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# Ion-Molecule Reactions in Carbonyl Sulfide-Hydrocarbon Mixtures

Akira MATSUMOTO, Satoshi OKADA,* Toshiyuki MISAKI,
Setsuo TANIGUCHI,* and Teruo HAYAKAWA

*Department of Chemistry, Faculty of Liberal Aarts and Sciences, University of Osaka Prefecture, Sakai, Osaka 593*
**Radiation Center of Osaka Prefecture, Sakai, Osaka 593*

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Thermal energy ion-molecule reactions in carbonyl sulfide–hydrocarbon (methane, acetylene and propylene) mixtures were studied using a mass spectrometer equipped with a pulsed ion source. The rate constants for sulfur atom transfer, sulfur ion transfer and sulfur ion addition reactions were measured.

Several papers have been published on ion-molecule reactions in mixtures of hydrocarbons and sulfur-containing compounds.[1-4] However, reactions leading to $RHS^+$ (RH represents saturated or unsaturated hydrocarbons) have not yet been reported with the exception of ethane studied by Dzidic *et al.*[2] They reported that $RHS^+$ is produced in a mixture of ethane and carbonyl sulfide exclusively *via* $S^+$ transfer from $COS^+$ to ethane, but is not produced in a mixture of methane or ethylene and carbonyl sulfide.

In the present work, further study of the reactions leading to $RHS^+$ and $RS^+$ in mixtures of hydrocarbons such as methane, acetylene and propylene and carbonyl sulfide has been carried out using a mass spectrometer equipped with a pulsed ion source. The rate constants of the reactions have been determined.

## Experimental

The operating characteristics of a pulsed ion source used in conjunction with a magnetic deflection instrument have been described previously;[5,6] only a brief description need be given here. Primary reactant ions were produced by an electron pulse of 0.2 μs duration and 10—16.3 V amplitude. Ions were extracted for mass analysis by applying a positive pulse of 1 μs duration and 10 V amplitude to the repeller plates. Primary and secondary ion currents were recorded as a function of the delay time between the ionizing pulse and the ion removal pulse. A repetition rate of 100 kHz was used.

In order to avoid the production of the excited ion $S^+(^2D^0)$, measurements were carried out at the electron energies below 16.7 eV (the appearance potential of $S^+(^2D^0)$ from COS).[7]

COS purchased from Matheson was purified by distillation under reduced pressure: analysis showed it to be more than 99.0% pure. $H_2S$ and $CS_2$ were detected as minor impurities. All other gases were Takachiho high purity grade (99.9%) and were used without further purification.

The rate constants of ion-molecule reactions studied were calibrated with reference to the reported rate constant, $k=1.22\times10^{-9}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$, for the hydrogen transfer reaction $CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$.[8]

## Results and Discussion

*$CH_4$–COS System.* The ion-molecule reactions for the formation of $CH_4S^+$ and $CH_3S^+$ ions in a $CH_4$–COS mixture were studied at total pressures up to $10^{-4}$ Torr in the ion source. At electron energies between 10 and 15 eV, the significant primary ions were $COS^+$, $CH_4^+$, $CH_3^+$, and $S^+$ in the ground state ($^4S^0$). The ion-molecule reactions forming $CH_4S^+$ and $CH_3S^+$ can be discribed by the scheme

$$CH_4 + COS^+ \longrightarrow CH_4S^+ + CO \qquad (1)$$

$$CH_4^+ + COS \longrightarrow CH_4S^+ + CO \qquad (2)$$

$$CH_4 + S^+ \longrightarrow CH_4S^+ \qquad (3)$$

$$CH_4 + COS^+ \longrightarrow CH_3S^+ + HCO \qquad (4)$$

$$CH_4^+ + COS \longrightarrow CH_3S^+ + HCO \qquad (5)$$

$$CH_3^+ + COS \longrightarrow CH_3S^+ + CO \qquad (6)$$

$$CH_4 + S^+ \longrightarrow CH_3S^+ + H \qquad (7)$$

The ion intensities of secondary ion $CH_4S^+$ ($m/e=48$) and $CH_3S^+$ ($m/e=47$) may be written:

$$I_{48} = (k_1I_{60}[CH_4] + k_2I_{16}[COS] + k_3I_{32}[CH_4])t + C_1 \qquad (I)$$

$$I_{47} = (k_4I_{60}[CH_4] + k_5I_{16}[COS] + k_6I_{15}[COS] + k_7I_{32}[CH_4])t + C_2 \qquad (II)$$

where $I_M$ is the intensity of ion ($m/e$=M), $k_i$ the rate constant of the $i$-th reaction, $t$ the reaction time, and $C_1$ and $C_2$ are constants.

In the formation of $CH_4S^+$, Reactions 1, 2, and 3 may be selected by choosing an appropriate electron energy. However, at lower electron energies (<15.1 eV) where only $COS^+$ and $CH_4^+$ are formed as significant primary ions, the amount of the secondary ion, $CH_4S^+$, formed was too small to determine the rate

TABLE 1. TOTAL RATE CONSTANTS UNDER VARIOUS CONDITIONS IN THE $CH_4$–COS SYSTEM

| Run | Electron energy (eV) | Pressure in reservoir (Torr) | | $I_{16}/I_{32}$ | $I_{60}/I_{32}$ | Total rate constant* |
|---|---|---|---|---|---|---|
| | | $CH_4$ | COS | | | |
| 1 | 15.8 | 83.08 | 53.05 | 4.22 | 15.1 | $7.53\times10^{-11}$ |
| 2 | 16.0 | 83.08 | 53.05 | 4.33 | 13.7 | $6.08\times10^{-11}$ |
| 3 | 14.4 | 74.55 | 55.03 | 10.55 | 67.1 | $11.89\times10^{-11}$ |
| 4 | 15.1 | 74.55 | 55.03 | 6.23 | 27.1 | $8.41\times10^{-11}$ |
| 5 | 14.7 | 76.66 | 51.25 | 10.56 | 66.4 | $12.64\times10^{-11}$ |
| 6 | 15.4 | 76.66 | 51.25 | 7.93 | 34.5 | $7.25\times10^{-11}$ |
| 7 | 15.1 | 81.57 | 49.63 | 8.90 | 38.6 | $9.43\times10^{-11}$ |
| 8 | 15.8 | 81.57 | 49.63 | 5.89 | 19.9 | $8.16\times10^{-11}$ |
| 9 | 15.8 | 85.76 | 64.88 | 4.16 | 19.4 | $8.08\times10^{-11}$ |
| 10 | 16.0 | 85.76 | 64.88 | 4.41 | 18.1 | $7.06\times10^{-11}$ |
| 11 | 14.7 | 86.50 | 68.29 | 7.78 | 62.5 | $10.52\times10^{-11}$ |
| 12 | 15.4 | 86.50 | 68.29 | 6.26 | 32.2 | $7.57\times10^{-11}$ |

*Total rate constants are expressed by ($k_1I_{60}/I_{32}+k_2I_{16}[COS]/I_{32}[CH_4]+k_3$) in $\mathrm{cm^3\ mol^{-1}s^{-1}}$.

constants $k_1$ and $k_2$ with sufficient accuracy. Therefore, the experiments were performed in the higher energy region ($<$16.7 eV) where Reactions 1, 2, and 3 occur simultaneously. From the results of Table 1 obtained under various conditions using least-squares means, the rate constants for Reactions 1, 2, and 3 were calculated to be $(3.8\pm0.1)\times10^{-13}$, $(6.0\pm0.1)\times10^{-12}$, and $(4.42\pm0.02)\times10^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The rate constant for S atom transfer from COS, $k_2$, is about 15 times that for S$^+$ ion transfer from COS$^+$, $k_1$. The rate constant for S$^+$ ion addition reaction, $k_3$, is about 7 times as large as $k_2$. It should be pointed that the formation of $CH_4S^+$, which was not observed by Dzidic *et al.*, has been confirmed. Furthermore, in the formation of RHS$^+$, S transfer from COS to RH$^+$ is faster process than S$^+$ transfer from COS$^+$ to RH in the $CH_4$–COS mixture. On the other hand, Dzidic *et al.* concluded that S$^+$ transfer from COS$^+$ to RH occurs exclusively in $C_2H_6$–COS mixture.

In the lower electron energy region ($<$14.25 eV, A.P. of $CH_3^+$ from $CH_4$), $CH_3S^+$ is produced by Reactions 4 and 5. Using Eq. (II), the rate constants $k_4$ and $k_5$ were determined to be $k_4=3.0\times10^{-12}$ and $k_5=1.6\times10^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$, respectively. However, in the high electron energy region ($14.25<E<16.7$ eV), Reactions 6 and 7 as well as 4 and 5 take place. The rate constants $k_6$ and $k_7$ were determined by substituting in Eq. (II) the above values for $k_4$ and $k_5$. Figure 1 shows a plot of $k_6+k_7I_{15}[\mathrm{COS}]/I_{32}[\mathrm{CH_4}]$ *vs.* $I_{15}[\mathrm{COS}]/I_{32}[\mathrm{CH_4}]$: the intercept and the slope correspond to $k_6=5.9\times10^{-10}$ and $k_7=9.5\times10^{-10}$ cm$^3$ mol$^{-1}$ s$^{-1}$. The rate constant $k_6$ obtained here is in good agreement with the $5.0\times10^{-10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ reported by Dzidic and co-workers.[2)]

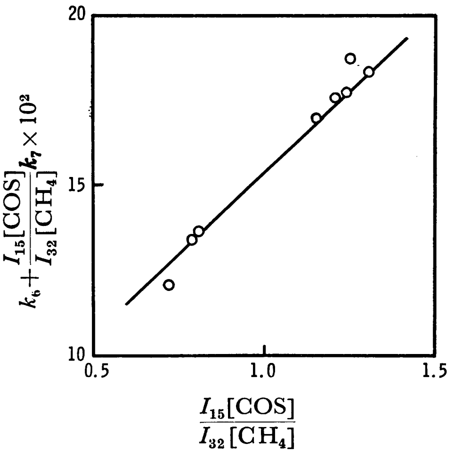

Fig. 1. Plots of $k_6+\frac{I_{15}[\mathrm{COS}]}{I_{32}[\mathrm{CH_4}]}k_7$ *vs.* $\frac{I_{15}[\mathrm{COS}]}{I_{32}[\mathrm{CH_4}]}$ in $CH_4$–COS system.

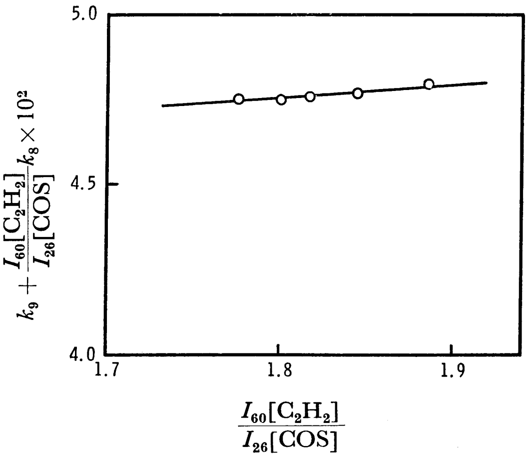

Fig. 2. Plots of $k_9+\frac{I_{60}[\mathrm{C_2H_2}]}{I_{26}[\mathrm{COS}]}k_8$ *vs.* $\frac{I_{60}[\mathrm{C_2H_2}]}{I_{26}[\mathrm{COS}]}$ in $C_2H_2$–COS system.

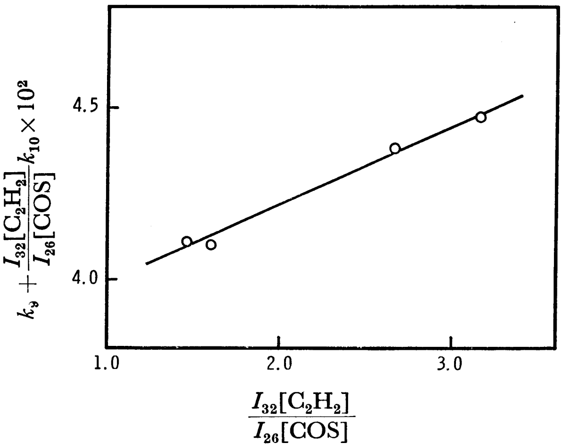

Fig. 3. Plots of $k_9+\frac{I_{32}[\mathrm{C_2H_2}]}{I_{26}[\mathrm{COS}]}k_{10}$ *vs.* $\frac{I_{32}[\mathrm{C_2H_2}]}{I_{26}[\mathrm{COS}]}$ in $C_2H_2$–COS system.

*$C_2H_2$–COS System.* In $C_2H_2$–COS mixtures, the ion $C_2H_2S^+$ is formed by the reactions such as

$$\mathrm{C_2H_2 + COS^+ \longrightarrow C_2H_2S^+ + CO} \tag{8}$$

$$\mathrm{C_2H_2^+ + COS \longrightarrow C_2H_2S^+ + CO} \tag{9}$$

$$\mathrm{C_2H_2 + S^+ \longrightarrow C_2H_2S^+} \tag{10}$$

Figure 2 shows the results obtained at lower electron energy where only $C_2H_2^+$ and COS$^+$ ions are formed as primary ions: the rate constants for Reactions 8 and 9 were determined to be $8.0\times10^{-11}$ and $1.3\times10^{-9}$ cm$^3$ mol$^{-1}$ s$^{-1}$, respectively. At higher electron energy, Reaction 10 also yields $C_2H_2S^+$. In Fig. 3 $k_9+k_{10}I_{32}[\mathrm{C_2H_2}]/I_{26}[\mathrm{COS}]$ is plotted *vs.* $I_{32}[\mathrm{C_2H_2}]/I_{26}[\mathrm{COS}]$—the value of $8.0\times10^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ obtained above is used for $k_8$. From the intercept and the slope $k_9=1.5\times10^{-9}$ and $k_{10}=8.0\times10^{-10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ were obtained. $k_9$ determined from Fig. 3 is in good agreement with $k_9$ obtained at lower electron energy.

As in the $CH_4$–COS system, the rate constant $k_9$ for S atom transfer from COS is about 17.5 times as large as $k_8$ for S$^+$ ion transfer from COS$^+$. On the other hand, the rate constant $k_{10}$ for the S$^+$ ion addition reaction is smaller than $k_9$ for S atom transfer reaction. The rate constant of $1.4\times10^{-9}$ cm$^3$ mol$^{-1}$ s$^{-1}$ for Reaction 9 is surprisingly large compared with the value[2)] of $4.7\times10^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$, reported for the same reaction of the fragment ion $C_2H_2^+$ from $C_2H_4$. The implication of this difference still remains to be determined.

The possible reactions to account for the formation of $C_2HS^+$ are

$$C_2H_2 + COS^+ \longrightarrow C_2HS^+ + CO + H \tag{11}$$

$$C_2H_2^+ + COS \longrightarrow C_2HS^+ + CO + H \tag{12}$$

$$C_2H^+ + COS \longrightarrow C_2HS^+ + CO \tag{13}$$

$$C_2H_2 + S^+ \longrightarrow C_2HS^+ + H \tag{14}$$

Thermochemical data shows that Reactions 11 and 12 are endothermic. Therefore, these processes are expected to occur only slightly. The secondary ion, $C_2HS^+$ was not detected in the low electron energy region where only $COS^+$ and $C_2H_2^+$ are observed as primary ions. After all, the formation of $C_2HS^+$ is attributed to Reactions 13 and 14. Rate constants of $1.1\times10^{-10}$ and $1.5\times10^{-9}$ cm$^3$ mol$^{-1}$ s$^{-1}$ for Reactions 13 and 14 were obtained from the results shown in Fig. 4.

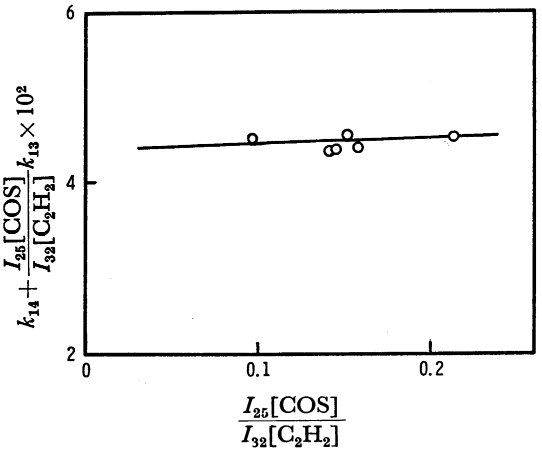

Fig. 4. Plots of $k_{14}+\frac{I_{25}[COS]}{I_{32}[C_2H_2]}k_{13}$ *vs.* $\frac{I_{25}[COS]}{I_{32}[C_2H_2]}$ in $C_2H_2$–COS system.

*$C_3H_6$–COS System.* In $C_3H_6$–COS mixtures, the following processes yielding $C_3H_6S^+$ were considered:

$$C_3H_6 + COS^+ \longrightarrow C_3H_6S^+ + CO \tag{15}$$

$$C_3H_6^+ + COS \longrightarrow C_3H_6S^+ + CO \tag{16}$$

$$C_3H_6 + S^+ \longrightarrow C_3H_6S^+ \tag{17}$$

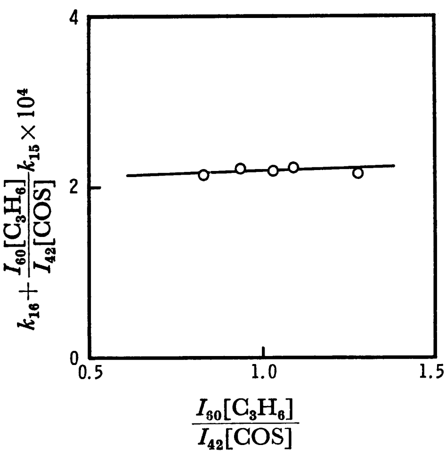

Fig. 5. Plots of $k_{16}+\frac{I_{60}[C_3H_6]}{I_{42}[COS]}k_{15}$ *vs.* $\frac{I_{60}[C_3H_6]}{I_{42}[COS]}$ in $C_3H_6$–COS system.

From the results shown in Fig. 5, obtained at lower electron energy where $C_3H_6^+$ and $COS^+$ are the only significant primary ions, the rate constants for Reactions 15 and 16 were determined to be $k_{15}=8.0\times10^{-14}$ and $k_{16}=9.3\times10^{-12}$ cm$^3$ mol$^{-1}$ s$^{-1}$. At higher electron energies, the Reaction 17 also occurs. $k_{17}$ was evaluated to be $4.6\times10^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$, in a manner similar to the case of $C_2H_2$–COS system.

The following processes involved in the $C_3H_5S^+$ formation are

$$C_3H_6 + COS^+ \longrightarrow C_3H_5S^+ + HCO \tag{18}$$

$$C_3H_6^+ + COS \longrightarrow C_3H_5S^+ + HCO \tag{19}$$

$$C_3H_5^+ + COS \longrightarrow C_3H_5S^+ + CO \tag{20}$$

$$C_3H_6 + S^+ \longrightarrow C_3H_5S^+ + H \tag{21}$$

Since Reactions 18 and 19 are endothermic, $C_3H_5S^+$ formation in $C_3H_6$–COS systems is attributed to Reactions 20 and 21. From the intercept and the slope of the plot of $k_{20}+k_{21}I_{32}[C_3H_6]/I_{41}[COS]$ *vs.* $I_{32}[C_3H_6]/$

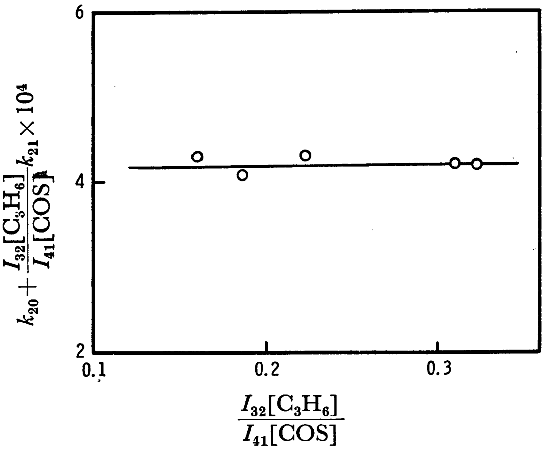

Fig. 6. Plots of $k_{20}+\frac{I_{32}[C_3H_6]}{I_{41}[COS]}k_{21}$ *vs.* $\frac{I_{32}[C_3H_6]}{I_{41}[COS]}$ in $C_3H_6$–COS system.

TABLE 2. RATE CONSTANTS IN COS-HYDROCARBON SYSTEMS

| Reaction | Rate constant cm$^3$mol$^{-1}$s$^{-1}$ |
|---|---|
| $CH_4$–COS system | |
| $CH_4+COS^+ \rightarrow CH_4S^++CO$ | $3.8\pm0.1\ \times10^{-13}$ |
| $CH_4^++COS \rightarrow CH_4S^++CO$ | $6.0\pm0.1\ \times10^{-12}$ |
| $CH_4+S^+ \rightarrow CH_4S^+$ | $4.42\pm0.02\times10^{-11}$ |
| $CH_4+COS^+ \rightarrow CH_3S^++HCO$ | $3.0\ \times10^{-12}$ |
| $CH_4^++COS \rightarrow CH_3S^++HCO$ | $1.6\ \times10^{-11}$ |
| $CH_3^++COS \rightarrow CH_3S^++CO$ | $5.9\ \times10^{-10}$ |
| $CH_4+S^+ \rightarrow CH_3S^++H$ | $9.5\ \times10^{-10}$ |
| $C_2H_2$–COS system | |
| $C_2H_2+COS^+ \rightarrow C_2H_2S^++CO$ | $8.0\ \times10^{-11}$ |
| $C_2H_2^++COS \rightarrow C_2H_2S^++CO$ | $1.4\ \times10^{-9}$ |
| $C_2H_2+S^+ \rightarrow C_2H_2S^+$ | $8.0\ \times10^{-10}$ |
| $C_2H^++COS \rightarrow C_2HS^++CO$ | $1.1\ \times10^{-10}$ |
| $C_2H_2+S^+ \rightarrow C_2HS^++H$ | $1.5\ \times10^{-9}$ |
| $C_3H_6$–COS system | |
| $C_3H_6+COS^+ \rightarrow C_3H_6S^++CO$ | $8.0\ \times10^{-14}$ |
| $C_3H_6^++COS \rightarrow C_3H_6S^++CO$ | $9.3\ \times10^{-12}$ |
| $C_3H_6+S^+ \rightarrow C_3H_6S^+$ | $4.6\ \times10^{-11}$ |
| $C_3H_5^++COS \rightarrow C_3H_5S^++CO$ | $1.8\ \times10^{-11}$ |

$I_{41}$[COS] shown in Fig. 6, the rate constants for Reactions 20 and 21 were determined to be $k_{20}=1.8\times10^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ and $k_{21}\leq10^{-13}$ cm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The small value of $k_{21}$ estimated for the highly exothermic reaction 21 suggests that the product ion, $C_3H_5S^+$ may be followed by fragmentation.

In the low electron energy region, the ion-molecule reactions yielding $CH_4S^+$, $C_2H_2S^+$, and $C_3H_6S^+$, in methane-COS, acetylene-COS and propylene-COS systems may be classified into three groups; $S^+$ ion transfer, S atom transfer and $S^+$ ion addition. As seen in Table 2, the rate constants for S atom transfer are very large compared with those for $S^+$ ion transfer in methane-COS and propylene-COS mixtures although not in acetylene-COS mixtures. In acetylene-COS mixtures, all the reactions are very fast compared with those in methane-COS and propylene-COS mixtures. This seems to be attributable to the triple bond of acetylene.

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