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## THE ABSORPTION SPECTRA, STRUCTURE AND DISSOCIATION ENERGIES OF THE GASEOUS HALOGEN CYANIDES

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### Introduction

Spectroscopic investigations have yielded a great deal of interesting and useful information regarding the nature and strength of binding in diatomic molecules, and it is now desirable to extend studies of this sort to cases of molecules built up of several atoms. Several attempts have been made to do this, but in many instances the results obtained are difficult to interpret in an exact way, since the nature and energy states of the products into which more complicated molecules may dissociate are not known. In order to obtain quantitative information regarding the strength of individual molecular bonds, it seems advantageous to proceed gradually from very simple to more complicated cases, and in particular to choose for study those molecules about whose possible dissociation products we known as much as possible.

For this reason the cyanides seem to be very well suited for study, since the lower energy states of the cyanide radical are well known. Two cyanides have already been investigated: potassium cyanide by Villars,<sup>1</sup> and hydrogen cyanide by Badger and Binder.<sup>2</sup> As the subject of the investigation here described we have chosen the halogen cyanides, because there has been considerable discussion as to the structure of these compounds without any very definite conclusion being arrived at, and because certain inconsistencies in the literature make an independent determination of their heats of formation of interest.

### Experimental Procedure

The substances used in the investigation were prepared as described below. In all cases chemically pure reagents were used.

**Cyanogen Chloride.**—In the preparation of this substance concentrated hydrochloric acid was dropped from a separatory funnel into an all-glass generator containing a solution of potassium chloride, potassium chlorate and potassium cyanide. The gas evolved was condensed in a receiver cooled with ice water. The liquid collected had a slight yellowish green tint which might have been due to the presence of some free chlorine. The liquid was then allowed to evaporate into the absorption cell, which consisted of a Pyrex tube 183 cm. in length, closed at the ends with quartz plates attached by sealing wax. When the absorption spectrum of the gas was photographed immediately after preparation, the chlorine bands as well as bands in the rather far ultraviolet due to cyanogen came out rather strongly. After the gas had stood for some time, these dis-

<sup>1</sup> D. S. Villars, *THIS JOURNAL*, **53**, 405 (1931).

<sup>2</sup> R. M. Badger and J. L. Binder, *Phys. Rev.*, **37**, 800 (1931).

appeared completely. No polymerization occurred even when the gas was kept in the tube for several days.

**Cyanogen Bromide.**—The preparation of this substance was similar to that of the chloride. Potassium bromide and bromate were used instead of the corresponding chlorine compounds. The gas was driven from the solution of these substances and potassium cyanide by heating to 70–80°, and was condensed as a solid in the form of white crystals in a receiver cooled in ice water. These crystals were then sublimed into the absorption cell and the pure solid condensed there could be preserved for over a month without any polymerization being evident. The gas used in the absorption experiments was that in equilibrium with the solid at room temperature, and was confined in an absorption cell 91 cm. in length.

**Cyanogen Iodide.**—In the preparation of this substance pure iodine was resublimed and dissolved in ether to which an excess of mercuric cyanide was then added. After vigorous shaking the solution became colorless, indicating the completion of the reaction. The mercuric iodide which precipitated and the excess mercuric cyanide were removed by filtration. On evaporation of the filtrate cyanogen iodide was obtained, mixed with considerable mercuric iodide. A purification by recrystallization from ether solution, and by sublimation, yielded a product with only a very faint orange tint. The 91-cm. absorption cell was used in this case; but, as the absorption of the gas in equilibrium with solid ICN at room temperature was rather small, it was found necessary to heat the absorption cell, which contained some crystals of the solid, to about 60°. In order to eliminate any absorption of free iodine which might be liberated by the dissociation of the compound, some cyanogen was introduced into the absorption cell. This gas gives rise to a set of discrete bands beyond  $\lambda 2100$ , which are easily identified and were in no way troublesome.

**Optical Apparatus.**—As a source of continuous spectrum in the ultraviolet a conventional hydrogen discharge tube was used. The spectra were photographed with a small Hilger quartz spectrograph. Eastman D-C ortho plates were used, and in order to obtain a greater sensitivity in the ultraviolet they were oiled with a light transformer oil which was found to be especially suitable for the purpose.

### Experimental Results and Discussion

In the case of each gas only continuous absorption was found, and a careful search failed to detect any discrete bands. The spectra of the three compounds are entirely similar except that in the order ICN, BrCN, CICN the absorption regions are displaced toward the short wave side, and the absorption becomes weaker in the same order. In the iodine compound two absorption regions were found, in the other cases only one, undoubtedly for the reason that the analogous second regions were further in the ultraviolet than could be reached by the quartz spectrograph. Since the absorption regions shade off rather gradually on the long wave side (and on the other side as well, where it can be observed) and since the apparent long wave limit shifts toward the red when the depth of absorbing gas is increased, it is not possible to give any definite long wave absorption limit. However, it is certain that absorption extends on the long wave side at least as far as the wave lengths given in Table I.

It is reasonable to assume that as a result of light absorption in the continuum of any of the halogen cyanides, a dissociation of the molecule

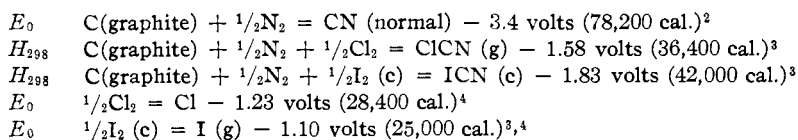
TABLE I  
LONG WAVE LENGTH LIMITS OF THE CONTINUOUS ABSORPTION OF THE HALOGEN  
CYANIDES

Gas	Region a		Region b		Upper limit for dissociation energy (volt-electrons)	
	$\lambda$	$\nu$	$\lambda$	$\nu$	a	b
ICN	> 2900	< 34470	> 2100	< 47600	4.26	5.88
BrCN	> 2450	< 40800			5.05	
CiCN	> 2270	< 44040			5.43	

takes place. This being the case, we may calculate from the long wave limit of the absorption region an upper limit for a dissociation energy of the molecule. Values so obtained are given in the right of Table I. Before discussing the nature of the dissociation products, we must consider the probable structure of the halogen cyanide molecules. As mentioned above there has been considerable discussion in this regard, though particularly relating to the molecules in solution. As regards the gaseous molecules, the similarity of the spectra, and the fact that they fall into a reasonable series, strongly indicates a similarity of structure for the three. In a previous paper<sup>2</sup> it has been shown that the hydrogen cyanide molecule has a linear structure represented by the formula HCN, and that the HNC molecule, if it exists, must be energetically very unstable. Similar but much stronger arguments may be advanced in this case. From a study of the heats of formation of carbon tetrachloride and carbonyl chloride we may estimate the energy of the carbon-chlorine bond to be of the order of 3.5-4.5 volts, while the energy of the nitrogen-chlorine bond is much smaller, say about 2 volts, as may be seen from data on nitrosyl chloride and nitrogen trichloride. Consequently a CINC molecule which would be formed from an excited CN radical, probably that in the <sup>2</sup>II state with 1.78 volts excitation energy, should lie at least 3.3 volts (75,000 cal.) higher in the energy scale than CiCN formed from the normal CN radical. Though CINC should consequently be very unstable, the argument of course does not exclude the possibility that isocyanide molecules may be produced under certain conditions, and may have a relatively long life-time. However, in the case of gaseous iodine cyanide it is known that an equilibrium is readily reached between this gas and iodine and cyanogen. It seems unlikely then that this gas can exist for an appreciable length of time in the unstable form. We shall assume for the time being that all three gases exist in the stable cyanide form, and as will be seen later this assumption is justified by the energy relations.

Since the optical dissociation energies are far too small to account for the splitting of the carbon nitrogen bond, we may conclude that the dissociation products are a CN radical and a halogen atom, one or both of which may be in excited states. We may compare the spectroscopic values with the dissociation energies of the molecules calculated from the chemical

heats of formation, the known energies of activation of the products, etc. The necessary data are expressed by the equations



Unfortunately heat data on BrCN are lacking. Specific heats are also lacking for correcting the chemical heats of formation at room temperature to the absolute zero, but in any case the correction will be small in comparison with the dissociation energies. The heat of sublimation of ICN is not known but we shall probably not be greatly in error if we estimate it at  $-0.4$  volt.

The dissociation energies of ClCN and BrCN into normal halogen atom and normal cyanide radical, and into normal halogen atom and excited CN radical ( ${}^2\Pi$  with 1.78 volts excitation energy), as calculated from the above data are tabulated in Columns 2 and 3, respectively, of Table II. In Columns 4 and 5 are given the spectroscopic values for all three substances.

TABLE II  
DISSOCIATION ENERGIES OF THE GASEOUS HALOGEN CYANIDES

Gas	Dissociation energy			
	From chemical data		From spectroscopic data	
	Products: halogen (normal) + CN (normal)	Products: halogen (normal) + CN* ( ${}^2\Pi$ )	(a)	(b)
ClCN	3.04 volts (74,700 cal.)	4.82 volts (112,000 cal.)	< 5.43 volts	..
BrCN	..	..	< 5.05 volts	..
ICN	2.27 volts (52,000 cal.)	4.05 volts (93,000 cal.)	< 4.26 volts	< 5.88 volts

It is seen that the energy of dissociation into normal products, calculated from the chemical heat of formation, is about what one would expect for the breaking of a carbon-halogen bond, and is much larger than would correspond to breaking a nitrogen-halogen bond. We may conclude that the molecules in their normal state are built from the normal CN radical and normal halogen atom. Since the spectroscopic dissociation energies are much larger than the energy of dissociation into normal products, dissociation by light absorption must result in at least one excited product. Since the lowest excitation energy of the iodine atom is 0.94 volt, it is evident that only one of the dissociation products of ICN can be excited when dissociation takes place as a result of absorption in region (a). The rough agreement between the spectroscopic value and the second chemical value in the table indicates that it is the CN which is excited. This is confirmed by the data on ClCN, since the excitation energy of chlorine is only 0.11 volt. The relatively large discrepancy in this case between the spectroscopic value and the second chemical value is to be explained by the

<sup>3</sup> "International Critical Tables."

<sup>4</sup> J. Franck, *Z. Electrochem.*, **36**, 581 (1930).

weak absorption of this gas, which leads one to estimate the long wave absorption limit relatively farther in the ultraviolet than in the other cases. To make the results strictly comparable it would have been necessary to use a much longer tube of gas than circumstances permitted.

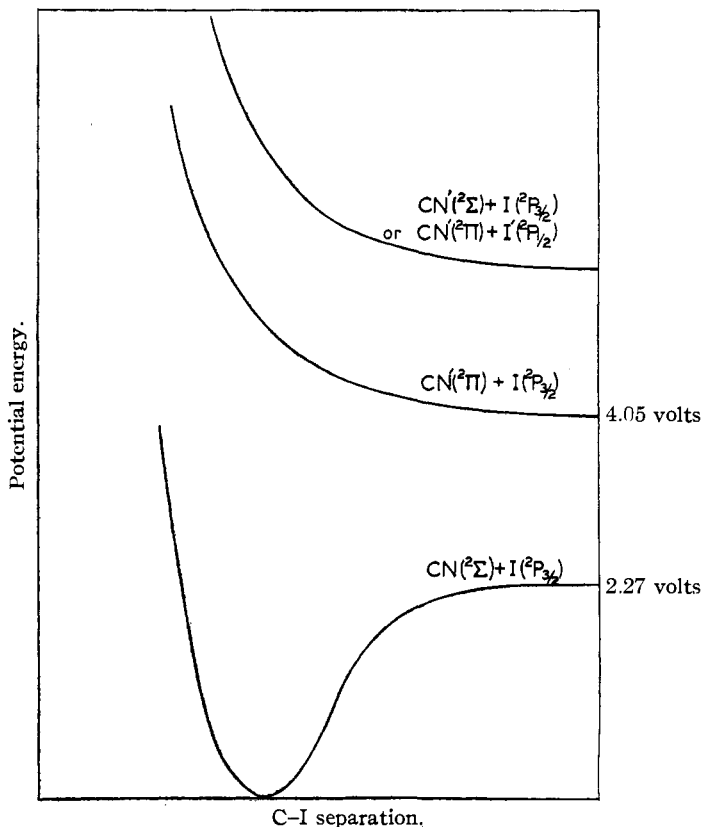


Fig. 1.—Approximate potential energy curves showing the potential energy of the ICN molecule as a function of the carbon-iodine separation, for three electronic states.

It is not possible to decide definitely whether absorption in the region (b) of ICN results in dissociation into an excited iodine atom with 0.94 volt energy and a CN radical ( $^2\Pi$ ) with 1.78 volts energy, or into a normal iodine atom and a CN radical ( $^2\Sigma$ ) with 3.19 volts energy.

Several attempts were made to demonstrate directly the nature of the dissociation products by fluorescence experiments, but unfortunately they were unsuccessful. One might expect that when the gases are illuminated with light of a wave length lying in the region of continuous absorption one should obtain the red cyanogen bands in fluorescence. The conditions are,

however, very unfavorable for obtaining such a fluorescence. The absorption, even at the maximum of the continuum, is not very strong and if one uses sufficient gas pressure to obtain appreciable absorption one should expect the fluorescence to be almost completely quenched. Some experiments were made in which ICN gas was illuminated with a mercury arc, and some in which BrCN was illuminated with a cadmium arc. No fluorescence was visible to the eye even under very satisfactory conditions as to a black background, etc. In an investigation using a very fast glass spectrograph and dicyanin plates it was found that any fluorescence present was weaker than stray light which was excluded as far as possible.

As noted above the chemical dissociation energies show that the halogen cyanide molecules in the lowest energy state are formed from normal halogen atom and normal cyanide radical. The nature of the absorption spectra is strong indication that in the two next higher excited electronic states we have a case of repulsion at all distances, or possibly a very small minimum in the potential energy curve at a relatively large distance of separation of halogen atom and cyanide radical. The probable state of affairs is represented in Fig. 1.

This is indeed what one should expect. The normal cyanide radical, since it is formed from a normal nitrogen atom and a carbon atom in the  $^5S$  state (tetravalent),<sup>5</sup> is capable of forming one shared electron pair bond between the carbon atom and some other atom and radical. The  $^2\Pi$  cyanide radical, on the other hand, is formed from the  $^3P$  carbon atom (divalent) and one should expect no tendency for molecule formation when an atom is brought up on the carbon side of this radical.

### Summary

1. The absorption of the gaseous halogen cyanides has been investigated in the ultraviolet. Regions of continuous absorption only were found, with the following long wave length limits: ClCN,  $\lambda > 2270$ ; BrCN,  $\lambda > 2450$ ; ICN,  $\lambda > 2900$  and  $\lambda > 2100$ .

2. The similarity of the spectra and their relation to each other suggest a similar structure for all three molecules.

3. Consideration of thermochemical and spectroscopic data together shows that in the normal state the halogen cyanide molecules are built from normal halogen atoms and normal cyanide radical, and in the first excited electronic state from normal halogen atom and an excited CN radical in the  $^2\Pi$  state. The structures are probably those represented by the formulas: ClCN, BrCN, ICN.

4. The thermochemical heats of formation of the ClCN and ICN seem to be in substantial agreement with the spectroscopic values.

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<sup>5</sup> Heitler and Herzberg, *Z. Physik*, **53**, 52 (1929).