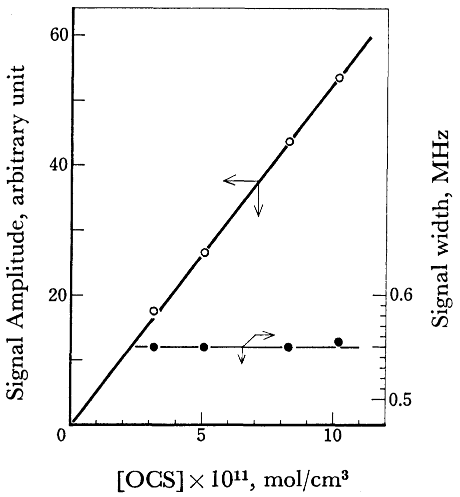

Fig. 3. Peak-to-peak amplitude and width of OCS first-derivative signal (12163 MHz) *vs.* OCS concentration. *T*: 27.5 °C, *P*: 0.0572−0.0591 Torr, He flow: 9.86 μmol/s, Noise level: 0.3 unit.

Determination of the Rate Constant k. In order to perform an exact analysis of a flow system, it would be necessary to employ a laborious treatment. In the present study it was assumed that the radial concentration gradients and axial diffusion rates were negligible and that the parabolic velocity distribution could be replaced by an average velocity (v). Furthermore it was assumed that Reaction 1 operated simply and other side reactions were ignored. Then the solution of the rate equation becomes

$$k\cdot t = -\frac{1}{[\mathrm{OCS}]_0-[\mathrm{O}]_0}\cdot\ln\frac{[\mathrm{O}]\cdot[\mathrm{OCS}]_0}{[\mathrm{O}]_0\cdot[\mathrm{OCS}]}. \qquad (2)$$

The present experiments were performed under a condition of a large excess of carbonyl sulfide, $[\mathrm{OCS}]_0 \gg [\mathrm{O}]_0$, so that [OCS] is essentially constant throughout the reaction. Equation 2 can be reduced under this condition, and replacement of $[\mathrm{O}]_0$ by $[\mathrm{SO}]_\infty$ yields

$$k\cdot[\mathrm{OCS}]_0\cdot t = \ln(1-[\mathrm{SO}]/[\mathrm{SO}]_\infty)^{-1}, \qquad (3)$$

where $[\mathrm{OCS}]_0$ is the initial concentration of carbonyl sulfide and $[\mathrm{SO}]_\infty$ the concentration of the SO radicals after infinite time. In Fig. 4, typical plots of $\ln(1-[\mathrm{SO}]/[\mathrm{SO}]_\infty)^{-1}$ *vs.* t are shown for various empirically adjusted values of $[\mathrm{SO}]_\infty$. It may be seen that initial time, $t=0$, can be arbitrarily chosen without loss of generality. As shown in Fig. 4, plots for $[\mathrm{SO}]_\infty=22$ (arbitrary units) produced a linear curve, while the others did not. The values of k obtained from the slopes of several such linear plots are given in Table 1, and the values of k determined by other workers using MS and ESR spectrometers are also listed for comparison. The values of v and $[\mathrm{OCS}]_0$ given in the table were determined at the pressure calculated for the center of the range of the OCS-injection point. The average k thus obtained was 7.1×10^9 cm³/mol·s, which agrees well with the values reported by other workers.

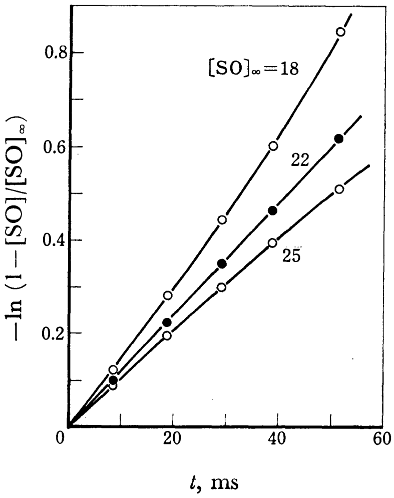

Fig. 4. Typical logarithmic plots of the SO appearance in the reaction of OCS+O→SO+CO for various empirically adjusted values of $[\mathrm{SO}]_\infty$.
T: 24.0 °C, P: 0.1304 Torr, v: 9.6 m/s, $[\mathrm{OCS}]_0$: 1.64×10^{-9} mol/cm³.

Reliability of the Observed Values. An important point in the kinetic studies by the measurement of a product species is how much the product may be lost by side reactions. The O/SO stoichiometry in Reaction 1 was thus examined by comparing $[\mathrm{O}]_0$ and $[\mathrm{SO}]_\infty$, because if the loss of SO by side reactions was significant, $[\mathrm{SO}]_\infty$ should be smaller than $[\mathrm{O}]_0$. In the case of Expt 1 in Table 1, $[\mathrm{O}]_0$ was found to be 2.1×10^{-11} mol/cm³ by the $\mathrm{NO_2}$-titration, while the adjusted $[\mathrm{SO}]_\infty$ value was 2.0×10^{-11} mol/cm³. This good agreement confirms the stoichiometry, and hence supports the assumption of the negligible side reactions. This result is concordant with that reported by Westenberg and deHaas,[8] who confirmed this stoichiometry under highly diluted conditions by monitoring both O and SO with an ESR spectrometer.

Table 1. The rate constant k for OCS+O → SO+CO

Expt No.	T (°C)	P (Torr)	v (m/s)	$[\mathrm{OCS}]_0$ (mol/cm³)	k (cm³/mol·s)
1	25.0	0.1298	9.4	1.57×10^{-9}	7.3×10^9
2	24.3	0.1304	9.6	1.64×10^{-9}	7.0×10^9
3[a]	24.0	0.1372	8.8	1.57×10^{-9}	7.1×10^9
					(av.$=7.1\times10^9$)
Ref. 5	25.0[b]			Detector: MS	6.7×10^9
6	25.0[b]			MS	6.0×10^9
7	room temperature			MS	5.5×10^9
8	24.0			ESR	8.5×10^9
9	24.0			ESR	7.2×10^9

a) Effect of metal surface was examined. b) The value calculated from the Arrhenius expression

The most serious difficulty of the microwave technique may arise from the possible effect of the metal surface of the Stark electrodes on the kinetic measurement, particularly in the case of transient species. In order to assess the error, k was determined when a gold-plated brass plate having almost the same surface area as the electrodes was inserted into the flow tube. The result is listed in Table 1 as Expt 3. Comparison of the results demonstrates that there was little difference in the values of k determined with and without the extra metal surface in the flow tube. Therefore, the surface of the Stark electrodes was considered to have little effect on the kinetic measurement.

The microwave absorption cell has a detection zone of about 3 cm. It takes about 2 ms for the flowing gas molecules to pass through the absorption cell. It is not always negiligibly small in comparison with the time range within which the reaction was monitored, but it may be reasonable to consider that the response of the spectrometer corresponds to the concentration at a fixed point in the cell.

The radial concentration gradients and the axial diffusion rate may be evaluated by the diffusion aspect of reactants, and the values of r^2/D and the ratio $k\cdot[\mathrm{OCS}]_0\cdot D/v^2$ are measures of them, where D denotes the diffusion coefficient of the O atoms in He and r the radius of the flow tube. Recently Goldberg and Crowe reported the value of D as 1300 cm²/s at 0.6 Torr and at 280 K.[17] The value corrected to 0.13 Torr is 6000 cm²/s, according to the relation $D=D_0(P_0/P)$ where D_0 is the diffusion coefficient at an arbitrary value of P_0,[18] the small contribution due to temperature dependence being ignored. Thus the value of r^2/D is 0.7 ms in He and $k\cdot[\mathrm{OCS}]_0\cdot D/v^2 \ll 1$. Therefore, the corrections for both effects may be negligible. In the case of the viscous pressure drop, it was about 7—9% within the range where the OCS-injection point was shifted. Westenberg and deHaas reported,[19] "Simply using the pressure at the center of the measurement section to compute flow velocity and reactant concentration yielded essentially the same rate constant as was obtained with more sophisticated corrections for the pressure drop." The effect was assumed to be of the same magnitude in our experiments, since the present conditions were almost the same as theirs.

On these basis the assumptions used in determining k were considered to be reasonable. Stability of the flow system as well as of the detection system was satisfactory, as was described in the previous section. Thus the origin of the errors in the measurement may be ascribed mainly to the relative readings of the signal amplitudes and to the determination of the slopes of the pseudo-first order plots. These measurement errors were roughly estimated to be about $\pm 10\%$.

The results obtained above demonstrate that the microwave spectroscopic technique offers a reliable and powerful means for gas kinetic studies, in spite of some limitations to its applications, *e.g.*, non-polar substances cannot be detected, and the applicable pressure-range is limited normally to 10^{-1}—10^{-2} Torr. Nevertheless, high specificity of the microwave spectrum makes this technique most suitable among the available techniques (ESR, MS, *etc.*) for reactions concerned with isotopic and geometric isomers. In addition to the determination of reaction rate constants, it may be possible by this technique to determine the life-time of transient species and the diffusion coefficients of gaseous substances regardless of their stabilities.

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