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Spectroscopic Measurements of Gaseous CN

I. Dissociation in the Electric Discharge

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Free CN radicals in the gaseous state are formed in the electric discharge through cyanogen. By the use of a very intense low pressure spark as a background the 0,0 and 1,1 bands of the ${}^{2}\Sigma \rightarrow {}^{2}\Sigma$ transition of CN have been observed in absorption at short intervals of time after the end of this discharge. The intensities of the lines of the bands were measured by means of microphotometer traces of the spectra and of the characteristic curve of the photographic plate. They were corrected for the incomplete resolution of the spectrograph, Relative concentrations of CN were calculated from the sums of the intensities of the lines. The rate of disappearance of CN after the end of the discharge was studied and found to be the same over a large range of pressure and dilution with argon. A mechanism is proposed to account for this. In all cases the disappearance was

INTRODUCTION

 $\mathbf{F}_{molecular}^{ROM}$ the known emission spectra of diatomic molecules their energy levels, electron configurations, and relative transition probabilities have been derived. Very little information about their lifetime, properties, or absolute concentrations and absolute transition probabilities has been found. While the properties of the stable molecules are well known, those of most free radicals like CN and NH are not. As shown by Oldenberg,¹ a study of the absorption spectra of the latter constitutes a valuable method for investigating them. The presence in the sun of OH, NH, CN, and CH is indicated by their absorption spectra,² but of these only OH has previously been studied carefully in the laboratory at room temperatures.¹ SH has been observed by Lewis and the author,3 and some of the aluminum halides have been found in absorption by Miescher⁴ at slightly higher temperatures. While the strongest absorption of most stable molecules lies in the far ultraviolet, that of most exponential with a mean half-life of 11 milliseconds. The half-life of the first excited vibration state was 3 milliseconds, during which time about 10,000 collisions occurred. By dilution of the cyanogen in the discharge tube with argon until the CN bands were no longer visible the partial pressure of CN could be calculated on the assumption that near this point all the cyanogen present was observed in the form of CN. The minimum detectable pressure of CN was of the order of 2×10^{-6} mm. The absolute f value of the ${}^{2}\Sigma \rightarrow {}^{2}\Sigma$ transition is 0.026 (±0.006). By using the corresponding absolute absorption coefficient and the observed temperature distribution in a carbon arc the partial pressure of CN present in an arc is calculated to be of the order of 10 mm,

common free radicals occurs in the visible or near ultraviolet. Thus spectroscopic investigation can be used to supplement chemical methods where the latter are weakest.

The violet ${}^{2}\Sigma \rightarrow {}^{2}\Sigma$ system of CN, the 0.0 band of which lies at λ 3883, is the resonance system of this molecule, and its absorption should constitute a sensitive test for the presence of free CN. Heretofore this band has been observed in absorption only as a result of thermal dissociation in the sun and stars² and in the laboratory.⁵ In the present work its lifetime, absorption coefficient, and other properties are studied at room temperature by means of its absorption spectrum. The method of observation is based on that used by Oldenberg in studying the lifetime of OH. The fundamental steps are:

- (1) Formation of the radicals by an electric discharge;
- (2) Passage of a brief flash of white light through the absorption tube immediately after the discharge;
- (3) Dispersion of the white light in a spectrograph of high resolving power;
- (4) Measurement of the amount of light absorbed by the lines of the CN band spectrum.

As no source has been found bright enough to allow this measurement to be made with a

^{*} Now with Standard Oil Development Company, Eilzabeth, New Jersey.

¹O. Oldenberg, J. Chem. Phys. 3, 266 (1935).
²H. N. Russell, Astrophys, J. 79, 317 (1934).
³M. Lewis and J. U. White, Phys. Rev. 55, 894 (1939).
⁴E. Miescher, Helv. Phys. Acta 9, 693 (1936).

⁵G. B. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. 1, 432 (1933).



FIG. 1. The vacuum system.

single flash of light, it is necessary to repeat the cycle many times and integrate the spectrum on a photographic plate.

Apparatus

The apparatus consisted of an absorption tube and vacuum system for flowing C_2N_2 through it continuously, a radiofrequency oscillator fitted with electrodes to pass a discharge through the absorption tube, a source of continuous radiation, a 21-foot concave grating spectrograph, and a synchronous motor driving the switches and an optical shutter.

The cyanogen was prepared in an all-glass system by heating Merck's C.P. grade $Hg(CN)_2$ in an electric furnace to 400°C, after a preliminary baking in vacuum at a lower temperature to drive off water vapor and adsorbed air. The cyanogen generator was specially designed with a movable heating coil and outlets at each end to reduce the losses from the sublimation of the $Hg(CN)_2$. The cyanogen thus made had a vapor pressure of 9.5 mm over dry ice which is so close to the 9.6 mm observed by Perry and Bardwell⁶ at this temperature that the gas was

used without further purification. The main part of the discharge tube was 70 cm long and 15 cm in diameter. Since cyanogen polymerizes in an electric discharge to dark brown, solid paracyanogen, special precautions had to be taken to keep the windows free of it. They were mounted on smaller tubes sealed on each end of the large one and further protected by a continuous flow of cyanogen from them toward the middle of the tube. The cyanogen was kept in a reservoir of large glass bulbs, from which its flow was regulated by a stopcock, and finally reclaimed over liquid air. As it was desired to flush out the discharge tube completely and remove all products of the preceding discharge between each cycle, a very rapid pumping system was required. A large mercury pump, backed by a Megavac pump, was able to flush out the discharge tube three times between each cycle at the lowest pressures used and 1.2 times at the highest. Pressures were read on a McLeod gauge and rates of flow on a previously calibrated pressure difference gauge across a constriction. By putting a dry-ice bath on a coil of glass tubing the mercury vapor was at first removed from the incoming gas. As it was latter found to have no effect, the coil was removed. After every 1000 cycles the paracyanogen was burned

⁶ J. H. Perry and D. C. Bardwell, J. Am. Chem. Soc. 47, 2629 (1925).

out of the discharge tube by a discharge through oxygen at low pressure. The exhaust from the pumping system was led at a pressure slightly below atmospheric to an aspirator where any cyanogen was washed down the drain with a large amount of water. Fig. 1 shows a diagram of the vacuum system.

The source of the background radiation was the Lyman continuum of a low pressure spark, which gave exposures about three hundred times as fast as the next best alternative, a tungsten strip filament bulb. Its characteristics, amply described in the literature,⁷ are ideal for taking a series of rapid snapshots. A $1-\mu f$ condenser was charged to 15,000 volts by a Thordarson transformer with a completely insulated secondary and kenotron rectifier tube and discharged through a 2-mm quartz capillary about 3 cm long. Breakdown was regulated by a tickler electrode in an auxiliary spark gap in series with the discharge tube. To make this reproducible the two sides of the auxiliary gap had to be held at equal and opposite potentials relative to the grounded tickler in the center. A high resistance with a grounded center across the condenser accomplished this and, with a milliammeter in series, served as a voltmeter.

The discharge that formed the CN radicals in the absorption tube was made with a radio-

⁷ J. A. Anderson, Astrophys. J. 75, 394–406 (1932).

frequency oscillator⁸ connected by a resonant transmission line to two large iron electrodes on each side of the absorption tube. These were bent around until the discharge appeared uniform throughout the tube. The oscillator was run with 60-cycle a.c. on the plate, and keyed by cutting off the filament power supply during the dead half-cycle. The water cooling leads were arranged so that when the main power supply was cut off the filament became much more positive than the grid. A milliameter in the d.c. power supply gave a ballistic reading of the intensity of each flash of the discharge. While it would not give quantitative relations without further calibration, it would give qualitative indications and show when discharges were of equal intensity.

The oscillator and spark discharge were coordinated accurately to a thousandth of a second by a switching system driven by a synchronous motor. In each circuit there were two switches in series, one on a fast and one on a slow shaft. The oscillator switches were arranged to pass one half-wave of 60-cycle a.c. every twenty seconds. The switches in the other circuit acted through a Ford ignition coil to break down the spark gap a short time later. The time interval between them was varied by adjusting the angle between the switches in the two circuits. An

⁸ D. H. Sloan, R. L. Thornton, and F. A. Jenkins, Rev. Sci. Inst. 6, 75 (1935).



FIG. 2. Wiring diagram.

optical shutter protected the plate from emission during the discharge. As a synchronous motor will run equally well on either sense of the current, a neon bulb was operated on half-wave rectified a.c. near a white mark on the switch to show by the stroboscopic effect in which position the motor was running (see Fig. 2).

As Oldenberg has pointed out,1 very high resolving power is needed to observe faint, narrow absorption lines like the individual ones in a band. The spectrograph was a 21-foot aluminum concave grating ruled 30,000 lines to the inch and giving a dispersion of 4.4 cm^{-1} per millimeter at λ 3883 in the second order. Its theoretical resolving power of 330,000 is about equal to the Doppler half-intensity width of the lines of the violet CN bands under the conditions here used. Actually the observed resolving power was about a third of the theoretical. Under these conditions only the areas of the lines could be measured directly, not the maxima of the absorption coefficients. A cylindrical lens of crystalline quartz placed in front of the plate as recommended by Oldenberg⁹ increased the intensity by a factor of fifteen.

All the exposures necessary to determine a rate constant under any set of conditions were put on the same plate. Also on the same plate there was put an exposure through a step weakener transmitting known fractions of the incident light. The step weakener was made of

⁹ O. Oldenberg, J. Opt. Soc. Am. 22, 441 (1932).

sputtered platinum on quartz and calibrated with a quartz photo-cell and monochromator. The weakener was used directly in front of the plateholder. Eastman 33 plates were used throughout and developed for five minutes in M-Q developer. Microphotometer traces of the spectra and of the calibration marks on each plate were made on a Zeiss recording microphotometer. The amounts of blackening corresponding to the different steps of the step weakener were measured on each plate and plotted against its known transmission intensities to get calibration curves for the different plates. The blackenings of the different lines and corresponding backgrounds were similarly measured and corrected to intensities by the calibration curve for the particular plate. The fraction of the incident light apparently absorbed by each line was obtained by dividing the corrected intensity of the line by that of the background. Several test calibrations that were made on one plate with the spark source at different sparking rates and with a tungsten filament bulb indicated that there was no trouble from the intermittency effect in this experiment. The probable error in the photometric measurements is of the order of ten percent.

MEASUREMENTS

A preliminary experiment with a d.c. discharge gave strong absorption of the CN band in the first order as explained in a previous communi-

TABLE I. Half-life of CN radicals in milliseconds as a function of pressure and dilution with argon.

	DILUTION WITH ARGON										
Pressure MM	Pure	9:1	99 : 1	999 : 1	9999	: 1 99,999 : 1					
0.15	10										
0.475	10, 8	11.5, 7.5			12	2					
1.5	11	13, 10			12	2					
4.75			9	15.5							



FIG. 3. Successive CN absorption spectra.

cation.¹⁰ It is now clear that the peculiar rate reported there was caused by a very short halflife coupled with the insufficient resolution in the first order of the grating and emphasized by the great intensity of the absorption. In a second preliminary experiment a radiofrequency discharge was used, but the contents of the discharge tube were only changed after every 500 flashes instead of after every flash. Although the correction for poor resolving power, derived later, was not applied, the weaker absorption made it less necessary. The order and rate of the disappearance were calculated approximately and found comparable to the final more accurate results.

On each plate of the final experiment, made with the apparatus described above, there were a number of exposures taken at intervals of 0.005 second after the end of the discharge. They were taken irregularly, rather than in the order of increasing time, to find out whether there was any effect of running the tube after it had been cleaned with oxygen. None was found. On some of the plates exposures were made with two different discharge intensities, and the rates for the two calculated independently. Plates were

taken under a large variety of conditions of pressure and dilution where a glow discharge could be maintained and the CN absorption spectrum observed. The intervals of dilution were factors of ten, of pressure the square root of ten. Twenty-two such plates were taken at all combinations of 0.15, 0.475, 1.5 and 4.75 mm total pressure and dilutions of zero, 9:1, 99:1, 999:1, 9999:1, and 99,999:1 except pure cyanogen at 4.75 mm and the lowest pressure and greatest dilution. All 22 of these showed visible absorption on the first exposure, but only on 16 does it last long enough to permit a measurement of its rate of disappearance. All but these 16 spaces are crossed off in Table I. and in the 9 of the 16 for which the calculations were made there are shown the corresponding half-lives of the CN radicals.

A typical series of exposures, with the times when they were taken, is shown in Fig. 3. As the overlapping of the lines of the P branch near the band head makes accurate measurements of their intensities impossible, only the first 18 lines of the R branch were used in the calculations.

The light source was so much more intense than the discharge that formed the CN radicals

¹⁰ J. U. White, J. Chem. Phys. 6, 294 (1938).

that their absorption spectrum could be observed at any time during the discharge without appreciable trouble from emission. A few exposures were taken during the discharge, including two at the two lowest partial pressures where absorption was observed. One of them shows that during the discharge there was about four times as much CN present as immediately after it. The lines of the weaker, 1,1 band, which were also observed in absorption on all the plates immediately after the discharge where the 0.0 band was intense, were measured and reduced in the same way as those of the 0,0 band.

The measurement of the areas of the absorption lines needed for the correction for incomplete resolution is the least accurate procedure in the experiment. As it was impractical to do this for every line, the areas and maxima of about 40 representative lines in different parts of the band were measured on large scale microphotometer traces and corrected with the calibration curve of the plate. The graph relating the two is shown in Fig. 4. It was found that for the first 18 lines the spin doublet separation was so much smaller than the effective resolving power that the ratio of area to maximum was constant. Beyond this point it began to increase. This graph was used to convert all the other maxima to areas.

CALCULATIONS

Correction for incomplete resolution

In the case of complete resolution of the line form the apparent fraction of light absorbed. which can be measured directly, is the true



FIG. 4. Relation between area and maximum intensity of the lines.

maximum fraction, for incomplete resolution it is always less than that. However, as the quantity of light absorbed is unaffected by the resolution, it can be measured directly in either case. It is then necessary to calculate the relation between the amount of light absorbed by a line and its true absorption coefficient. The methods of Frost¹¹ and of van Wijk¹² for measuring relative concentrations cannot be used in the case of CN because they depend on comparing two lines of equal intensities and the same line form. The unresolved spin doubling of CN makes every line different, even though all appear the same. Neglect of this results in serious errors.

When light passes through a thin layer of an absorbing mixture, a certain fraction of its intensity, called the absorption coefficient, a, is removed, per unit thickness traversed. If x is the thickness of the absorbing layer, I_0 the initial intensity of the light, and I the intensity at any other point,

$$I = I_0 e^{-ax}$$

The quantity, a, is a characteristic for any material and proportional to the amount of it present. The total amount of light absorbed, A, is obtained by integration with respect to frequency.

$$A = \int_0^\infty [I_0(\nu) - I(\nu)] d\nu = I_0 \int_0^\infty (1 - e^{-a(\nu)x}) d\nu,$$

assuming $I_0(v)$ to be constant. While the quantity, A, could be measured directly for the different lines in the band, it is more convenient to measure the maxima of the lines and convert them to areas as explained above. If the true form of the absorption line is known, its maximum can be calculated from A. At pressures below five millimeters and at room temperatures pressure broadening, Stark effect, and natural breadth are all negligible compared to Doppler broadening. The spin doublet separation is theoretically proportional to $K+\frac{1}{2}$. These two facts, together with the theoretical intensity ratios of the doublets, have been assumed to give the true forms of the doublets. The problem then becomes

¹¹ A. A. Frost, D. W. Mann, and O. Oldenberg, J. Opt. Soc. Am. 27, 147 (1937). ¹² W. R. van Wijk and A. J. van Koeveringe, Proc. Roy.

Soc. A132, 98 (1931).



FIG. 5. Relation between absorption coefficient and amount of light absorbed.

one of converting the total amounts of light absorbed to the true absorption coefficients under the above assumptions. If μ =molecular weight, R=gas constant, T=absolute temperature, c=velocity of light, and ν =frequency, the form of a line broadened by the Doppler effect is given by

$$a(\nu) = \exp\left((-\mu/2RT)(c^2/\nu^2)(\nu-\nu_0)^2\right).$$

If b is the relative intensity and $\nu_1 - \nu_2$ the separation of a doublet, the form of the absorption coefficient of a double line becomes

$$a(\nu) = a \left[\exp\left((-\mu c^2/2RT\nu^2)(\nu - \nu_1)^2 \right) + b \exp\left((-\mu c^2/2RT\nu^2)(\nu - \nu_2)^2 \right) \right].$$

The total amount of light absorbed by this doublet, in absolute frequency units, is

$$A = I_0 \int_0^\infty \left[1 - \exp\left(-ax \left\{ \exp\left(-\frac{\mu}{2RT} \frac{c^2}{\nu^2} (\nu - \nu_1)^2\right) + b \exp\left(-\frac{\mu}{2RT} \frac{c^2}{\nu^2} (\nu - \nu_2)^2\right) \right] \right] d\nu$$

If we set

$$s = (2RT/\mu)^{\frac{1}{2}} v_0/c$$

and change variables by

$$v = sy + (v_1 + v_2)/2,$$

 $r = (v_2 - v_1)/2s,$

this becomes

$$A = I_0 s \int_{-\frac{\nu_2 + \nu_1}{2s}}^{\infty} [1 - \exp -xa\{e^{-(y+r)^2} + be^{-(y-r)^2}\}] dy.$$

If the absorption is very weak this can be simplified and integrated directly.

$$A = I_0 sax \sqrt{\pi(1+b)}.$$

By means of the doublet separation of 0.037A for line 28 given by Birge¹³ and the intensity

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¹³ R. T. Birge, Astrophys. J. 55, 280 (1922),



FIG. 6. Absorption coefficient against initial energy level.

formulas from Jevons¹⁴ the values of, s, r, and b were calculated for the first eighteen lines of the R branch of the 0,0 band in the ${}^{2}\Sigma \rightarrow {}^{2}\Sigma$ transition.

$$s = 0.0395$$
, $r = 0.115(K + \frac{1}{2})$, $b = \frac{2K + 1}{2K - 1}\frac{K - 1}{K + 1}$

where K is the rotational quantum number of the higher level of the transition. The integral was evaluated numerically for values of ax=0.5, 1, 2, 3, 4, and 6 for each of the lines K=2, 4.7, 10, and 20.5. Curves of A/I_{0S} were plotted against ax for these lines, and those for the intermediate ones were interpolated between them. The correction to the integral for temperatures other than 300°K was calculated to be less than 1 percent for every 12°. It was neglected. The curves are shown in Fig. 5 as functions of A/I_{0S} , and of the observed maxima of absorption.

Calculation of relative concentrations

Under the conditions of very weak absorption, the amount of light absorbed is directly proportional to the number of absorbing molecules. For stronger absorption the linear relation with concentration holds only for the integrated absorption coefficient, B, rather than for the amount of light removed. The absorption coefficients found above were integrated over all frequencies and summed over all the lines of the R branch of the band. The first 18 lines were

¹⁴ W. Jevons, Report on Band Spectra, p. 137.

measured directly; the others were predicted by the Boltzmann distribution at the observed rotational temperature. The final quantity, $\sum_{\kappa} B$, is a direct measure of the amount of CN present in the tube. Fig. 6 shows the logarithm of each absorption coefficient divided by its *i* factor plotted against the energy of the initial level of the line. The slope of this curve equals -1/T. The rotational temperatures found in this way varied from 350°K at the end of the discharge down to 320°K after a hundredth of a second.

RESULTS

Reaction kinetics

The mechanism of the disappearance of the CN radicals after their formation in the discharge has been studied in detail. Concentrations were measured as functions of time over a large range of pressure and dilution. In all cases the reaction was found to be first order, i.e., the rate of disappearance was proportional only to the concentration of CN present. Fig. 7 shows a graph of the averages of the points from several plates plotted against time on semi-log paper to find out if there is any departure from the first-order rate law. The unit of concentration is the partial pressure of CN as found below. There



FIG. 7. Mean disappearance of CN concentration.

was no dependence on total pressure or on partial pressure of cyanogen. There was a qualitative relationship with the intensity of the discharge forming the CN; the more vigorous the discharge, the more rapid the disappearance. The longest observed lifetime was 1/15 second, the mean half-life 11 milliseconds. The half-life as a function of total pressure and dilution with argon is shown in Table I. The probable errors in the table are of the order of one millisecond. The intervals of pressure and dilution were so chosen that the partial pressure of cyanogen remains constant on moving diagonally down to the right in the table. In the cases where two discharge intensities were used, both half-lives are given, the one corresponding to the more intense discharge coming first.

The conceivable reactions by which a radical might disappear are: (1) direct recombination to cyanogen; (2) addition to cyanogen; (3) reaction on the walls limited by the rate of diffusion to them; (4) reaction on the walls limited by the wall area; (5) ionization by loss or addition of an electron; (6) reaction with some product formed during the discharge. The first four of these are each impossible, because: (1) the reaction is not second order in CN; (2) the reaction is invariant to the partial pressure of

 TABLE II. Appearance potentials, excitation potentials, and relative abundances of particles present in the discharge.

PARTICLE	Appearance Potential in Volts	Relative Abundance	Excitation Potential in Volts	
$\begin{array}{c} C_2 N_2^+ \\ C N^+ \\ C_2^+ \\ C N^+ \\ C N \\ A^+ \\ A \end{array}$	14.1 21.3 18.6 19.8 6.0 15.5	3.4 0.7 0.2 0.1	3.2, 1.3 11.5	

cyanogen; (3) the reaction is invariant to the total pressure; (4) the reaction chamber is so large that the diffusion coefficient would have to be about 50 times that of nitrogen to account for the observed half-life on this basis.

Number (5) does not disagree with any of the observed evidence. As the CN radical resembles a halogen atom electronically, it is practically certain not to lose an electron outside of a discharge. It might, however, pick up a free electron or even remove one from some other neutral molecule. The presence of enough free electrons to account for the disappearance for more than 0.001 second is impossible. If electrons are being removed from some molecule, the observed rate should be pressure dependent, and the molecule must be present in equal quantities in the cyanogen and in commercial argon. Thus the last mechanism is the only one remaining.

Number (6) is in agreement with the observed

TABLE III. Ratio of intensities of 0,0 to 1,1 Band for different pressures and dilutions.

PRESSURE MM	Pure	9:1	99:1	999 : 1	9999 : 1
0.15 0.475 1.5 4.75	0.088 Trace Trace	0.18 0.081	0.49 0.24	0.22	0.42 0.26

increase in rate with discharge intensity and with the findings of the two preliminary experiments described above. It explains the more rapid rate found in the first experiment using a directcurrent discharge instead of radiofrequency to produce the dissociation. It can be further limited by the results of the second, when the gas in the discharge tube was only changed every 500 flashes. As the rate of disappearance was then about the same, the only conclusion is that the reaction involved an ion that subsequently was neutralized between flashes. Any reasonable mechanism must give the proper end product, paracyanogen, when all the reactions are completed. A mechanism that meets all these requirements can be built on a theory of the condensation of the radicals on active centers of complex ions formed in the discharge. The ions known to occur in a discharge through cvanogen,¹⁵ along with their ionization potentials, relative abundances, and other useful data, are given in Table II. The first step is the formation during the discharge of a complex ion by the addition of a CN radical to one of those in Table II. As the most abundant of these is the only one that will give a polymer of cyanogen on neutralization of the addition product, the

¹⁵ J. T. Tate, P. T. Smith, and A. L. Vaughan, Phys. Rev. 48, 525 (1935).

indicated first step is

$$CN + C_2N_2^+ \rightarrow C_3N_3^+.$$

The amount of $C_2N_2^+$ formed in a weak discharge through cyanogen is independent of the pressure for the same applied voltage. The failure to observe any emission spectrum of argon indicates that even at considerable dilution most of the positive current was being carried by cyanogen ions. Therefore down to the limit of observation of strong absorption by CN radicals one should expect about the same number of $C_2N_2^+$ ions to be formed.

The density of ions needed to carry the current is very much less than the concentration of cyanogen put in the tube, even at the greatest dilutions where rate measurements could be made. If each of the ions formed adds a CN by the equation above, at the end of the discharge there is always about the same number of complex ions left in the tube. They are so large that they do not diffuse rapidly to the walls, but stay in the gas. The observed disappearance of the CN radicals after the discharge is by a chain of successive additions to these complexes:

$$C_3N_3^++CN \rightarrow C_4N_4^+$$

 $C_4N_4^++CN \rightarrow C_5N_5^+$, etc.

The complexes formed should have enough vibrational and rotational energy levels to absorb the excess energy in the collisions in the absence of any third bodies. This mechanism is in complete harmony with the work of Hogness and Liu-Sheng T'sai¹⁶ on the photopolymerization of cyanogen. From the quantum yield in the absence of ions they postulated an addition of CN to a cyanogen molecule. The failure to observe this reaction in the present work only indicates that it is very slow compared to the addition to the ion.

Persistence of vibration

The distribution of the CN radicals in the rotation levels of the ground state is about what is predicted by the Boltzmann theory. There is a small temperature inhomogeneity in the lowest levels, but it is not large enough to be very significant. The case of vibration is entirely



FIG. 8. CN absorption against partial pressure of cyanogen.

different. In equilibrium at 330°K, 1/8000 of the radicals should be in the first vibration level. Actually at the end of the discharge an appreciable fraction has been observed in this state in all cases. The fraction is larger at low pressures and large dilutions. In one case the band still remained with measurable intensity 5 milliseconds after the discharge. From this observation the half-life of the vibrating state was calculated to be 3 milliseconds, or one-fourth that of the ground state. The pressure dependence shown in Table III indicates that some of the excited radicals are being reduced to the ground state by collisions, as well as being destroyed completely. During a half-life the radicals suffer about 10,000 collisions with argon atoms. This confirms predictions of the persistence of vibration from the increase of the velocity of sound at high frequencies and the work of Dwyer¹⁷ on iodine vapor. The persistence of the vibrations is naturally dependent on the nature of the gas present. In commercial argon they last about ten times as long as in pure cyanogen.

Absolute concentrations and f values

When the cyanogen in the discharge tube was diluted with argon, the intensity of the CN spectrum remained about constant for a while, then fell off slowly, and finally disappeared quite suddenly. A series of measurements of the absorption intensity near the point of disappearance were taken, some during the discharge and some immediately after it. The relative concentrations, $\sum B$, calculated from them are shown in Fig. 8 as functions of the partial pressure of

¹⁶ T. R. Hogness and Liu-Sheng T'sai, J. Am. Chem. Soc. 54, 123 (1932).

¹⁷ R. J. Dwyer, J. Chem. Phys. 7, 40 (1939).

cyanogen present. The graph of those after the discharge against the partial pressure of cyanogen remains about level until the dilution is 10,000: 1, when it falls off sharply but does not pass through the origin. The graph of those during the discharge is parallel to the other but displaced to lower concentrations. The final slope of the two curves is taken as a limiting relation between the partial pressures of cyanogen and CN. The latter must be less than or equal to what would be obtained if all the cyanogen present were dissociated to CN. If the dissociation had been caused by a much shorter and more intense discharge, the points could be corrected back to zero time, when they should lie on a line through the origin. Although this correction could not be made completely, the graph during the discharge shows a large improvement over the other. If it could be made the fraction dissociated would be found to increase regularly with dilution until it approached and flattened out at a limiting value. If we take the final slope of the two graphs as the best value and remember that a molecule of cyanogen dissociates to two CN radicals, the partial pressure of CN in millimeters is $(0.0075/x)\sum_{K}B$ for room temperatures, where, if the absorption is weak, $\sum_{K} B/I_0 x$ is the total amount of light absorbed per centimeter by the R branch of the band. This must be corrected for the number of molecules in higher vibrational levels. At these pressures and dilutions the ratio of the intensities of the 0,0 and 1,1 bands, obtained from Table III, was 0.45. Dividing by 0.87, the ratio of the relative probabilities of these transitions,¹⁸ the ratio of the populations of these levels is 0.52. If the vibrational levels are populated according to an exponential distribution with 0.52 as the ratio of the second to the first, the total population is 2.1 times that of the ground level. Dividing by this, the partial pressure of CN in millimeters is

$$P_{\rm CN} = \frac{0.0035}{x} \sum_{\kappa} B.$$

All the absolute concentrations have been calculated with this limiting figure. The question of how close to the limit the dissociation actually is will be discussed in a later paper, where it will

¹⁸ L. S. Ornstein and H. Brinkman, Proc. Amsterdam Acad. **34**, 1 (1931).

be shown that the dissociation is almost complete.

For very weak absorption the total light removed by a single line in cm^{-1} is

$$A = I_0 sax \sqrt{\pi} = B.$$

In terms of the total absorption per cm of the R branch of the band,

$$A = 0.0081 \frac{I_0 i e^{-\epsilon/kT}}{x} \sum_{K} B,$$

where ϵ is the energy of the initial level of the particular line considered. The total absorption can also be expressed in the form given by dispersion theory. Korff and Breit¹⁹ give as the formula for the same quantity,

$$A = \frac{\pi F_s e^2}{mc^2} I_0,$$

where e is the charge on the electron, M its mass, and F_s the number of dispersion electrons per cubic centimeter. If we eliminate A, the density of dispersion electrons for each line is

$$F_0 = 9.2 \times 10^9 \frac{i e^{-\epsilon/kT}}{I_0 x} \sum_{\kappa} B.$$

The density of molecules causing this line is the total density present times the fraction in the proper state to absorb it. The density under standard conditions is 2.70×10^{19} molecules/cc, which corresponds to 2.94×10^{16} at 330° K and 1 millimeter pressure. The number in any state is

$$N = 2.94 \times 10^{16} p \frac{(K+1)e^{-\epsilon/kT}}{\sum_{K} (2K+1)e^{-\epsilon/kT}}$$

where p is in millimeters.

$$N = 8.4 \times 10^{11} \frac{\sum B}{x} (K+1)e^{-\epsilon/kT}.$$

The absolute f value is defined as the number of dispersion electrons per molecule for a particular line.

$$f = \frac{F_s}{N} = 0.012 \frac{K+1}{K+\frac{1}{2}}$$
$$= 0.012(\pm 0.003)$$

¹⁹ A. Korff and G. Breit, Rev. Mod. Phys. 4, 471 (1932).

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for large values of K. The f value for the whole band including the P branch is twice this. f=0.022. For the whole ${}^{2}\Sigma \rightarrow {}^{2}\Sigma$ transition including the 0.1 band with a relative probability of 0.16^{15} , $f = 0.026 \ (\pm 0.006)$. As this is based on the upper limit for the concentration of CN, it is only a lower limit for the f value. This value should be compared with 0.00013 found by Oldenberg²⁰ for OH. It agrees quite well with Mulliken's²¹ prediction based on absorption in the sun that transition probability of the violet CN band system is about a thousand times greater than that of the OH system. The value may also be compared with that for the D lines of sodium, f = 99.7 percent.

Application to carbon arc

The absolute absorption coefficient can also be expressed in terms of a mean collision cross section. Thus light of the proper frequency passing through a cloud of CN radicals at room temperature is half-absorbed if each photon passes within 25A of a radical in the proper state to absorb it. Considering only one molecule and light of the proper frequency with respect to its motion the radius of absorption is of the order of ten times this.

In the ordinary carbon arc the CN bands are observed to have a different rotational temperature in the core and the outer part. If much CN

were present, the radiation from the core would all be absorbed in the outer part. Lochte-Holtgreven and Maecker²² have found a bend in the temperature curves for the cores corresponding to this effect. If the light in their case is assumed to be half-absorbed by a layer three millimeters thick, allowing a factor of five for the difference in line widths, there must be 8×10^{13} radicals per cc absorbing the most intense lines. Adding for all the rotation and vibration levels there must be a total of about two hundred times this, or 2×10^{16} radicals per cc in the arc. This corresponds to a partial pressure of about $\frac{1}{2}$ millimeter at room temperatures or 10 millimeters at the temperature of the arc.

In conclusion I should like to mention the possible errors in this work. All parts of the apparatus were carefully designed and constructed, and whenever an improvement was thought possible, they were rebuilt. By stroboscopic tests the timing was found to be correct to better than a thousandth of a second. The probable photometric errors were of the order of ten percent. While undetected variations in the discharge through cyanogen may have introduced small numerical errors, they cannot have been large enough to affect the nature of the conclusions. The greatest uncertainty, which lies in the assumption of complete dissociation of the cyanogen to CN at very great dilution, will be considered in detail in a later paper.

²⁰ O. Oldenberg and F. H. Rieke, J. Chem. Phys. 6, 439 (1938). ²¹ R. S. Mulliken, Astrophys. J. **89**, 283 (1939).

²² W. Lochte-Holtgreven and H. Maecker, Zeits. f. Physik 105, 1 (1937).