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# ADVERTISEMENT



# Collision Reactions of Negative Ions in Several Sulfur Compounds and in Their Mixtures with ClCN

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The formation of the principal negative ions in COS,  $CS_2$ ,  $H_2S$ , and  $CH_3SH$  and their collision reactions in mixtures of these compounds with ClCN have been studied. A time-of-flight mass spectrometer fitted with a high pressure source was employed. By comparing ionization efficiency curves for the various resonances occurring, it has been shown that the principal reactions in the above mentioned systems involve attack of S<sup>-</sup> or HS<sup>-</sup> on ClCN to yield SCN<sup>-</sup> and CN<sup>-</sup>. The rate of formation of CN<sup>-</sup> is approximately 100 times that of SCN<sup>-</sup>. Rate constants have been determined for the various reactions.

#### INTRODUCTION

The formation of secondary negative ions in the gas phase has been reported by several workers.<sup>1-13</sup> Since our knowledge regarding the types of reactions which produce secondary negative ions is still limited, a study of the interaction of a group of negative ions with neutral molecules has been undertaken. In this paper, the results of a study of the reactions of negative ions in mixtures of ClCN with CS<sub>2</sub>, COS, H<sub>2</sub>S, and CH<sub>3</sub>SH are presented. The investigation was carried out to identify the reactions occurring and to provide information on the rates of the reactions.

## EXPERIMENTAL

The reactions reported in this paper were investigated using a Bendix time-of-flight mass spectrometer, which is equipped with a high pressure source capable of operating up to 100  $\mu$ Hg.<sup>9,14</sup> From empirical observations, we found that improved resolution was obtained when a positive ion focus pulse was applied to the ion grid No. 1. A circuit diagram is shown in Fig. 1. The optimum focus pulse was usually found experimentally at a field strength of about 270 V/cm.

To improve the stability of emission, we employed a Lambda power supply, Model LH121B FM, set to maintain the filament current at a constant value usually chosen between 2.50 and 2.70 A dc. Filament life was comparatively short with all of the compounds employed in this study, but was especially short with  $CH_3SH$  when a filament life of only 4–5 h was realized.

In most experiments, 1:1 mixtures of the gases studied were introduced into the ion source as described earlier.9,14 Procedures for determining the variation of ion intensity as a function of reaction time (RT) and pressure were identical to those presented earlier.<sup>9,14</sup> It has been assumed that collection efficiencies and multiplier response do not depend on the mass of the ion collected. The electron energy scale was calibrated using the onsets of  $O^-$  from  $SO_2$  and  $SF_6^-$  from  $SF_6$ , respectively, at 4.29,10,12,15 and 0.0 eV. 9(a),9(b),16 Reaction rate constants reported in Table I were measured by varying the ion residence time or the pressure of one component. Plots of the ratio of secondary to initial primary ion currents versus reaction time or pressure gave straight lines from which the rate constants were evaluated. Semilog plots were used to calculate the rate of disappearance of reactants.

Heats of formation employed in the calculations are summarized in Table II. The materials used in this study were commercial products: carbonyl sulfide (97.5%), cyanogen chloride (97%), hydrogen sulfide (99.6%), and methyl mercaptan (99.5%) were purchased from the Matheson Company, Inc. Spectroquality carbon disulfide was obtained from Matheson, Coleman and Bell. All compounds were used without additional purification.

The reactions of negative ions investigated in this

System	Electron energy eV	Rates of formation in cm <sup>3</sup> molecule <sup>-1</sup> ·sec <sup>-1</sup>						Approximate rates of disappear- ance in cm <sup>3</sup> molecule <sup>-1</sup> .sec <sup>-1</sup>		
		Reactant <sup>a</sup>		Secondary ion	$K_{RT}  imes 10^{10}$ b	K <sub>P</sub> ×10 <sup>10</sup> c	$ar{K}  imes 10^{10} \ \mathrm{d}$	Ion	$\frac{1}{K_{RT} \times 10^{10}}$	$\frac{10^{10} \text{ sol}}{K_P \times 10^{10} \text{ c}}$
CICN-CS <sub>2</sub>	3.6	S-	(3)	SCN-	0.23	0.20	$0.22 \pm 0.02$	S-	5.1	13.6
$ClCN-CS_2$	6.1	S-	(3)	SCN~	0.37	0.35	$0.36 {\pm} 0.01$	S-	•••	9
ClCN-COS	2.1	S-	(7)	SCN-	0.25	0.24	$0.24 \pm 0.01$	S-	11.6	8.3
ClCN-H <sub>2</sub> S	3.0	HS-	(12)	SCN-	0.57	0.52	$0.54 \pm 0.02$	HS-	7.5	7.7
ClCN-H <sub>2</sub> S	9.6	S-	(11)	SCN-	0.58	0.39	$0.49 \pm 0.09$	S-	7.0	10.7
ClCN-CH <sub>3</sub> SH	0.7	CN-	(17)	SCN~	0.50	0.52	$0.51 \pm 0.01$	•••	•••	•••
CICN-COS	2.0	$S^{-}$	(4)	$CN^{-}$	9.2	•••	•••	•••	•••	•••

TABLE I. Rate measurements.

<sup>a</sup> Numbers refer to reactions listed in Table III.

<sup>b</sup> Obtained from intensities-ratio versus reaction-time plots.

<sup>c</sup> Obtained from intensities-ratio versus pressure plots.

<sup>d</sup> Errors give the uncertainty related to the arithmetic mean of  $K_{RT}$  and  $K_P$ .

work were studied at low electron energies ( $\leq 10 \text{ eV}$ ), where ions are formed by dissociative resonance capture processes. The reactant (precursor) ion is usually easily identified since the primary ion and the secondary ion exhibit identical resonance capture curves. If a secondary ion can arise from primary ions which have different resonance potentials, the secondary ion efficiency curve will appear at different electron energies corresponding to the resonance potentials of the primary ions.

The electron energies at which maxima in the resonance capture curves were observed for the dominant negative ions are presented in Table III. The probable process for the formation of each of these negative ions is also reported. The resonance capture curves are shown in Figs. 2–5 for the systems ClCN-CS<sub>2</sub>, ClCN-COS, ClCN-H<sub>2</sub>S, and ClCN-CH<sub>3</sub>SH, respectively, and in Fig. 6 for CH<sub>3</sub>SH alone. Some experimental parameters and ratios of the instrumental sensitivities,  $\Sigma$ , at which the efficiency curves were recorded are also given. In Fig. 3, two sets of points are plotted to indicate the degree of reproducibility of the data, which we consider to be satisfactory. Data points were omitted from the other curves for the sake of clarity.

## **RESULTS AND DISCUSSION**

#### Studies of Individual Compounds

# ClCN

The principal negative ions detected when only CICN was studied were CN- and Cl-. The CNion was about 10 times as intense at the maximum of its resonance capture curve as was Cl<sup>-</sup> at its maximum. The CN<sup>-</sup> efficiency curve was recorded several times at different experimental conditions, and we always noticed a lack of reproducibility. However, it exhibits a low-energy resonance peak with the maximum between 0.5 and 1.0 eV, and a high-energy one which reaches its maximum at 5.5-6.0 eV. The intensities of the two resonances are comparable. Also, Cl<sup>-</sup> shows two resonances. The low-energy peak occurs at the same electron energy as the low-energy resonance of CN<sup>-</sup>. The other resonance has its maximum at about 7.0 eV. The  $Cl^-$  ion formed at the lower electron energy might be the result of a simple dissociative capture process. Alternatively, Reaction (19), which is exothermic by 1.9 eV, might account for the presence of the low energy peak:

$$CN^{-} + ClCN \rightarrow Cl^{-} + (CN)_2.$$
(19)

The difficulty of getting reproducible results from ClCN alone prevented our determining the origin of Cl<sup>-</sup> in the low-energy region. The Cl<sup>-</sup> resonance at 7 eV does not coincide with the higher CN<sup>-</sup> resonance curve and so must arise from a direct dissociative

TABLE II. Heats of formation of ions and neutrals used in this study.

	$\Delta H_f$ in kcal/mole	Ref.
Н	52.095	a
С	171.291	a
$CH_2$	93.7	a
$CH_3$	33.2	a
0-	24.29	a
$CH_4$	-17.88	a
CN-	25.1	21
CO	-26.416	a
$C_2H_6$	-20.24	a
S	66.636	a
S-	17.42	а
HS	34.10	а
HS-	-19.0	b
$H_2S$	-4.93	a
Cl	29.082	a
Cl-	-58.8	a
HCl	-22.062	a
OCN-	-19	9(b)
CS	56	a
$CH_3S$	30.5	с
CH₃SH	-5.34	a
$(CN)_2$	73.84	a
SCN	84	20
SCN-	-4	9(b)
COS	-33.96	а
ClCN	32.97	a
CH <sub>3</sub> SCH <sub>3</sub>	-8.90	a
$CS_2$	28.05	a
SCl <sub>2</sub>	-4.7	a

<sup>8</sup> D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Natl. Bur. Std. (U.S.), Tech. Note 270-3 (1968). <sup>b</sup> J. I. Brauman and K. C. Smyth, J. Am. Chem. Soc. **91**, 7778 (1969).

<sup>o</sup> H. Mackle and R. G. Mayrick, Trans. Faraday Soc. 58, 33 (1962).

resonance capture process. Some data on Cl<sup>-</sup> and CN<sup>-</sup> were reported by Herron and Dibeler.<sup>17</sup>

At source pressures greater than 15  $\mu$ Hg, a slight ion current due to ClCN<sup>-</sup> was detected. Its intensity was a direct function of the pressure, up to the highest value tried, 24  $\mu$ Hg, and increased irregularly with increasing electron energy. No clear evidence of electron transfer reactions, such as (20) and (21), was obtained in our experiments:

$$CN^{-}+CICN^{-}+CN,$$
 (20)

$$Cl^{-}+ClCN\rightarrow ClCN^{-}+Cl.$$
 (21)

Further study would be required to ascertain the cause of the lack of reproducibility and the origin of  $ClCN^{-}$ .

COS and  $CS_2$ 

COS and CS<sub>2</sub> have been studied in low as well as high pressure sources by a number of workers.<sup>3,9(a),10,15,18</sup> Our results agree very well with the previous ones at comparable experimental conditions. The most intense negative ion produced in dissociative resonance capture



FIG. 1. Circuit for transformation of ion focus pulse from negative to positive. UTC H-47 pulse transformer can replace PIC C81 with corresponding change in terminations.  $S_1$  switch DPDT.

processes at source pressures of 5–10  $\mu$ Hg from COS was S<sup>-</sup>. The maximum S<sup>-</sup> ion current was found at 2.1±0.1 eV. The weak ionization efficiency curve of O<sup>-</sup> exhibits two resonances with onsets and maxima, respectively, at 3.8±0.2, 5.5±0.2, and 6.8±0.2, 8.9±0.2, in fairly good agreement with other authors.<sup>9(a),10</sup> These last data were obtained at a pressure of 7  $\mu$ Hg, with the mass spectrometer operating at its highest sensitivity. The low-energy O<sup>-</sup> resonance involves little or no excess energy and the width of the O<sup>-</sup> peaks reflect this. The O<sup>-</sup> peak at the higher energy resonance appeared to be considerably broadened but its intensity was too small to permit reliable measurement.

The ionization efficiency curve of S<sup>-</sup> from  $CS_2$ shows three maxima at  $3.5\pm0.1$ ,  $6.0\pm0.1$  and  $9.5\pm0.1$ eV; a reproducible shoulder occurs at about 7.7 eV. The formation of S<sup>-</sup> is to be attributed to Reaction (2) at all resonances. The reaction

$$CS_2 \rightarrow C + S + S^- \tag{22}$$

is endothermic by 9.9 eV and so is probably not responsible for the peak at 9.5 eV.

$$H_2S$$

In studies with only  $H_2S$  in the source,  $HS^-$  was the most intense negative ion with a resonance maximum at  $3.0\pm0.1$  eV. The maximum of the principal resonance capture curve for  $S^-$  was recorded at  $9.6\pm0.1$  eV.



FIG. 2. Ionization efficiency curves in the ClCN-CS<sub>2</sub> system. Reaction time = 0.750  $\mu$ sec;  $p(ClCN) = 14 \ \mu$ Hg;  $p(CS_2) = 15 \ \mu$ Hg;  $\Sigma(CN^-): \Sigma(S^-): \Sigma(SCN^-) = 1:1:100; (-) CN^-; (----)S^-; (-) SCN^-.$ 

Ion	System	Reaction	El	ectron energy in	eV (res	onance	maximum) ª	∆ <i>H</i> reaction in eV
CN- S-	ClCN-CS <sub>2</sub>	$ClCN \rightarrow CN^{-} + Cl$ $CS_{2} \rightarrow S^{-} + CS$	(1) (2)	0.5	5. 3.5	.6 5.9	9	+0.92 5 +2.0
SCN-		$S^++ClCN\rightarrow SCN^-+Cl$	(3)		3.6	6.1	9.2	-1.1
CN- CICN-COS CN-		$ClCN+S^{-}\rightarrow CN^{-}+SCl$ $ClCN\rightarrow CN^{-}+Cl$	(4) (5)	2.0	6.9			-0.7(?) +0.92
S SCN		$S^++ClCN\rightarrow SCN^-+Cl$	(0) (7)	2.1				+1.1 -1.1
CN- S- HS- SCN- SCN-	CICN-H <sub>2</sub> S	$ClCN \rightarrow CN^{-} + Cl$ $H_{2}S \rightarrow S^{-} + H_{2}$ $H_{2}S \rightarrow HS^{-} + H$ $S^{-} + ClCN \rightarrow SCN^{-} + Cl$ $HS^{-} + ClCN \rightarrow SCN^{-} + HCl$	(8) (9) (10) (11) (12)	1.1 3 3	5.0 5.0	6.0	9. 9.	$ \begin{array}{r} +0.92 \\ 5 +0.97 \\ +1.6 \\ 6 -1.1 \\ -1.7 \end{array} $
CN <sup></sup> S <sup>-</sup> HS <sup>-</sup> CH₃S <sup>-</sup> SCN <sup></sup> SCN <sup></sup>	ClCN-CH₃SH	$ClCN\rightarrow CN^{-}+Cl$ $CH_{3}SH\rightarrow S^{-}+CH_{4} (?)$ $CH_{3}SH\rightarrow HS^{-}+CH_{3}$ $CH_{3}SH\rightarrow CH_{3}S^{-}+H$ $CN^{-}+CH_{3}SH\rightarrow SCN^{-}+CH_{4}$ $S^{-}+ClCN\rightarrow SCN^{-}+Cl$	<ul> <li>(13)</li> <li>(14)</li> <li>(15)</li> <li>(16)</li> <li>(17)</li> <li>(18)</li> </ul>	1.0 1.9(?) 1.9 0.7	5	6.0 .2	8.2 8.4 8.2 8.3	+0.92 +0.21 +0.85 +1.9(?) -1.8 -1.1

TABLE III. Energy maxima of dominant negative ions.

<sup>a</sup> In most cases the standard deviation is  $\pm 0.1$  eV.



FIG. 3. Ionization efficiency curves in the ClCN-COS system. Reaction time=0.500  $\mu$ sec;  $p(ClCN) = 11 \ \mu$ Hg;  $p(COS) = 8 \ \mu$ Hg;  $\Sigma(CN^{-}): \Sigma(S^{-}): \Sigma(SCN^{-}) = 10:1:200$ . Each efficiency curve is formed by two sets of experimental points to give an example of reproducibility. The second set was recorded two hours after the first one. First set: ( $\blacktriangle$ ) CN<sup>-</sup>; ( $\bigcirc$ ) S<sup>-</sup>; ( $\blacksquare$ ) SCN<sup>-</sup>. Second set:  $\triangle$ ,  $\bigcirc$ ,  $\square$ .

F1G. 4. Ionization efficiency curves in the ClCN-H<sub>2</sub>S system. Reaction time=0.750  $\mu$ sec;  $p(ClCN) = 13 \ \mu$ Hg;  $p(H_2S) = 12 \ \mu$ Hg;  $\Sigma(CN^-): \Sigma(S^-): \Sigma(HS^-): \Sigma(SCN^-) = 2:2:1:100;$  (--) CN<sup>-</sup>; (-----) S<sup>-</sup>; (-----) HS<sup>-</sup>; (--) SCN<sup>-</sup>.



FIG. 5. Ionization efficiency curves in the ClCN-CH<sub>3</sub>SH system. Reaction time =0.750  $\mu$ sec;  $p(ClCN) = 21 \ \mu$ Hg;  $p(CH_3SH) = 21 \ \mu$ Hg;  $\Sigma(CN^-) : \Sigma(S^-) : \Sigma(HS^-) : \Sigma(CH_3S^-) : \Sigma(SCN^-) = 1:8:40:8:80; (--) CN^-; (----) S^-; (-----) HS^-; (-----) SCN^-.$ 

Two lower energy peaks with maxima at about 2.9 and 6.4 eV were much weaker and are not shown in Fig. 4. Onsets and spectra were reported by Kraus<sup>15</sup> and agree satisfactorily with our values. The formation of S<sup>-</sup> at 9.6 eV could occur either by Reaction (9) with loss of H<sub>2</sub> or by Reaction (23) with loss of 2H:

$$H_2S \rightarrow S^- + 2H, \qquad \Delta H = +5.5 \text{ eV}.$$
 (23)

Ample energy is available for either process and either would involve a large amount of excess energy. However, even with Reaction (9), essentially all of the excess energy would reside in the neutral hydrogen product leaving only a modest amount ( $\approx$ 9 kcal/mole) of translational energy with the S<sup>-</sup> (see discussion below).

# $CH_3SH$

We have studied CH<sub>3</sub>SH alone at 16  $\mu$ Hg. Although the intensities were very low, three ionic species were detected: S<sup>-</sup>, CH<sub>3</sub>S<sup>-</sup> and HS<sup>-</sup>, the latter being the weakest and just detectable. We show in Fig. 6 the result of our investigation: S<sup>-</sup> reaches a maximum at  $8.3\pm0.2$  eV; CH<sub>3</sub>S<sup>-</sup> exhibits three resonance peaks with maxima at  $1.9\pm0.2$ ,  $4.9\pm0.2$ , and  $8.3\pm0.2$  eV, respectively. HS<sup>-</sup> gave a signal that was too small to provide reproducible information. However, three peaks with maximum intensities at about 1.9, 4.8, and 9.0 eV seemed to occur, although only the third one was characterized and fairly well reproduced four times.

If we take the maximum of 1.9 eV as the mean energy required to form CH<sub>3</sub>S<sup>-</sup>, we compute  $\Delta H_f(CH_3S^-) \leq -13$  kcal/mole. This is less than would be computed from  $\Delta H_f(CH_3S)$  and its electron affinity of 32 kcal/mole.<sup>19</sup> The latter value appears much too small so our value is the preferred one.

It is not possible with our data to be certain which resonances from  $CH_3SH$  are due to direct decomposition and which to ion-molecule reactions. A pressure study might have resolved these uncertainties but the experimental problems of handling  $CH_3SH$  made such a study impractical. There is little doubt that the  $CH_3S^-$  formed at the 1.9-eV and 4.9-eV resonances are primary decomposition products. However, at the 8.3-eV resonance some 6.4 eV excess energy is involved. The translational energy may be calculated from the relation<sup>20</sup>

$$E_t = E^* / \alpha N, \tag{24}$$

where  $E_t$  is total translational energy,  $E^*$  is total excess energy, N is the degrees of vibrational freedom in the parent ion and  $\alpha$  is an empirical constant which is 0.42 for dissociative resonance capture processes.<sup>21</sup> For Reaction (16) with  $E^*=6.4$  eV,  $E_t=1.3$  eV, almost all of which is carried by the hydrogen. The remaining 5.1 eV would remain as internal energy, probably largely vibrational, in the CH<sub>3</sub>S<sup>-</sup> ion. Since



FIG. 6. Ionization efficiency curves for CH<sub>8</sub>SH. Delay time off;  $p(CH_3SH) = 16 \ \mu$ Hg;  $\Sigma(S^-): \Sigma(HS^-): \Sigma(CH_3S^-) = 1:5:2;$  (----) S<sup>-</sup>; (-----) HS<sup>-</sup>; (-----) CH<sub>3</sub>S<sup>-</sup>.

this is much greater than the approximately 2-eV electron affinity that we estimate for  $CH_3S$ , it seems very probable that the electron would be lost and the ion would not be observed at this high-energy resonance. On the other hand,  $CH_3S^-$  might be formed by ion-molecule reaction with S<sup>-</sup> at this energy, as discussed below.

The onset of the S<sup>-</sup> resonance curve from  $CH_3SH$  seems to be above 5 eV so that three different processes can lead to its formation: (14), (25), and (26). Reaction (27) or other fragmentation processes might also contribute at energies higher than 8.4 eV:

$$CH_3SH \rightarrow S^- + H + CH_3$$
,  $\Delta H = +4.7 \text{ eV}$ , (25)

 $CH_3SH \rightarrow S^- + H_2 + CH_2, \qquad \Delta H = +5.0 \text{ eV}, (26)$ 

$$CH_3SH \rightarrow S^- + 2H_2 + C, \qquad \Delta H = +8.4 \text{ eV}.$$
 (27)

If Reaction (14) occurs at the high (8.3 eV) resonance maximum, it involves 8.1 eV of excess energy. For  $E^*=8.1$  eV,  $E_t=1.6$  eV and  $E_t(S^-)=0.56$  eV. The total available internal energy is 6.5 eV. The excited electronic states of S- are not known but S- is isoelectronic with Cl and would be expected to have similar electronic states. The lowest excited states of Cl are the  ${}^{2}P_{1/2}$  state at 0.11 eV and the  ${}^{4}P$  state at 8.9 eV. Clearly, neither of these states can account for the high resonance curve for  $S^-$ . The internal energy must therefore reside in the CH<sub>4</sub> fragment. However, if this is principally in vibration, CH<sub>4</sub> can be expected to decompose to either  $H+CH_3$  or  $H_2+CH_2$ . Thus, it seems probable that Reaction (25) or (26) accounts for the formation of S<sup>-</sup> at the high dissociative resonance capture energy.

If S<sup>-</sup> undergoes ion-molecule reactions with CH<sub>3</sub>SH to give CH<sub>3</sub>S<sup>-</sup> and HS<sup>-</sup>, only processes (28), (29), and (30) would be allowed. The process

$$S^+CH_3SH \rightarrow CH_3S^-+HS$$
,  $\Delta H \leqslant +0.39 \text{ eV}$ , (28)

is slightly endothermic but since S<sup>-</sup> appears to be formed with an average translational energy of 0.56 eV, sufficient energy is available to overcome this barrier and permit reaction to occur. Further, if Reaction (28) is assumed to occur, the rate constant for the reaction can be estimated from the data in Fig. 6 to be about  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup>·sec<sup>-1</sup>. This is a reasonable value. On the whole, then, we deduce that CH<sub>3</sub>S<sup>-</sup> is probably formed by Reaction (28) at the high-energy resonance.

The mode of formation of  $HS^-$  is not so readily deduced. This ion could be formed by dissociative resonance capture at each of the energies observed. Although the distribution of vibrational energy in Reaction (15) cannot be predicted reliably, the vibrational energy of  $HS^-$  at 9 eV would be only about 1 eV if the internal energy is assumed to distribute equally among the vibrational modes of  $HS^-$  and  $CH_3$ . If these assumptions are correct, there is no evident reason why  $HS^-$  might not be formed as a primary ion at all of the observed resonances. However,

the coincidence of the resonances of  $HS^-$  with the lower resonances of  $CH_3S^-$  suggest the possibility that  $HS^-$  might result from the reaction

$$CH_3S^-+CH_3SH\rightarrow HS^-+CH_3SCH_3.$$
 (29)

This reaction would be exothermic and the curves in Fig. 6 suggest that the reaction would be comparatively slow, as might be expected. In the highenergy resonance region,  $HS^-$  might be formed either by Reaction (29) or by the reaction

$$S^{-}+CH_{3}SH \rightarrow HS^{-}+CH_{3}S$$
 (30)

which is slightly exothermic. Since  $CH_3S^-$  appears to be a secondary ion at these conditions,  $HS^-$  would be a ternary product if it is formed by Reaction (29). Thus, Reaction (30) appears to be the more probable of the two ion-molecule reactions that might form  $HS^-$ . However, it should be emphasized that  $HS^$ could be formed by electron impact and we can only conclude that our data do not permit a decision.

# Reactions in Mixtures of Sulfur Compounds with CICN

The principal collision reactions of negative ions in mixtures of ClCN with COS,  $CS_2$ ,  $H_2S$ , and  $CH_3SH$  have been studied. In all of these mixtures, the principal product ions were  $CN^-$  and  $SCN^-$ , the former being formed at about 100 times the rate of the latter. Both were formed principally by attack of S<sup>-</sup> or HS<sup>-</sup> upon ClCN.

The reaction sequences suggested in Table III are supported by capture maxima in the resonance curves and their general shapes. The neutral products in the negative ion-molecule reactions are selected on the assumption that the above mentioned reactions are exothermic. In Tables I and III, we report the most significant results and the rate constants for the reactions studied. Table III, as well as Figs. 2–5, shows that the SCN<sup>-</sup> ionization efficiency curves match the primary ion resonance capture curves for S<sup>-</sup> or HS<sup>-</sup>.

#### Formation of SCN-

The system ClCN-CS<sub>2</sub> is to be regarded with particular attention since the secondary ion curve reproduces very closely that of S<sup>-</sup> (Fig. 2). Both curves exhibit well marked shoulders, not reported in Table III, at  $7.6\pm0.2$  for SCN<sup>-</sup> and  $7.7\pm0.2$  eV for S<sup>-</sup>, the latter corresponding to a well-known resonance maximum.<sup>9(a),9(b),10,15,18</sup>

The reaction of  $CN^-$  with  $CS_2$ , COS,  $H_2S$ , or  $CH_3SH$  to give  $SCN^-$  involves a removal of the S atom. This seems to occur only for the mixture  $ClCN-CH_3SH$  according to Reaction (17), although there is very slight evidence that a similar process would also take place in the system  $ClCN-CS_2$  as the  $SCN^-$  efficiency curve shows a well-shaped and reproducible shoulder at  $1.5\pm0.2$  eV which might represent a combination of the formation of  $SCN^-$  by both S<sup>-</sup> and  $CN^-$ . If Reaction (31), exothermic by 0.05 eV, occurs, the

SCN- ionization efficiency curve would exhibit a reaction. However, our data show that some SCNpeak in correspondence with the low-energy resonance of CN<sup>-</sup>:

$$CN^{-}+CS_{2} \rightarrow SCN^{-}+CS.$$
 (31)

The SCN<sup>-</sup> peak could, however, be shifted and partly covered because of the larger production of SCNdue to the reaction between S<sup>-</sup> and ClCN. The rate of reaction for process (31) is  $0.03 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>·sec<sup>-1</sup>.

An extension of the reaction sequence would be to consider the system ClCN-CH<sub>3</sub>SCH<sub>3</sub> where the ion-molecule reaction

$$CN^{-}+CH_{3}SCH_{3}\rightarrow SCN^{-}+C_{2}H_{6}$$
 (32)

is exothermic by 1.8 eV. An experiment was carried out in which a mixture of ClCN and CH<sub>3</sub>SCH<sub>3</sub> was studied. Up to an ion source pressure of 40  $\mu$ Hg and residence times of 2.0 µsec, SCN<sup>--</sup> could not be detected at the resonance maxima for CN<sup>-</sup>. A possible explanation is that the reaction may be sufficiently slow that it would not be possible to observe the production of SCN-.

The formation of SCN<sup>-</sup> might have been expected to occur in correspondence with the high energy resonance capture in the CN<sup>-</sup> ionization efficiency curve. Figures 3-5 show that no observable amount of SCN<sup>-</sup> is formed at 6.9 and 6.0 eV. As the reactions

$$CN^{-}+COS \rightarrow SCN^{-}+CO,$$
 (33)

$$CN^{-}+H_2S \rightarrow SCN^{-}+H_2,$$
 (34)

and (17) are exothermic by 0.93, 1.0, and 1.8 eV, respectively, we can tentatively assume that the high energy at which the above mentioned processes should occur is sufficient to cause the electron to be ejected from SCN<sup>-</sup> and, hence, the latter could not be formed; i.e., that associative detachment reactions occur. In fact, Reaction (1) is endothermic by 0.92 eV and at 6.0 eV the excess energy is about 5 eV. From relationship (24)  $E_t = 3.0$  eV. As  $E_t(CN^-) = 1.7$  eV, the total excess energy with which CN<sup>-</sup> is formed is 3.6-3.7 eV, probably enough to cause associative detachment reactions.

We have already seen that S<sup>-</sup> from CH<sub>3</sub>SH at high energy carries a very small amount of kinetic energy (0.56 eV). We have applied the same procedure to the high energy resonance peaks of the systems ClCN-H<sub>2</sub>S and ClCN-CS<sub>2</sub>. Reactions (9) and (23) are endothermic by 0.97 and 5.5 eV, respectively. At 9.6 eV, where the dissociative resonance capture curve reaches its maximum, only the first one involves a marked excess energy (8.6 eV). The translational energy of  $S^-$  is 0.44 eV, too low to inhibit the formation of  $SCN^-$  by associative detachment. Reaction (2) is endothermic by about 2.0 eV. At 9.5 eV the translational energy of S<sup>-</sup> is about 2.6 eV. This energy, combined with the exothermicity of Reaction (3), might be sufficient to cause an associative detachment

is formed.

# Formation of CN<sup>-</sup>, Cl<sup>-</sup>, and ClCN<sup>-</sup>

The behavior of these mixed systems is complicated by the fact that, in many instances, ions from each component can react with the opposite parent molecule, often to form the same product. Thus, although we do not have proof that CN<sup>-</sup> reacts to give negative ions other than SCN-, S- seems to react with ClCN according to Reactions (4), (35), and (36):

$$S^++ClCN^++S,$$
 (35)

$$S^++ClCN\rightarrow Cl^-+SCN.$$
 (36)

Reaction (35) has been studied for mixtures of ClCN-CS<sub>2</sub> and ClCN-COS at average pressures and with reaction times up to  $1.250 \ \mu sec.$  Our data show that there is a definite possibility of electron transfer reaction even if, due to the very low intensity of ClCN<sup>-</sup>, we were unable to get quantitative results. The heat of formation of ClCN- is not available in the literature. The formation of Cl<sup>-</sup> has been investigated only for the system ClCN-COS. The electron energy was set at the maximum of the S<sup>-</sup> resonance capture curve; the rate constant we obtained by varying the ClCN pressure is  $3 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup>·sec<sup>-1</sup>. The experiment was carried out with a residence time of 0.750  $\mu$ sec. This reaction is exothermic by 1.1 eV.

Table III shows where CN<sup>-</sup> maxima occur. The low-energy maximum is found at 0.5, 1.0, 1.1, and 2.0 eV. This shifting might be partly attributed to some side reactions which lead to the formation of CN<sup>-</sup> as secondary ion; i.e., S<sup>-</sup>, HS<sup>-</sup>, or CH<sub>3</sub>S<sup>-</sup> would react with ClCN to give CN<sup>-</sup>. The shift is noticeably marked in the presence of COS, when CN<sup>-</sup> seems to be formed mainly via Reaction (4) to such a degree that the CN<sup>-</sup> peak due to the electron impact ionization is completely covered by that determined by the ion-molecule reaction. As COS gives S<sup>-</sup> with a very good ionization vield, we assume that Reaction (4)occurs to a large extent because of the high concentration of S<sup>-</sup> even at relatively low pressures. For CN<sup>-</sup> to be formed by attack of S- on ClCN, the neutral product would have to be SCl since, if the S and Cl atoms were formed, the reaction would be endothermic by some 3 eV. However,  $\Delta H_f(SCl)$  is not known and must be estimated. If the Pauling<sup>22</sup> method is employed, we find D(S-Cl) to be 87 and  $\Delta H_f(SCl)$  to be 9 kcal/mole. If the average bond strength of  $SCl_2(g)$ , computed from known heats of formation, is employed, we obtain  $\Delta H_t(SCl) = +31$  kcal/mole. Taking the smaller value, Reaction (4) is exothermic. Taking the high value, (4) is endothermic by 0.2 eV. However, at the resonance maximum for S<sup>-</sup> production about 1 eV excess energy is involved and we estimate some 0.3 eV of this would appear as translational energy of  $S^{-}$ . This is sufficient for Reaction (4) and thus either

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value for  $\Delta H_f(SCl)$  would lead to reaction. However, we do not have a satisfactory explanation for the shift in the CN<sup>-</sup> high-energy resonance. This maximum is always found about 5 eV above the low-energy one.

No OCN- was detected in this study. Dillard et al.9(c) reported its formation by the reaction

$$O^+ ClCN \rightarrow OCN^- + Cl$$
 (37)

when employing SO<sub>2</sub> and N<sub>2</sub>O as sources of abundant amounts of O<sup>-</sup>. The O<sup>-</sup> ion from COS, however, is formed in very small quantities so that any OCNformed would be in too small amount to be detected.

## **Rate Constants**

Rate constants for several reactions have been determined and the results are summarized in Table I. The rate constants for the formation of SCNfrom either S<sup>-</sup> or HS<sup>-</sup> fall in the range  $0.2-0.6 \times 10^{-10}$  $cm^3$  molecule<sup>-1</sup>·sec<sup>-1</sup>. Agreement of the constants obtained by varying pressure or time is quite good in all but one case (S<sup>-</sup> from H<sub>2</sub>S) and is fairly satisfactory in that one. It will be noted that the rate constants for the formation of SCN<sup>-</sup> are essentially the same for the low resonances of  $S^-$  from  $CS_2$  and COS. The rate constants are somewhat larger at the high-energy (6.1 eV) resonance from CS<sub>2</sub> and the resonance (9.6 eV)from  $H_2S$ . The low resonances from  $CS_2$  and COSinvolve about 1.0-1.5 eV excess energy and the S<sup>--</sup> would have about 0.3-0.5 eV of translational energy. The S<sup>-</sup> formed at the higher (6.1 eV) resonance of  $CS_2$  must have considerable translational energy, probably about 1.2 eV. The S<sup>-</sup> from H<sub>2</sub>S, however, probably has only some 0.3-0.4 eV translational energy. Thus, the differences observed in the rate constant for the formation of SCN- from S- do not appear to correlate with the translational energy of the S<sup>-</sup>. Consequently, we cannot explain these differences unless they represent the precision of our measurements. While we think our results are more precise than this, we have no other explanation to offer.

Table I also includes values of the rate constant for the disappearance of S<sup>-</sup>. These data are only approximate although in all but one instance the agreement of  $K_{RT}$  and  $K_{P}$  is reasonably good. The decay of  $S^-$  can be attributed largely to attack on ClCN to form CN<sup>-</sup> and this is borne out by one example in which the rate constant for the formation of CNagrees quite closely with that for the loss of S<sup>-</sup>. Values of  $K_{RT}$  would be expected to be greater than  $K_P$  by the amount of reaction of S<sup>-</sup> to form  $S_2^{-.9(a),10,18}$  How-

ever, with all compounds except COS this reaction seems to be quite slow and, unfortunately, with COS the measurement was not made. It is evident, however, that S<sup>-</sup> reacts primarily to form CN<sup>-</sup> and that the reaction to form SCN<sup>-</sup> is about 2 orders of magnitude smaller.

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(1959)

<sup>2</sup> C. E. Melton and P. S. Rudolph, J. Chem. Phys. 33, 1594 (1960).

<sup>3</sup> K. Kraus, W. Müller-Duysing, and H. Neuert, Z. Naturforsch. **16a**, 1385 (1961).

<sup>4</sup> R. K. Curran, Phys. Rev. 125, 910 (1962).

<sup>5</sup> B. P. Burtt and J. Henis, J. Chem. Phys. 41, 1510 (1964). <sup>6</sup> F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. 45, 1844 (1966).

J. F. Paulson, Advan. Chem. Ser. 58, 28 (1966).

<sup>8</sup> B. C. De Souza and J. H. Green, J. Chem. Phys. 46, 1421

(1967). <sup>9</sup> (a) J. G. Dillard and J. L. Franklin, J. Chem. Phys. 48, <sup>1</sup> T. Franklin, J. Chem. Phys. 2349 (1968). (b) J. G. Dillard and J. L. Franklin, J. Chem. Phys. 48, 2353 (1968). (c) J. G. Dillard, J. L. Franklin, and W. A. Seitz, J. Chem. Phys. 48, 3828 (1968).

<sup>10</sup> K. A. G. MacNeil and J. C. J. Thynne, J. Phys. Chem. 73, 2960 (1969)

<sup>11</sup> K. A. G. MacNeil and J. C. J. Thynne, J. Phys. Chem. 74, 2257 (1970).

12 K. A. G. MacNeil and J. C. J. Thynne, Intern. J. Mass Spectry. Ion Phys. **3**, 455 (1970). <sup>13</sup> D. Vogt, B. Hauffe, and H. Neuert, Z. Physik **232**, 439

(1970)

<sup>14</sup> J. L. Franklin, Y. Wada, P. Natalis, and P. M. Hierl, J. Phys. Chem. 70, 2353 (1966).

<sup>15</sup> K. Kraus, Z. Naturforsch. 16a, 1378 (1961).

 <sup>16</sup> R. E. Fox and R. K. Curran, J. Chem. Phys. **34**, 1595 (1961).
 <sup>17</sup> J. T. Herron and V. H. Dibeler, J. Am. Chem. Soc. **82**, 1555 (1960)

<sup>18</sup> F. H. Dorman, J. Chem. Phys. 44, 3856 (1966).

<sup>19</sup> F. M. Page and G. C. Goode, Negative Ions and the Magnetron (Wiley, New York, 1969).

<sup>20</sup> M. A. Haney and J. L. Franklin, J. Chem. Phys. 48, 4093 (1968)

<sup>21</sup> J. J. De Corpo, D. A. Bafus, and J. L. Franklin J. Chem. Phys.
 54, 1592 (1971).
 <sup>22</sup> D(S-Cl) has been estimated with the Pauling geometric

mean rule23 combined with the electronegativities of S and Cl which difference has been taken equal to  $0.58.^{44} D(S-S) = 101 \text{ kcal/mole}^{25}$  and D(CI-CI) = 58.2 kcal/mole from Table II.

<sup>23</sup> L. Pauling, The Nature of the Chemical Bond (Cornell U. P.,

Ithaca, N.Y., 1967), 3rd ed. <sup>24</sup> F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry

(Interscience, New York, 1967), 2nd ed., p. 103.

<sup>25</sup> J. Drowart and P. Goldfinger, Quart. Rev. (London) 20, 545 (1966).