

strong evidence of the occurrence of (1) in this gas phase radiolysis system. Since there is nothing unique about the reaction rate of (1), we conclude that these results support the view that ion-molecule reactions are of general importance in gas-phase radiation chemistry.

An alternate possibility to the gaseous-ion sensitization is excited atom sensitization, because the quantity  $\frac{BZ}{W}$  should also be proportional to the rate of formation of excited species. Thus the mode of hydrogen atom formation might be



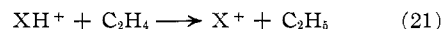
It is not possible to refute this completely, but it would seem that if (19) were occurring to any great extent, then as the sensitizer pressure was increased, the probability of deactivation by  $X^* + X$  collisions would become more probable than (19). This would result in a non-linearity of  $R_{C_2H_6} + R_{C_3H_8} + R_{C_4H_{10}}$  with sensitizer pressure, as has been observed for the rate of ethylene consumption as a function of argon pressure in studies of the ethyl-

ene-argon systems.<sup>5</sup> The corresponding dissipation of charge in  $X^+ + X$  collisions is not possible.

It is not at present possible to rule out the protonation of ethylene by  $XH^+$ , *viz.*



However, the formation of  $C_2H_5^+$  would not be expected to lead to the same products as hydrogen atom formation in the presence of ethylene, unless every  $C_2H_5^+$  was neutralized to  $C_2H_4 + H$ . This latter event would, of course, be kinetically indistinguishable from (1) followed by neutralization of  $XH^+$  and  $H_3^+$ . The reaction



can be ruled out on energetic grounds.

**Acknowledgments.**—The author wishes to acknowledge fruitful discussions with Dr. J. H. Futrell, the assistance of Messrs. C. W. Bell and T. P. Gorman in carrying out the experimental work and the help of Mr. E. E. Poirot with the calculations.

BAYTOWN, TEXAS

[CONTRIBUTION FROM THE MASS SPECTROMETRY SECTION, NATIONAL BUREAU OF STANDARDS]

## Electron Impact Study of the Cyanogen Halides<sup>1</sup>

BY JOHN T. HERRON AND VERNON H. DIBELER

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Mass spectra and appearance potentials are reported for the principal ions of cyanogen chloride, bromide and iodide. Using these data, the following thermochemical values have been computed:  $\Delta H_f^{\circ}CN = 89 \pm 2$  kcal./mole;  $\Delta H_f^{\circ}CN^- = 15 \pm 4$  kcal./mole,  $E.A.(CN) = 74 \pm 4$  kcal./mole.

### Introduction

The cyanogen halides form an interesting series of compounds bearing certain resemblances to mixed halogen compounds in the ease with which they form negative ions. Furthermore, they provide a homologous series containing the CN group, of which the heat of formation, ionization potential and electron affinity are of interest for numerous thermochemical applications.

Recent studies of the ionization-dissociation processes in cyanogen,  $C_2N_2$ , have been reported by McDowell and Warren,<sup>2</sup> Kandel,<sup>3</sup> and by Stevenson.<sup>4</sup> The only published appearance potential for the cyanogen halides is also due to Stevenson,<sup>4</sup> but is limited to the  $Cl^+$  ion of cyanogen chloride. As some uncertainties remain in the interpretation of the dissociation process in cyanogen chloride and cyanogen, further work including the halogenated series seems to be warranted. An additional incentive is the reliable determination of heats of formation of cyanogen chloride, bromide and iodide by Lord and Woolf.<sup>5</sup>

(1) This research was performed as part of the National Bureau of Standards' Free Radical Research Program supported by the Department of the Army.

(2) C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

(3) R. J. Kandel, *J. Chem. Phys.*, **22**, 1496 (1954).

(4) D. P. Stevenson, *ibid.*, **18**, 1347 (1950).

(5) G. Lord and A. A. Woolf, *J. Chem. Soc.*, 2546 (1954).

### Experimental

The mass spectrometer was essentially the conventional 60° sector-type instrument. Magnetic scanning was used at a constant ion accelerating potential of 5000 volts. Mass spectra were obtained using 70 v. electrons.

Usual procedures for appearance potential studies were employed. That is, the anode of the ion source was operated at about the same potential as the ionization chamber. The ion repeller was biased 3 v. positive with respect to the ionization chamber when studying positive ions and 1.5 v. negative for negative ions. The temperature of the ion source was about 250°.

Appearance potential measurements were made by varying the electron energy by means of a Shallcross decade potentiometer across a carefully regulated and measured 100.0 v. power supply. The electron accelerating voltage was usually varied in 0.1 v. steps.

The electron energy scale for positive ions was calibrated by means of argon, using the spectroscopic ionization potential of 15.76 e.v.<sup>6</sup>

In the case of negative ions, no single calibration point was found acceptable over the required energy scale. It was found necessary to separate negative ions into two energy ranges, *i.e.*, 0 to 2 ev. and above 2 ev. Furthermore each range required an optimum setting of source magnet and emission control to attain stable operation.

Ion currents were measured with a 10-stage electron multiplier, vibrating reed electrometer and recording potentiometer. Under favorable conditions, the minimum detectable current was estimated to be  $10^{-18}$  amp.

Table I lists the negative ions used as calibration points. Positive ion appearance potentials were evaluated by normalizing the slopes of the unknown and reference curves, plotting on a semi-log scale and determining the voltage in-

(6) C. E. Moore, *Natl. Bur. Standards Circular*, 467 (1949).

TABLE I

Molecule	Ion	NEGATIVE ION CALIBRATION POINTS		Method
		Probable process	A.P. (ev.)	
CO	O <sup>-</sup>	CO(1Σ <sup>+</sup> ) → C <sup>+</sup> ( <sup>2</sup> P) + O <sup>-</sup> ( <sup>2</sup> P)	20.902 ± 0.02	Calcd. <sup>a</sup>
	O <sup>-</sup>	CO(1Σ <sup>+</sup> ) → C( <sup>3</sup> P) + O <sup>-</sup> ( <sup>2</sup> P)	9.6 ± 0.2	Elect. impact <sup>b</sup>
O <sub>2</sub>	O <sup>-</sup>	O <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> ) → O <sup>-</sup> ( <sup>4</sup> S) + O <sup>-</sup> ( <sup>2</sup> P)	17.264 ± 0.009	Calcd. <sup>a</sup>
	O <sup>-</sup>	O <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> ) → O( <sup>3</sup> P) + O <sup>-</sup> ( <sup>2</sup> P)	4.53 ± .03	R.p.d. elect. impact <sup>c</sup>
HCl	Cl <sup>-</sup>	HCl(1Σ <sup>+</sup> ) → H( <sup>2</sup> S) + Cl <sup>-</sup> ( <sup>1</sup> S)	0.62 ± .05	R.p.d. elect. impact <sup>d</sup>
SF <sub>6</sub>	SF <sub>6</sub> <sup>-</sup>	SF <sub>6</sub> → SF <sub>6</sub> <sup>-</sup>	0.0	R.p.d. elect. impact <sup>e</sup>

<sup>a</sup> L. M. Branscomb, *J. Chem. Phys.*, **29**, 452 (1958). <sup>b</sup> H. D. Hagstrum, *ibid.*, **23**, 178 (1955). <sup>c</sup> D. C. Frost and C. A. McDowell, *THIS JOURNAL*, **80**, 6183 (1958). <sup>d</sup> R. E. Fox, *J. Chem. Phys.*, **26**, 1281 (1957). <sup>e</sup> W. M. Hickam and R. E. Fox, *ibid.*, **25**, 642 (1956).

terval between the nearly linear portions of the normalized curves.

Cyanogen chloride was prepared by the reaction of hydrochloric acid with a mixture of mercuric cyanide and potassium chlorate. The gas evolved was passed over solid potassium hydroxide, to remove water and unreacted hydrochloric acid.

Cyanogen bromide was obtained from a commercial source, and cyanogen iodide was supplied through the courtesy of Dr. D. E. Mann, National Bureau of Standards.

The cyanogen halides were shaken with mercury before use to remove free halogen. The bromide and iodide compounds also were held at -70° and pumped for about one-half hour to remove any volatile impurities. Mass spectral analyses showed these impurities: in CNCl, HCN, 0.5%, HCl 0.2%, hydrocarbon 3%; CNBr, HCN, 0.2%, HBr 0.2%; CNI, HCN, 1.5%, CNBr, 0.5%.

Several attempts to prepare CNF by various means were uniformly unsuccessful. Although Cosslett<sup>7</sup> reported the preparation of cyanogen fluoride by the reaction of cyanogen iodide with silver fluoride at 220°, all subsequent attempts to repeat this preparation have failed.<sup>8</sup> It now seems certain that Cosslett's product was principally a mixture of CO<sub>2</sub> and SiF<sub>4</sub>.

### Results and Discussion

Mass spectra of the cyanogen halides are given in Table II. The lower masses of the CNCl ( $m/e < 20$ ) are in some doubt due to the correction

TABLE II

Ion	MONOISOTOPIC MASS SPECTRA		
	CNCl	CNBr	CNI
C <sup>+</sup>	(2.36)	0.54	0.25
N <sup>+</sup>	0.94	0.12	.04
CN <sup>+</sup>	5.83	1.17	.86
X <sup>+</sup>	9.15	10.25	27.33
CX <sup>+</sup>	2.97	1.54	1.39
NX <sup>+</sup>	.....	0.03	0.03
CNX <sup>+</sup>	100.0	100.0	100.0
X <sup>+-</sup>	.....	0.13	0.82
CX <sup>++</sup>	0.03	0.03	0.02
CNX <sup>++</sup>	1.63	3.36	3.13
CN <sup>-</sup>	0.003	0.06	0.007
Max.	.064	.76	.005
X <sup>-</sup>	.001	.0002	~ .0001
Max.	.002	.005	~ .0001

for presence of a non-separable hydrocarbon impurity in the cyanogen chloride. The mass spectrum of cyanogen chloride differs somewhat from that reported by Stevenson.<sup>4</sup> However, Stevenson's data were obtained at 55° and 1000 v. ion acceleration voltage. Like the halogen molecules, the molecular ions are by far the most abundant.

Fragment ions resulting from the rupture of the CN-X bond show interesting variations. The

(7) V. E. Cosslett, *Z. anorg. Chem.*, **201**, 75 (1931).

(8) H. J. Callomon, H. W. Thompson, F. A. Anderson and B. Bak, *J. Chem. Soc. (London)*, 3709 (1953).

X<sup>+</sup> ion increases from 9.2% (sum of the isotopes) in CNCl, to 10.3% in CNBr, and 27.3% in CNI, whereas the abundance of the CN<sup>+</sup> ion decreases from 7.6% in CNCl to 0.86% in CNI. Apparently this is related to the difference in the ionization potential of the CN radical (14.6 ev.) and of the halogen atoms as the latter decreases from Cl (13.01 ev.) to I (10.45 ev.).

Doubly charged ions of the molecule and of fragment ions are observed in each instance. There is some indication of the rearrangement ions, NX<sup>+</sup>. Negative halogen ions and CN<sup>-</sup> ions are observed in each case.

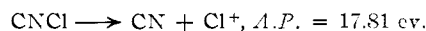
Negative ion abundances are tabulated at 70 ev. except for the resonant processes which are reported for the apparent maximum cross sections for the dissociative attachment process and are related to the most abundant positive ion measured at 70 ev.

Table III summarizes the measured appearance potentials along with the postulated reaction mechanisms.

Standard deviations are given for the positive ions. In the case of the negative ions, where the number of measurements was much smaller, the uncertainties have been estimated.

**Positive Ions. CNX<sup>+</sup>.**—The molecular ionization potentials are reported here for the first time. These values are very nearly equal to the ionization potentials of the halogen atoms:  $I(\text{Cl}) = 13.0$ ,  $I(\text{Br}) = 11.84$  and  $I(\text{I}) = 10.45$  ev. and suggest that ionization occurs by removal of a non-bonding electron from the halogen atom in the molecules.

**X<sup>+</sup>.**—Stevenson<sup>4</sup> measured the Cl<sup>+</sup> appearance potential from cyanogen chloride and attributed it to the process



from

$$A(\text{Cl}^+) = \Delta H_f \text{CN} + \Delta H_f \text{Cl}^+ - \Delta H_f \text{CNCl} + E_e + E_{k.e.}$$

where  $E_e$  is any electronic excitation energy and  $E_{k.e.}$  is the total excess kinetic energy possessed by the neutral and charged fragments, it follows that

$$\Delta H_f \text{CN} \leq A(\text{Cl}^+) + \Delta H_f \text{CNCl} - \Delta H_f \text{Cl}^+$$

Substituting Stevenson's measured  $A(\text{Cl}^+)$  from Table III and the heats of formation from Table IV gives  $\Delta H_f(\text{CN}) \leq 113$  kcal./mole.

Stevenson suggested that in this reaction the CN radical was in the A<sup>2</sup>Π electronic state ( $E_e = 26.4$  kcal./mole<sup>9</sup>). If this is the case, the heat of

(9) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

TABLE III  
 APPEARANCE POTENTIALS IN CYANOGEN HALIDES AND CYANOGEN

Process	This work		Other work	
	Pos. ion (ev.)	Neg. ion (ev.)	Pos. ion (ev.)	Neg. ion (ev.)
(CN) <sub>2</sub> → (CN) <sub>2</sub> <sup>+</sup>			13.57 ± 0.02 <sup>2</sup>	
→ CN <sup>+</sup> + CN			20.75 ± .04 <sup>3</sup>	
→ CN <sup>-</sup> + CN		4.4 ± 0.3		4.4 ± 0.2 <sup>2</sup>
CNCl → CNCl <sup>+</sup>	12.49 ± 0.04			
→ CCl <sup>+</sup> + N	17.2 ± .2			
→ CN <sup>+</sup> + Cl	18.3 ± .2			
→ CN <sup>+</sup> + Cl <sup>-</sup>	15.5 ± .2	15.5 ± .3		
→ CN + Cl <sup>+</sup>	17.9 ± .1		17.81 ± .2 <sup>3</sup>	
→ CN <sup>-</sup> + Cl <sup>+</sup>	13.6 ± .1	13.3 ± .3		
→ CN <sup>-</sup> + Cl		0.4 ± .3		
→ CN + Cl <sup>-</sup>		6.7 ± .3		
? → Cl <sup>-</sup>		~0 ± .3		
CNBr → CNBr <sup>+</sup>	11.95 ± .08			
→ CBr <sup>+</sup> + N	17.4 ± .2			
→ CN <sup>+</sup> + Br	18.3 ± .1			
→ CN <sup>+</sup> + Br <sup>-</sup>	14.6 ± .1	~12		
		~15		
→ CN + Br <sup>+</sup>	16.2 ± .1			
→ CN <sup>-</sup> + Br <sup>+</sup>	11.9 ± .2	<12		
→ CN <sup>-</sup> + Br		~0		
→ CN + Br <sup>-</sup>		4.1 ± .3		
? → Br <sup>-</sup>		~0		
CNI → CNI <sup>+</sup>	10.98 ± .05			
→ CI <sup>+</sup> + N	17.6 ± .3			
→ CN <sup>+</sup> + I	18.1 ± .1			
→ CN <sup>+</sup> + I <sup>-</sup>	.....	.....		
→ CN + I <sup>+</sup>	14.3 ± .1			
→ CN <sup>-</sup> + I <sup>+</sup>	9.8 ± .1	9.8 ± .3		
→ CN <sup>-</sup> + I		~0		
→ CN + I <sup>-</sup>		2.6 ± .3		

TABLE IV

## HEATS OF FORMATION

Substance	$\Delta H_f$ 298°, kcal./mole	Ref.	Substance	$\Delta H_f$ 298°, kcal./mole	Ref.
C <sub>2</sub> N <sub>2</sub>	73.84	<sup>a</sup>	CN <sup>+</sup>	419	<sup>d</sup>
CNCl	31.6	<sup>b</sup>	Cl <sup>+</sup>	329	<sup>d</sup>
CNBr	43.3	<sup>b</sup>	Br <sup>+</sup>	300	<sup>d</sup>
CNI	52.4	<sup>b</sup>	I <sup>+</sup>	267	<sup>d</sup>
CN	89	<sup>c</sup>	CN <sup>-</sup>	15	<sup>c</sup>
Cl	29.0	<sup>a</sup>	Cl <sup>-</sup>	-59	<sup>d</sup>
Br	26.7	<sup>a</sup>	Br <sup>-</sup>	-57	<sup>d</sup>
I	25.5	<sup>a</sup>	I <sup>-</sup>	-48	<sup>d</sup>
N	113.0	<sup>a</sup>			

<sup>a</sup> F. D. Rossini, *et al.*, Natl. Bur. Standard Circular 500 (1952). <sup>b</sup> Ref. 5. <sup>c</sup> This work. <sup>d</sup> F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y. 1957.

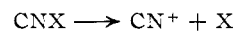
formation of ground state CN is  $\leq 113 - 26 \leq 87$  kcal./mole.

McDowell and Warren<sup>2</sup> have criticized this mechanism on the grounds that there is no *a priori* reason to expect dissociation to lead to formation of an excited rather than ground state CN radical. They suggested that kinetic energy may have been involved in the dissociation, and that the results were fortuitous. Although it is not possible to make any unequivocal choice between mechanisms without kinetic energy measurements of the fragment ions, our data can be consistently interpreted on the basis of the mechanism of Stevenson. The values so obtained for  $\Delta_f H$ -CN(X<sup>2</sup>Σ) are 89, 90 and 89 kcal./mole from the

chloride, bromide and iodide, respectively. The average value from all our data is

$$\Delta_f H_{CN}(X^2\Sigma) \leq 89 \pm 2 \text{ kcal./mole}$$

**CN<sup>+</sup>**.—We have identified the higher CN<sup>+</sup> appearance potential with the process



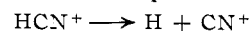
The heat of formation of CN<sup>+</sup> can be calculated from

$A.P. (CN^+) = \Delta_f H_{CN^+} + \Delta_f H_X - \Delta_f H_{CNX} + E_c + E_{k.e.}$   
from which

$$\Delta_f H_{CN^+} \leq A.P. (CN^+) + \Delta_f H_{CNX} - \Delta_f H_X$$

Using the measured CN<sup>+</sup> appearance potentials from Table III and the heats of formation of the cyanogen halides and halogen atoms from Table IV,  $\Delta_f H_{CN^+} \leq 425, 439$  and  $444$  kcal./mole from the chloride, bromide and iodide compounds, respectively.

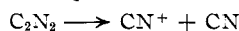
The heat of formation of CN<sup>+</sup> also can be calculated from the appearance potential of the CN<sup>+</sup> ion from HCN.<sup>4</sup> For the process



$$\Delta_f H_{CN^+} \leq 426 \text{ kcal./mole}$$

The value for  $\Delta_f H_{CN^+}$  has some bearing on the mode of dissociation of cyanogen. Kandel<sup>3</sup> has measured the appearance potential of CN<sup>+</sup> from C<sub>2</sub>N<sub>2</sub> as  $20.75 \pm 0.04$  ev. and has determined that 0.57 ev. total excess kinetic energy was involved in the process.

If the dissociation process can be represented by



then the appearance potential can be calculated from

$$A(\text{CN}^+) = \Delta H_f \text{CN}^+ + \Delta H_f \text{CN} - \Delta H_f \text{C}_2\text{N}_2 + E_0 + E_{k.e.}$$

from which

$$\Delta H_f \text{CN} = A(\text{CN}^+) + \Delta H_f \text{C}_2\text{N}_2 - \Delta H_f \text{CN}^+ - E_0 - E_{k.e.}$$

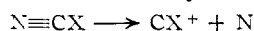
Using Kandel's values for  $A(\text{CN}^+)$  and  $E_{k.e.}$ ,  $\Delta H_f \text{C}_2\text{N}_2$  from Table III, and  $\Delta H_f \text{CN}^+ \leq 426$  from Stevenson's measurements on HCN, we obtain  $\Delta H_f \text{CN} \geq (113.2 - E_0)$  kcal./mole.

The value 113.2 is almost certainly too high for ground state CN. Brewer, *et al.*,<sup>10</sup> have determined  $\Delta H_f \text{CN} = 94$  kcal./mole by a thermochemical method. Likewise, McDowell and Warren<sup>2</sup> found  $\Delta H_f \text{CN} = 92.7$  kcal./mole from an electron impact study of cyanogen and methyl cyanide.

An interpretation consistent with that adopted for the cyanogen halides would place the CN radical in the  $A^2\Pi$  state, and hence lead to  $\Delta H_f \text{CN} \geq 113.2 - 26.4 \geq 86.8$  kcal./mole.

**CX<sup>+</sup>.**—The normal order of appearance potentials in a halogen series is chloride > bromide > iodide. For the CX<sup>+</sup> ions of the cyanogen halides, this order is reversed.

The ions must be formed by the simple process



The ionization potentials of the CX<sup>+</sup> ions can be calculated from

$$A(\text{CX}^+) = D(\text{N} \equiv \text{CX}) + I(\text{CX}) + E_0 + E_{k.e.}$$

from which

$$I(\text{CX}) \leq A(\text{CX}^+) - D(\text{N} \equiv \text{CX})$$

The values calculated in this manner using a value of 160 kcal./mole for  $D(\text{N} \equiv \text{CX})$  are  $I(\text{CCl}) \leq 10.2$  ev.;  $I(\text{CBr}) \leq 10.5$  ev.; and  $I(\text{CI}) \leq 10.8$  ev. Within the extreme limits of estimated uncertainties in the measurement together with plausible small variations in  $D(\text{C} \equiv \text{N})$  due to the nature of halogen substitution, the observed  $I(\text{CX})$  values may be considered very nearly equal. By direct measurement, Reed and Sneddon<sup>11</sup> found  $I(\text{CCl}) = 12.9$  and  $I(\text{CBr}) = 10.4$  ev. The latter is in good agreement with present results, but the value for  $I(\text{CCl})$  is in serious disagreement. It is interesting to note that the above calculations result in upper limits to the ionization potential and that excess electronic or kinetic energy would result in smaller values for the ionization potentials than those indicated.

**Ion-pair Processes.**—Several positive and negative ion appearance potentials have been identified as ion-pair processes. These are of special interest as there is as yet no experimental evidence to support the existence of excited states of negative atomic ions<sup>12</sup> and any excess energy of the products is likely to be kinetic energy.

Because of the greater reliability of the positive ion energy scale and the fact that positive ion ap-

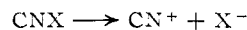
(10) I. Brewer, L. K. Templeton and F. A. Jenkins, *THIS JOURNAL*, **73**, 1462 (1951).

(11) R. I. Reed and W. Sneddon, *Trans. Faraday Soc.*, **54**, 301 (1958).

(12) L. M. Branscomb, "Negative Ions," *Advances in Electronics and Electron Physics*, Academic Press, Inc., New York, N. Y., 1957.

pearance potentials are based on a much larger number of measurements than the corresponding negative ion appearance potentials, all calculations are made using positive ion appearance potentials.

**X<sup>-</sup>, CN<sup>+</sup>.**—This ion pair is produced by the process



for which we can write

$$A(\text{CN}^+) = A(\text{X}^-) = \Delta H_f \text{CN}^+ + \Delta H_f \text{X}^- - \Delta H_f \text{CNX} + E_0 + E_{k.e.}$$

hence

$$\Delta H_f \text{CN}^+ \leq A(\text{CN}^+) + \Delta H_f \text{CNX} - \Delta H_f \text{X}^-$$

Substitution of the measured appearance potentials from Table III and heats of formation from Table IV results in  $\Delta H_f \text{CN}^+ \leq 448$  and 437 kcal./mole for the chloride and bromide, respectively. These values are considerably greater than the lowest value calculated in a previous section for  $\Delta H_f \text{CN}^+$  of 424 kcal./mole and suggests that in the present case the appearance potentials contain either kinetic or electronic excitation energy terms of about 1 and 0.6 ev., respectively.

In the case of cyanogen bromide, it was found that the Br<sup>-</sup> ionization efficiency curve had a resonance type maximum at the foot of the curve, so that no unambiguous single onset energy could be determined.

**CN<sup>-</sup>, X<sup>+</sup>.**—The process in this case is



and

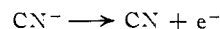
$$A(\text{CN}^-) = A(\text{X}^+) = \Delta H_f \text{CN}^- + \Delta H_f \text{X}^+ - \Delta H_f \text{CNX} + E_0 + E_{k.e.}$$

hence

$$\Delta H_f \text{CN}^- \leq A(\text{X}^+) + \Delta H_f \text{CNX} - \Delta H_f \text{X}^+$$

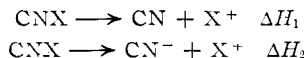
and  $\Delta H_f \text{CN}^- \leq 16, 18, 11$  kcal./mole for the chloride, bromide and iodide, respectively. The mean value from all determinations was  $\Delta H_f \text{CN}^- \leq 15 \pm 4$  kcal./mole.

The electron affinity of CN can be calculated directly from



for which  $\Delta H = EA(\text{CN}^-) = \Delta H_f \text{CN} - \Delta H_f \text{CN}^-$  hence  $EA(\text{CN}^-) = (89 \pm 2) - (15 \pm 4) = 74 \pm 6$  kcal./mole.

The electron affinity of CN also can be obtained from the processes



from which

$$\text{CN}^- \longrightarrow \text{CN} + e^-, \quad \Delta H = EA(\text{CN}^-) = \Delta H_1 - \Delta H_2$$

Thus by taking differences between the measured X<sup>+</sup> appearance potentials for every individual experiment (assuming the neutral CN is produced in the  $A^2\Pi$  state), we calculate  $EA(\text{CN}^-) = 74 \pm 4$  kcal./mole ( $3.2 \pm 0.2$  ev.).

Bakulina and Ionov<sup>13</sup> measured the electron affinity of CN by surface ionization of KCN and KCNS on a hot tungsten wire. At 2210, 2230 and 2440°K., the values found were 69 to 74 kcal./

(13) I. N. Bakulina and N. I. Ionov, *Doklady Akad. Nauk S.S.S.R.*, **99**, 1023 (1954).

mole for KCN and 69 to 76 kcal. for KCNS. The mean value, 72 kcal./mole, is in good agreement with the present calculation, although the temperature dependence of their results creates some uncertainty.

**Negative Ions by Resonance Capture.  $X^-$ .**—Figure 1 shows an ionization efficiency curve for the  $Br^-$  ion from cyanogen bromide. The small resonance peak near zero volts may be due to a small HBr impurity. The main peak has an onset of  $4.1 \pm 0.3$  ev. In the case of the iodide no peak was observed near zero volts, the main peak having an onset of  $2.6 \pm 0.3$  ev. On the other hand the chloride had a large peak at or near zero volts and a second peak with an onset of  $6.7 \pm 0.3$  ev. We are not certain as to the origin of the first  $Cl^-$  maximum.

If the process is represented by

$$CNX \rightarrow CN + X^-$$

the appearance potential can be calculated from

$$A(X^-) = \Delta H_f CN + \Delta H_f X^- - \Delta H_f CNX + E_e + E_{k.e.}$$

For  $E_{k.e.}$  and  $E_e$  zero, the values so obtained are  $-0.04$ ,  $-0.43$  and  $-0.43$  ev. for the chloride, bromide and iodide respectively. This would indicate that the measured values contain from 2.2 to 6.7 ev. excess energy.

**$CN^-$ .**—This ion is formed by the process



The onset for this process is nearly zero volts for the bromide and iodide and about 0.4 ev. for the chloride.

The appearance potential can be calculated from

$$A(CN^-) = \Delta H_f CN^- + \Delta H_f X - \Delta H_f CNX$$

assuming no excess energy is involved in the dissociation. The calculated values are 0.6, 0.0 and

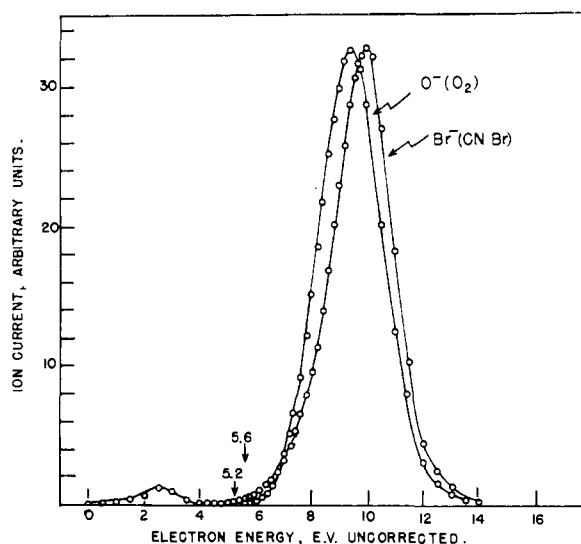


Fig. 1.—Ionization efficiency curve for  $Br^-$  from  $CNBr$ .

$-0.4$  ev. for the chloride, bromide and iodide, respectively. The experimental and calculated values are sufficiently close to indicate that only relatively small amounts of excess kinetic energy can be involved in the dissociation.

### Summary

Appearance potential measurements of both positive and negative ions of the cyanogen halides lead to consistent values for the heat of formation of the  $CN$  radical of 89 kcal./mole and of the  $CN^-$  ion of 15 kcal./mole. Thus the ionization potential of the  $CN$  radical is 337 kcal. (14.6 ev.) and the electron affinity is 74 kcal. (3.21 ev.).

WASHINGTON, D. C.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, KYUSHU UNIVERSITY]

## Effect of Temperature on Ultraviolet Absorption Spectra of Benzoic Acids and its Relation to Hydrogen Bonding

BY MITSUO ITO, HIDEO TSUKIOKA AND SUNAO IMANISHI

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The near ultraviolet absorption spectra of benzoic acids in petroleum ether were measured at various temperatures ranging from  $+100$  to  $-180^\circ$ . At low temperatures absorption bands due to dimers appear at wave lengths greater than those of monomer bands for all the substances investigated. Effect of hydrogen bonding on the absorption spectra of benzoic acid was also studied at low temperatures for the solution systems containing proton donating or accepting molecules. The results show that the direction of spectral shift due to hydrogen bond formation is determined whether benzoic acid behaves as a proton donor or a proton acceptor in hydrogen bonding. The observed spectral shifts are discussed qualitatively.

### Introduction

In a previous paper it was reported that absorption spectra of benzoic acids near 2800 Å. show a remarkable effect of concentration in non-polar hydrocarbon solvents which was interpreted in terms of equilibria between monomer and dimer forms of solute molecules.<sup>1</sup> Hydrogen bonding, through which benzoic acids associate into dimers, is in general a weak binding and its effect on electronic absorption spectra is usually small. To be able to estimate such a small effect, the electronic

(1) M. Ito, *J. Mol. Spectroscopy*, in press.

absorption bands must be sharp enough. Unfortunately, the absorption spectrum of benzoic acid in the region near 2800 Å. is considerably broadened and exhibits only a very vague vibrational structure even with a solution in a non-polar solvent, contrary to the cases of other monosubstituted benzenes which exhibit generally sharp absorption bands.

In order to investigate this apparently small effect of hydrogen bonding on the absorption spectra of benzoic acids, measurements were made at low temperatures by utilizing the fact that