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ION-MOLECULE REACTIONS OF SULFUR IONS ($^4S^0$ AND $^2D^0$ STATES) AND CARBONYL SULFIDE IONS IN CARBONYL SULFIDE SYSTEM

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Ion-molecule reactions in pure COS have been studied using a pulsing method. The reactions including the excited S^+ for S_2^+ formation have been identified and the rate constants measured. The fraction of the excited state present in the S^+ ions formed at electron energy 18.3 eV was estimated to be 0.36.

The populations of various ionic states of atoms and molecules resulting from electron impact ionization have recently been determined by measuring the attenuation of ion beam.[1~5] However, the knowledge on their reactivities or the cross sections of the reactions which the excited ions perform is rather limited. As to sulfur atomic ions, Lindholm[2] showed that the S^+ formed by 100 eV electron impact ionization of H_2S, COS and SF_6, contained $^4S^0$ (40 %) and $^2D^0$ (60 %) states. Harrison[6] also reported that there were two ionic states of the S^+, which showed different disappearance rates, in the 55 eV electron impact ionization in H_2S system, though there was no assignment about the disappearance processes.

In the present work, an attempt has been made to determine the respective rate constants of S_2^+ formation in COS system, especially each of the reaction, $S^+ + COS \rightarrow S_2^+ + CO$, for S^+ ($^4S^0$) and S^+ ($^2D^0$) states separately. It has been demonstrated that S^+ in the excited state ($^2D^0$) has a higher reactivity compared with that of the ground state ions ($^4S^0$).

The experiments were performed on a Hitachi RMU-5G mass spectrometer provided with the pulsed ion source.[7] The COS purchased from Matheson Gas Products was purified by vacuum distillation; analysis showed it to be more than 99 % pure. H_2S and CS_2 were detected as minor impurities. The rate constants of ion-molecule reactions studied were calibrated by the rate constant, $k = 1.22 \times 10^{-9}$ cm^3 $molecule^{-1}$ sec^{-1}, which was reported by Gupta and co-workers,[8] for the hydrogen transfer reactions: $CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$.

The ionization efficiency curves measured for COS^+, S^+ and Kr^+ as a reference of energy correction, are given in Figure 1. In the cases of Kr^+ and S^+, the cuneate lines were observed.

The ionization potentials of COS and the appearance potentials of S^+ are given in Table 1. The energy correction was made by using the spectroscopic ionization potential, 13.996 eV of Kr.[9] As seen in Table 1, the appearance potential of S^+ ($^4S^0$) is consistent with the second ionization potential of COS. This shows that S^+ are produced via the curve crossing between $\tilde{A}^2\Pi$ and $\tilde{B}^2\Pi$ states of COS^+, as

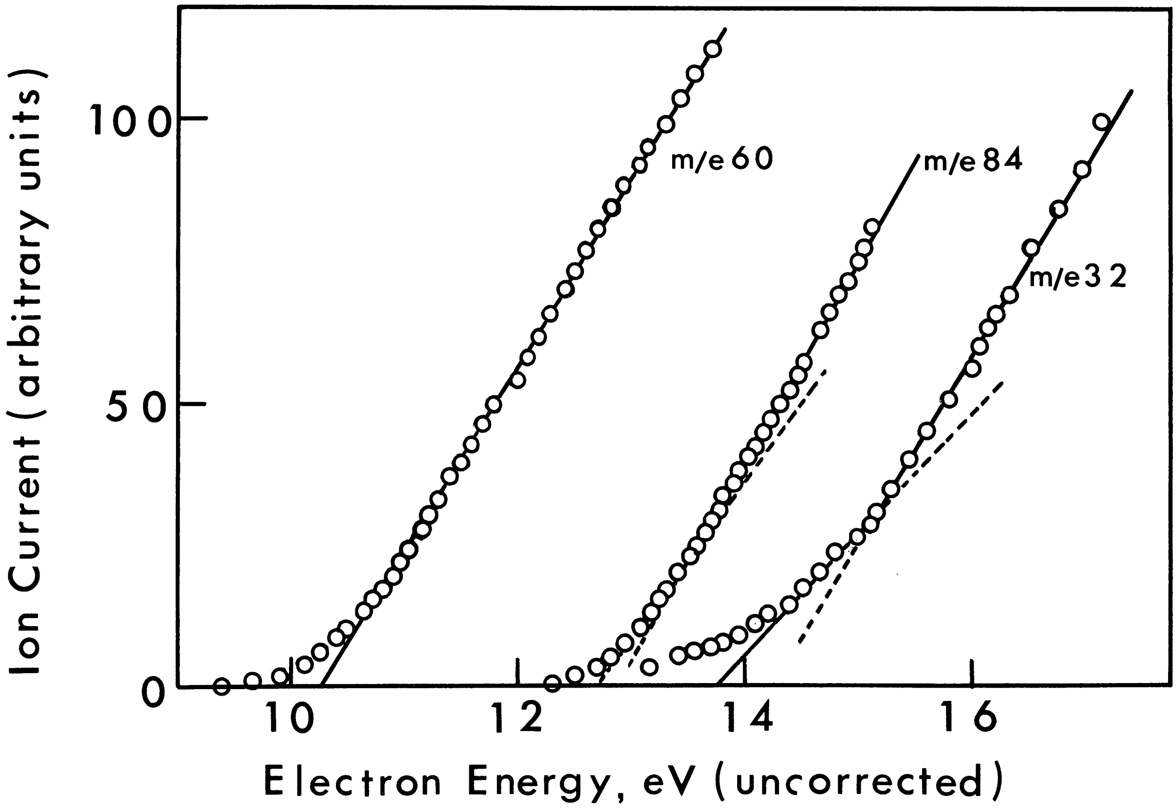

Figure 1. Ionization efficiency curves of COS^+ (m/e 60), S^+ (m/e 32) and Kr^+ (m/e 84) for COS-Kr.

Table 1. Ionization potentials and appearance potentials for ions in COS system.

Ion	I.P. or A.P. (eV)	
	This work	Ref. 8
COS^+ ($\tilde{X}^2\Pi$)	11.6	11.18, 11.23
COS^+ ($\tilde{A}^2\Pi$)		15.08
COS^+ ($\tilde{B}^2\Pi$)		16.04
S^+ ($^4S^0$)	15.1	
S^+ ($^2D^0$)	16.7	

reported by Brundle and Turner.[10)] Therefore, we may regard that COS^+ observed at higher electron energy than the appearance potential of S^+ ($^4S^0$), 15.1 eV, is still in the ground state ($\tilde{X}^2\Pi$). The energy difference between the appearance potentials obtained for S^+ ($^4S^0$) and S^+ ($^2D^0$) is 1.6 eV, which agrees with the difference, 1.8 eV, between their recombination energies.[4)] The cuneate line for S^+ in Figure 1 may be empirically expressed by

$$I_1 = 14.54(V - 1.326) - 199.6 \qquad V \leq 16.7 \qquad [\text{ I-a }]$$

$$I_2 = 27.85(V - 1.326) - 398.8 \qquad V \geq 16.7 \qquad [\text{ I-b }]$$

where I_1 and I_2 are ion intensities of S^+ in arbitrary units, V electron energy in electron volt, 16.7 the appearance potential of S^+ ($^2D^0$), and 1.326 the calibration energy based on the ionization potential for Kr^+.

If we assume reasonably that the ionization efficiency curve of S^+ ($^4S^0$) at the higher electron energy range than the appearance potential of S^+ ($^2D^0$) can be expressed by the empirical formula [I-a], the fraction, f(V) of the excited state S^+ ($^2D^0$) to the total S^+ ($^4S^0$ and $^2D^0$) at electron energy, V eV, can be given by the following

$$f(V) = \frac{I_2 - I_1}{I_2} = \frac{I^*_{32}}{I_{32} + I^*_{32}} = \frac{13.31V - 216.8}{27.85V - 435.7} \qquad V \geq 16.7 \qquad [\text{ II }]$$

where I_{32} and I^*_{32} are the ion intensities of S^+ ($^4S^0$) and S^+ ($^2D^0$), respectively. Even at the highest electron energy, 18.3 eV, the ion intensity ratios of the sulfur containing primary ions were $COS^+ : S^+ : CS^+ : OS^+$ = 945 : 100 : 2.93 : 0.02. So, the significant reaction processes forming S_2^+ in this system are considered to be as

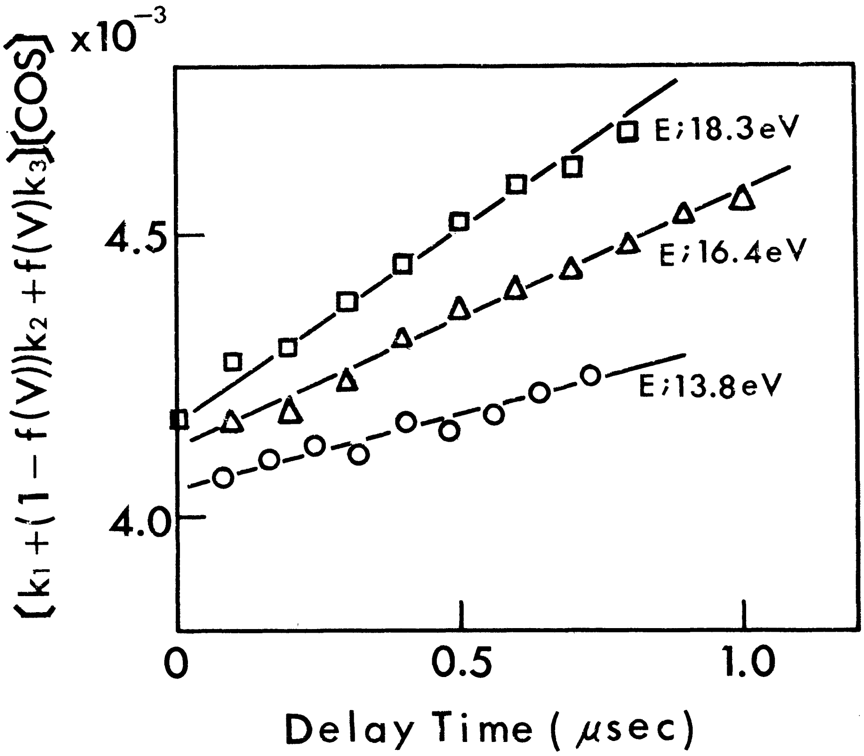

Figure 2. Plots of $[k_1 + (1 - f(V))k_2 + f(V)k_3][COS]$ vs delay time at 13.8, 16.4 and 18.3 eV, electron energy in COS system.

follows:

$$COS^+ (\tilde{X}^2\Pi) + COS \longrightarrow S_2^+ + 2CO, \quad \Delta H = -19.6 \text{ kcal/mol} \qquad (1)$$

$$S^+ (^4S^0) + COS \longrightarrow S_2^+ + CO, \quad \Delta H = -75 \text{ kcal/mol} \qquad (2)$$

$$S^+ (^2D^0) + COS \longrightarrow S_2^+ + CO, \quad \Delta H = -112 \text{ kcal/mol} \qquad (3)$$

Hence, the secondary ions S_2^+ as a function of reaction time is given by

$$I_{64} = [I_{60}k_1 + (I_{32} + I_{32}^*)((1 - f(V))k_2 + f(V)k_3)][COS]t + C \qquad [\text{ III }]$$

where k_1, k_2 and k_3 are the rate constants for reactions (1), (2) and (3) respectively, I_{64} the ion intensity of S_2^+, I_{60} the ion intensity of COS^+, t the reaction time and C a constant. Selecting energy of ionizing electron, each of the reactions (1), (2) and (3) can be separated. Figure 2 shows the I_{64}/I_{60} vs reaction time plots obtained at 13.8, 16.4 and 18.3 eV. At 13.8 eV the reaction (1) occurs, at 16.4 eV the reactions (1) and (2), and at 18.3 eV the reactions (1), (2) and (3), respectively. At 18.3 eV, it can be estimated according to Eq.(II) that 64 % of the S^+ ions primarily produced are in $^4S^0$ state and the remainder in $^2D^0$ state. From the slopes of the plots and the ion intensity ratio, we can obtain the rate constants of the reactions (1), (2) and (3), as given in Table 2.

Table 2. Rate constants in COS system.

Reaction	k (cm^3 $molecule^{-1}$ sec^{-1}) X 10^{11}		
	This work	Ref. 11	
		Pressure method	Pulsing method**
(1)	3.9_7	3.7	32
(2)	$11._6$	24*	54
(3)	$33._1$		

* This rate constant would correspond to $[(1 - f(20))k_2 + f(20)k_3]$.

** Measured under the conditions of $P_{N_2} \simeq 2$ Torr and $P_{COS} \simeq 5$ mTorr.

The values obtained for k_1 of 3.9_7 X 10^{-11} and for k_2 of $11._6$ X 10^{-11} are only ~1/8 of 32 X 10^{-11} and ~1/5 of 54 X 10^{-11} measured by Dzidic and co-workers$^{11)}$ using a quite different pulsing method, respectively. As having been already discussed by Dzidic and co-workers, their measurement of k_1 would contain the large contribution of the charge exchange reaction between COS^+ and H_2S as an impurity. As to k_2, similarly, it is possible to account for their anomalously large value by postulating the occurrence of the charge exchange reaction between S^+ and H_2S.$^{12)}$ However, the values for k_1 of 3.9_7 X 10^{-11} and for $[(1 - f(V))k_2 + f(V)k_3]$ of $19._4$ X 10^{-11} (f(V) = 0.36, at V = 18.3 eV), which corresponds to $22._2$ X 10^{-11} (f(V) = 0.41, at V = 20 ev), are rather in good agreement with 3.7 X 10^{-11} and 24 X 10^{-11} calculated from their cross section measurement at electron energy 20 eV by using the Stevenson relationship. The result that the reactivity of the excited state S^+ ($^2D^0$) for S_2^+ formation is about 3 times as great as that of the ground state S^+ ($^4S^0$) despite the high exothermicity of their reactions is of some interest. Implication of this result, however, still remains to be inquired.

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