



# Reactions of Negative lons in the Gas Phase. II. NH2-

John G. Dillard and J. L. Franklin

Citation: The Journal of Chemical Physics **48**, 2353 (1968); doi: 10.1063/1.1669436 View online: http://dx.doi.org/10.1063/1.1669436 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/48/5?ver=pdfcov Published by the AIP Publishing

## Articles you may be interested in

Equilibrium electrontransfer reactions in the gas phase involving longlived negative ion radicals J. Chem. Phys. **68**, 3309 (1978); 10.1063/1.436138

Mobilities and reactions of negative ions in CO2 gas J. Chem. Phys. **64**, 4228 (1976); 10.1063/1.431995

Thermal energy reactions of negative ions with H atoms in the gas phase J. Chem. Phys. **58**, 5841 (1973); 10.1063/1.1679215

Hydration of Negative Ions in the Gas Phase J. Chem. Phys. **49**, 817 (1968); 10.1063/1.1670145

Reactions of Negative Ions in the Gas Phase. III. The Formation of OCN–J. Chem. Phys. **48**, 3828 (1968); 10.1063/1.1669696



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 132.174.255.116 On: Mon, 22 Dec 2014 13:58:21

## Reactions of Negative Ions in the Gas Phase. II. NH<sub>1</sub>-

JOHN G. DILLARD\* AND J. L. FRANKLIN

Department of Chemistry, Rice University, Houston, Texas

(Received 9 October 1967)

In mixtures of ammonia with carbon disulfide and carbonyl sulfide the NH2<sup>-</sup> ion is formed with considerable abundance and reacts to form several other negative ions. The principal products of reaction with CS2 were HS-, CS2-, and SCN-. The principal products of reaction with COS were HS-, NH2S-, and OCN-. The rates of the various reactions are similar to those of many positive-ion-molecule reactions. The heats of formation of SCN- and OCN- ions were determined from appearance potentials of these ions from CH<sub>3</sub>NCS and CH<sub>3</sub>NCO to be -4 and -19 kcal/mole, respectively.

### INTRODUCTION

Charge-transfer processes in pure carbon disulfide and in mixtures of ammonia and carbon disulfide have been studied previously.<sup>1</sup> The dominant secondary negative ion in both systems was CS<sub>2</sub><sup>-</sup>, formed by charge exchange with CS<sup>-</sup> in pure CS<sub>2</sub> and produced via electron transfer from HN<sub>2</sub><sup>-</sup> in the mixture of ammonia and carbon disulfide. The experiments by Kraus and co-workers<sup>1</sup> were conducted at relatively low pressures so the formation of other secondary negative-ion products was not observed. In our efforts to better understand ion-molecule reactions of negative ions, we have studied the reactions of NH2- formed via dissociative resonance capture from NH<sub>3</sub>, with CS<sub>2</sub> and COS at source pressures up to about 50  $\mu$ . This paper presents appearance potentials determined from the maxima in the resonance capture process for the primary and secondary ions observed, upper limits for heats of formation of the secondary negative ions calculated from the ion-molecule reactions observed, and rate constants for the formation of the secondary negative ions.

#### **EXPERIMENTAL**

The study of negative ion-molecule reactions was carried out using a Bendix time-of-flight mass spectrometer (Model 12-101) employing techniques described earlier.<sup>2</sup> Sample gases were stored in separate vessels where each reservoir had a volume of 6 liters. The gases were introduced into the mass spectrometer through separate stainless-steel valves and gold leaks of identical size. In all experiments 1:1 mixtures of NH<sub>3</sub> and CS<sub>2</sub> or COS were studied.

Appearance potentials for resonance processes were determined for ions from pure NH<sub>3</sub>, CS<sub>2</sub>, and COS at a pressure of 10  $\mu$ . The electron energy scale was calibrated using the onset of  $O^-$  formation in SO<sub>2</sub> at 4.2 eV, the electron energy where maximum O<sup>-</sup> current was observed in the resonance capture process from SO<sub>2</sub> at 5.0 eV,<sup>3</sup> and the resonance capture process for  $SF_6^$ at 0 eV.4

The intensity of an ion at a particular pressure was determined by scanning the negative-ion mass spectrum as a function of electron energy. The variation of negative-ion current was plotted against electron energy for each ion. The intensity of the ion at the maximum in the resonance curve was taken as the ion-current value for that pressure. The resonance maximum was then determined at each pressure studied to establish the change in negative-ion current with pressure. In the rate measurements employing variation in time delay, the ion-source pressure was maintained at 25  $\mu$  and the resonance capture curve was determined as described above for each time delay reported.

The materials used in this study were purchased from commercial sources. Ammonia and carbonyl sulfide were obtained from the Matheson Company, Inc. The stated purities of the compounds were 99.99% and 97.5%, respectively. Reagent-grade carbon disulfide was a product of Matheson, Coleman & Bell. Methyl isocyanate was obtained from Ott Chemical Company and methyl isothiocyanate was purchased from Aldrich Chemical Company. All compounds were used without additional purification.

Heats of formation used in the calculations are given in Table I.<sup>5-11</sup>

<sup>\*</sup> Present address: Department of Chemistry, Virginia Poly-technic Institute, Blacksburg, Va. 24060. <sup>1</sup> K. Kraus, W. Muller-Duysing, and H. Neuert, Z. Naturforsch

<sup>16</sup>a, 1385 (1961).

<sup>&</sup>lt;sup>2</sup> (a) J. G. Dillard and J. L. Franklin, J. Chem. Phys. **48**, 2347 (1968), preceding paper; (b) J. L. Franklin, Y. Wada, P. Natalis, and P. M. Hierl, J. Phys. Chem. **70**, 2353 (1966).

<sup>&</sup>lt;sup>8</sup> K. Kraus, Z. Naturforsch. 16a, 1378 (1961).
<sup>4</sup> R. E. Fox and R. K. Curran, J. Chem. Phys. 34, 1595 (1961).
<sup>5</sup> H. O. Pritchard, Chem. Rev. 52, 529 (1953).
<sup>6</sup> D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, Natl. Bur. Std. (U.S.) Tech. Note 270.1 (1965) 270-1 (1965)

<sup>&</sup>lt;sup>7</sup> JANAF Thermochemical Tables, D. Stull, Ed. (Dow Chemi-

<sup>&</sup>lt;sup>1</sup> JANAF Thermochemical Tables, D. Stull, Ed. (Dow Chemical Co., Midland, Mich.).
<sup>8</sup> B. G. Hobrock, R. C. Shenkel, and R. W. Kiser, J. Phys. Chem. 67, 684 (1963).
<sup>9</sup> R. N. Dixon, Can. J. Phys. 38, 10 (1960).
<sup>10</sup> S. Sunner, Acta Chem. Scand. 9, 837 (1955).
<sup>11</sup> F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe, Natl. Bur. Std. (U.S.) Circ. 500 (1952).



FIG. 1. Representative ionization efficiency curves for negative ions in the  $CS_2$ -NH<sub>8</sub> system (the highest resonance capture for S<sup>-</sup> is not shown).

## **RESULTS AND DISCUSSION**

The resonance potential maxima for negative ions and the probable processes for the formation of the ions are listed in Table II. The H<sup>-</sup> ion from NH<sub>3</sub> occurs in our instrument in considerably less abundance than does  $NH_2^-$  and the maximum of the H<sup>-</sup> ionization efficiency curve occurs about 2 eV above that of  $NH_2^-$ . Since the ionization efficiency curves of the various secondary

TABLE I. Heats of formation employed in these studies.

ions discussed herein matched very closely those of  $\rm NH_2^-$  we conclude that H<sup>-</sup> played very little if any part in the reactions discussed below. It should be mentioned that our observations are somewhat at variance with those of Melton.<sup>12</sup> He observed H<sup>-</sup> in greater abundance than we did and the maximum in the ionization efficiency curve for H<sup>-</sup> in his instrument occurred only about 0.5 to 1 eV above that of NH<sub>2</sub><sup>-</sup>. Since the electron-voltage scale of the ionization

TABLE II. Resonance dissociative capture maxima for negative ions.

	ATT (NA)				
 М	(kcal/mole)	Reference	Process	Electron energy (eV)	
$\rm NH_2^-$	15	5		6 2 1 0 2	
HS-	-6.6	3	$N_3 \rightarrow N_2 + n$	$0.3 \pm 0.2$	
NH3	-11.02	6	$CS_2 \rightarrow S^- + CS$	$3.5 \pm 0.2$	
COS	33.96	6		$6.1 \pm 0.2$	
$CS_2$	28.05	6		$7.9 \pm 0.3$	
$H_2S$	-4.93	6	$CS_2 \rightarrow CS^- + S$	$6.1 \pm 0.2$	
CO	-26.42	6	CS+CS <sup>-</sup> →CS <sup>-</sup> +CS	$6.1 \pm 0.2$	
HNCS	30.5	6		0.1_0.2	
HNCO	-27.9	7	COS→S <sup>-</sup> +CO	$2.1 \pm 0.2$	
NCS	97	8		$(0.1 \pm 0.3 \text{ (onset)})$	
NCO	17	9	CH₃NCS→NCS <sup>-</sup> +CH₃	{	
CH₃NCS	27.1	10		$(1.5\pm0.3 \text{ (max)})$	
CH₃NCO	-11.5ª	11		$(1.1 \pm 0.3 \text{ (onset)})$	
$CH_3$	33.2	6	CH₃NCO→NCO <sup>−</sup> +CH₃		
$H_2O$	-57.80	6		$(2.7\pm0.3 \text{ (max)})$	

 $^{a}\Delta H_{f}(\rm CH_{4}NCO)_{\ell}$  obtained from  $\Delta H_{f}(\rm CH_{4}NCO)_{\ell}=-21.5$  kcal/mole and an estimated heat of vaporization of 10 kcal/mole.

<sup>12</sup> C. E. Melton, J. Chem. Phys. 45, 4414 (1966).





efficiency curve for  $NH_2^-$  was reported by Melton as uncorrected, comparison of the absolute values of electron energy for the two studies is not possible.

In Figs. 1 and 2 we show the change in negative-ion current as a function of electron energy in the mixtures  $NH_3-CS_2$  and  $NH_3-COS$ , respectively. In Figs. 3 and 4, respectively, are plots of fractional abundance of negative-ion intensities against pressure in the  $NH_3-CS_2$  and  $NH_3-COS$  systems. These show the depletion of  $NH_2^-$  ion abundance and the increase of secondary-ion abundances with pressure. From the general characteristics of the resonance curve and other considerations discussed below we conclude that the following reactions of negative ions occur in the  $NH_3-CS_2$  and  $NH_3-COS$  mixtures:

$$NH_3 + e^- \rightarrow NH_2^- + H, \qquad (1)$$

$$NH_2^- + CS_2 \rightarrow CS_2^- + NH_2, \tag{2}$$

$$NH_2^{-}+CS_2 \rightarrow HS^{-}+HNCS, \qquad (3)$$

$$NH_2^- + CS_2 \rightarrow SCN^- + H_2S, \qquad (4)$$

$$NH_2^-+COS \rightarrow NH_2S^-+CO,$$
 (5)

$$NH_2^-+COS \rightarrow HS^-+HNCO,$$
 (6)

$$NH_2^-+COS \rightarrow OCN^-+H_2S.$$
 (7)

$$CS_2^-$$

The formation of  $CS_2^-$  is believed to occur predominantly via electron transfer from  $NH_2^-$  with some minor contribution from the charge-transfer process with CS<sup>-</sup>. The production of  $CS_2^-$  from charge transfer with negative sulfur seems unlikely, since  $CS_2^-$  is not observed at lower electron energies where the first resonance capture peak for negative sulfur is observed.

The analogous charge-transfer reaction

$$NH_2$$
 +  $COS \rightarrow COS$  +  $NH_2$ 

was not observed. It may be that the intensity of COS<sup>-</sup> was so low that we could not detect it.

HS-

The  $HS^-$  ion might be formed by any of the following reactions since all these reactant negative ions are observed in resonance capture reactions in the 5.5-6.5-eV region:

$$S^+ + NH_3 \rightarrow HS^- + NH_2,$$
 (8)

$$CS^{-}+NH_{3}\rightarrow HS^{-}+CH_{2}N, \qquad (9)$$

$$NH_2^- + CS_2 \rightarrow HS^- + HNCS,$$
(10)

$$NH_2^-+COS \rightarrow HS^-+HNCO.$$
 (11)

Reaction (8) might occur in the  $NH_3:CS_2$  mixture at three resonance energies, 3.5, 6.1, and 7.9 eV, as given in Table II. From the resonance curve shown in Fig. 1 for  $HS^-$  it is evident that no formation of  $HS^$ is observed at the low energy nor at the highest resonance potentials for S<sup>-</sup>. Certainly it is possible that S<sup>-</sup>, formed at the intermediate resonance potential from



FIG. 3. Fractional abundance of negative ions in an NH<sub>3</sub>: SO<sub>2</sub> mixture.

 $CS_2$  may contain some excess energy which is necessary in the reaction to form HS<sup>-</sup>, but this is surely speculative. No HS<sup>-</sup> is observed in the NH<sub>3</sub>: COS system at the S<sup>-</sup> resonance potential which is similar to what we observed for S<sup>-</sup> from CS<sub>2</sub> at low energies. Furthermore, Reaction (8) is endothermic by approximately 1 eV, if we assume that  $S^-$  is in its ground state, and that  $\Delta H_f(\text{HS}^-)$  in Table I is a reasonable value. The  $\Delta H_f(HS^-)$  calculated from the appearance potential of HS<sup>-</sup> from H<sub>2</sub>S reported by Kraus<sup>3</sup> may include excess energy. If this is corrected for the excess energy, the resulting  $\Delta H_f(\text{HS}^-)$  would be more negative, tending to make Reaction (8) more nearly exothermic. Thus we cannot exclude Reaction (8) as the mode of formation of HS<sup>-</sup> at high electron energies, but we feel that the reaction is not the dominant mode of formation of HS<sup>-</sup>.

Reaction (9) involving  $CS^-$  as the reactant ion is excluded as the precursor in the HS<sup>-</sup> formation, since the fractional abundance of  $CS^-$  remained essentially constant throughout the pressure range studied as indicated in Fig. 3.

Thus, Reaction (10) appears to be the major reaction pathway for the formation of  $HS^-$  in the NH<sub>3</sub>:CS<sub>2</sub> system. Reaction (10) as written is exothermic by about 0.8 eV.

In the  $NH_3$ : COS system, the interpretation is more straightforward. The only reasonable reaction for HS<sup>-</sup> formation is that given by Eq. (11). As mentioned

TABLE III.	Rate constants, units of cubic centimeter	s per
	molecule • second.*	

	COS-NH <sub>8</sub>	CS <sub>2</sub> -NH <sub>3</sub>
$(k_1+k_2)_{\tau}$	4.65×10 <sup>-10</sup>	9.22×10 <sup>-10</sup>
$(k_1+k_2)_p$	8.71×10 <sup>-10</sup>	9.76×10 <sup>-10</sup>
$k_{\tau}$ (NH <sub>2</sub> <sup>-</sup> disappearance)	4.59×10 <sup>-10</sup>	13.4×10 <sup>-10</sup>

\* Further studies of the reactions of NH2<sup>-</sup> and also of PH2<sup>-</sup> with a series of organic molecules are in progress.

above, we did not detect HS<sup>-</sup> at the resonance potential for  $S^-$  from COS, so Reaction (8) is not responsible for production of HS<sup>-</sup> in this system. From the heats of formation in Table I, Reaction (11) is calculated to be exothermic by about 0.7 eV.

#### OCN- and SCN-

The reactions producing OCN- and SCN- are given by Eqs. (4) and (7). The SCN<sup>-</sup> ion was not detected in the study with NH<sub>3</sub> and COS.

To aid in our understanding of the ion-molecule reactions producing OCN<sup>-</sup> and SCN<sup>-</sup> we have measured the appearance potentials of OCN- and SCN- from CH<sub>3</sub>NCO and CH<sub>3</sub>NCS, respectively. Using the onset energies given in Table II combined with the heats of formation in Table I and Reactions (12) and (13), we calculate that  $\Delta H_f(SCN^-) = -4$  kcal/mole, and  $\Delta H_f(OCN^-) = -19 \text{ kcal/mole:}$ 

$$CH_3NCO + e^{-} \rightarrow NCO^{-} + CH_3,$$
 (12)

$$CH_3NCS + e^{-} \rightarrow NCS^{-} + CH_3.$$
 (13)

These values represent upper limits to the actual heats of formation, since it was not possible to measure translational energy for these ions because of their very low intensity.

The heat of formation of OCN<sup>-</sup> has not been measured previously, so we suggest our value as the "best" value available. However, Napper and Page13 have determined  $\Delta H_f(NCS^-)$  to be 38.5 kcal/mole. In addition to our determination of  $\Delta H_f(SCN^-)$  here, we have examined a series of negative-ion-molecule reactions in which SCN<sup>-</sup> is the dominant secondary ion.<sup>14</sup> From the series of reactions producing SCN- the upper limit for  $\Delta H_f(SCN^-) = -4$  kcal/mole is to be preferred.

The heats of formation of NCO and NCS radicals have been determined in this laboratory.<sup>15</sup> This was done by measuring the appearance potentials of CH<sub>3</sub><sup>+</sup> from CH<sub>3</sub>NCO and CH<sub>3</sub>NCS. The CH<sub>3</sub>+ was formed in each case with excess translational energy and when due allowance is made for the corresponding amount of excess internal energy the heats of formation of NCO and NCS are found to be 16.5 and 77 kcal/mole, respectively. Our value for NCO is in good agreement with that of Dixon<sup>9</sup> but our value for NCS is considerably less than that of Hobrock et al.8 We are inclined to think our lower value is the better one, since allowance was made for excess energy in its measurement. Using the above values for the heats of formation of the NCO and NCS radicals and the corresponding



FIG. 4. Fractional abundance of negative ions in an NH<sub>3</sub>: COS mixture.

negative ions we calculate  $E_A(NCO)$  and  $E_A(NCS)$  to be 36 and 81 kcal/mole, respectively.

The reactions which are proposed in Eqs. (4) and (7) are the only reasonable reactions for the formation of OCN<sup>-</sup> and SCN<sup>-</sup>. From the equation and heats of formation given above, Reaction (4) is exothermic by 2.3 eV, and Reaction (7) by 0.2 eV. It is surprising that no SCN<sup>-</sup> was observed in the reaction of NH<sub>2</sub><sup>-</sup> with COS. The reaction

$$NH_2^{-} + COS \rightarrow SCN^{-} + H_2O \tag{14}$$

is exothermic by 1.9 eV and therefore thermodynamically possible. It might be suggested that the  $NH_2^{-}$  ion has a preferred direction of attack on COS but this is pure speculation. For the present we have no reasonable explanation why the reaction should not be observed.

## NH<sub>2</sub>S-

The reaction of  $NH_2^-$  with COS produced  $NH_2S^-$ . The NH<sub>2</sub>S<sup>-</sup> ion was not detected in the system NH<sub>3</sub>- $CS_2$ . From Eq. (5) we calculate an upper limit for  $\Delta H_f(\mathrm{NH}_2\mathrm{S}^-)$  to be 7 kcal/mole.

#### **RATE CONSTANTS**

The rate constants calculated from changes in primary- and secondary-ion currents as a function of pressure (at constant time) and as a function of time (at constant pressure) compare with rates for other negative ion-molecule reactions. The determination of

<sup>&</sup>lt;sup>18</sup> R. Napper and F. M. Page, Trans. Faraday Soc. 59, 1086 (1963).

<sup>&</sup>lt;sup>14</sup> The reactions involve CN<sup>-</sup> and R<sub>2</sub>S molecules and a complete report of the results will appear in the future. <sup>15</sup> M. A. Haney and A. L. Yergey III (private communication).



the rate constants is complicated by the fact that the primary ion reacts to form two or more products. A semilog plot of the  $NH_2^-$  ion intensity against time gives a straight line with  $CS_2$ .

Since  $NH_2^-$  is the precursor of both  $CS_2^-$  and  $HS^-$ , and since the secondary ions are of nearly equal intensity, it appears that the rates of formation of  $HS^$ and  $CS_2^-$  are very similar. Thus, we can calculate the sum of the rates for production of  $HS^-$  and  $CS_2^-$  and get an idea of the order of magnitude of the rates. Using an approach similar to that of Shannon and Harrison<sup>16</sup> it can be shown that for the reactions

$$NH_2^{-} + CS_2^{-} + NH_2, \qquad (2)$$

$$NH_2^-+CS_2^{\to}HS^-+HNCS,$$
 (3)

$$I^{\circ}_{\rm NH_2}/(I_{\rm HS} + I_{\rm CS_2}) = [(k_1 + k_2)\tau(\rm CS_2)]^{-1} + 1.$$
 (15)

Thus a plot of  $I^{\circ}_{\mathrm{NH}_2}$ -/ $(I_{\mathrm{HS}}$ -+ $I_{\mathrm{CS}_2}$ -) vs  $\tau^{-1}$  should give a straight line of intercept 1 and slope of  $[(k_1+k_2)(\mathrm{CS}_2)]^{-1}$  from which  $k_1+k_2$  can be evaluated. An analogous plot of ion-current ratio vs  $(\mathrm{CS}_2)^{-1}$ should give a slope of  $[(k_1+k_2)\tau]^{-1}$ .

To be precise, the rate of Reaction (4) leading to the formation of NCS<sup>-</sup> should also be included in the derivation of Eq. (15). However, this reaction is quite slow and its neglect introduces only a very small error

in the results. This procedure has also been applied to the  $NH_3$ -COS system in which the principal secondary ions were HS<sup>-</sup> and  $NH_2$ S<sup>-</sup>. Again the intensity of NCO<sup>-</sup> was sufficiently small that it was neglected in the computation of the rate constants. A typical plot of

$$I^{\circ}_{\rm NH_2}$$
-/( $I_{\rm HS}$ -+ $I_{\rm CS_2}$ -) vs  $\tau^{-1}$ 

according to Eq. (15) is given in Fig. 5.

The results for  $(k_1+k_2)$  for both systems and obtained by variation of both time delay and pressure are given in Table III. In addition, the rate constant for the disappearance of  $NH_2^-$  is given for both systems. Agreement is reasonably good for the  $NH_3$ -CS<sub>2</sub> system. The  $NH_2^-$  decay and  $(k_1+k_2)$ , values for the  $NH_3$ -COS system agree very well, but the  $(k_1+k_2)_p$  value is quite high. We cannot be certain, but we are inclined to question this value and, indeed, to place more reliance upon the values obtained by time variation. The latter can be obtained quite quickly, whereas the pressure studies are relatively slow, so that there is time for conditions in the instrument to change in the course of the study.

#### ACKNOWLEDGMENTS

The authors wish to express their appreciation for the support of the Robert A. Welch Foundation. Also, we wish to acknowledge the help of William A. Seitz in the analysis of the data.