Kinetics and Dynamics on the Formation of $S_2(X^3\Sigma_g^-, a^1\Delta_g)$ in the $S(^1D)$ + OCS Reaction

Jun Yamashita[1], Hirofumi Takahashi[1], Kenichi Orimi[1], Tsubasa Hashimoto[1], Hiroshi Kohguchi[1], and Katsuyoshi Yamasaki[1,*]

[1] Department of Chemistry, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan
* Corresponding author: kyam@hiroshima-u.ac.jp

Photolysis of calbonyl sulfide (OCS) is a good source of $S(^1D)$; nevertheless, there have been few reports[1,2] on the rate coefficients of the reaction of $S(^1D)$ with OCS. The reaction of $S(^1D)$ with OCS has three exothermic channels.

$$S(^1D) + OCS \rightarrow S_2(X^3\Sigma_g^-) + CO \qquad \Delta_r H^\circ_{298} = -228 \text{ kJ mol}^{-1} \quad (1)$$

$$\rightarrow S_2(a^1\Delta_g) + CO \qquad \Delta_r H^\circ_{298} = -172 \text{ kJ mol}^{-1} \quad (2)$$

$$\rightarrow S(^3P) + OCS \qquad \Delta_r H^\circ_{298} = -110 \text{ kJ mol}^{-1} \quad (3)$$

The heats of reactions of channels 1 and 2 are large enough to generate vibrationally excited $X^3\Sigma_g^-$ and $a^1\Delta_g$ states up to $v = 29$ and 22, respectively; however, van Veen et al.[1] observed the only level $v = 0$ of the $X^3\Sigma_g^-$ state, and Richter et al.[3] reported the highest populated vibrational level of the $a^1\Delta_g$ state to be $v = 6$. In this paper, the authors have determined the rate coefficient of the $S(^1D)$ + OCS reaction and detected the vibrational levels of $S_2(X^3\Sigma_g^-, a^1\Delta_g)$ higher than those reported previously.

A gaseous mixture of OCS(3–40 mTorr)/He(10 Torr) in a flow cell at 298 K was irradiated with a KrF laser (248 nm) to generate $S(^1D)$ in the photolysis of OCS. The two electronic states $X^3\Sigma_g^-$ and $a^1\Delta_g$ of S_2, produced in the $S(^1D)$ + OCS reaction, were probed with laser-induced fluorescence (LIF) via the $B^3\Sigma_u^- - X^3\Sigma_g^-$ and $f^1\Delta_u - a^1\Delta_g$ transitions, respectively. In the present measurement, vibrational levels at least $v = 15$ of $X^3\Sigma_g^-$ and $v = 10$ of $a^1\Delta_g$ were detected. Time-resolved LIF intensities of the production of the $X^3\Sigma_g^-$ state were recorded at various OCS pressures as shown in Figure 1, giving the overall rate coefficient of the $S(^1D)$ + OCS reaction to be $[3.2 \pm 0.2(2\sigma)] \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

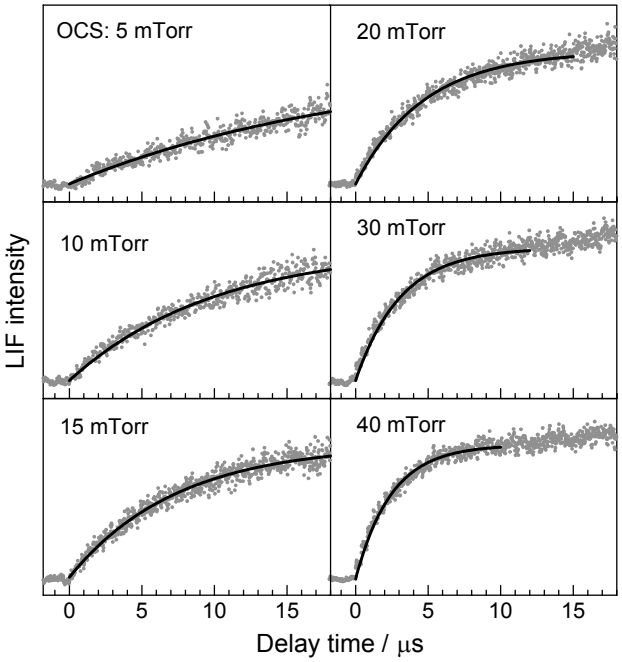

Figure 1. Time-resolved LIF intensities of 3–1 band of $S_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$ transition recorded at different pressures of OCS. p_{He} = 10 Torr. •: observed data and —: simulation.

THURSDAY

References

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