

The Absorption Spectra and Dissociation Energies of Cyanic Acid and Some Isocyanates

ShoChow Woo and TaKong Liu

Citation: *The Journal of Chemical Physics* **3**, 544 (1935); doi: 10.1063/1.1749723

View online: <http://dx.doi.org/10.1063/1.1749723>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/3/9?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Dissociation of multiply ionized isocyanic acid through electron impact](#)

J. Chem. Phys. **120**, 123 (2004); 10.1063/1.1630310

[Vibrational spectroscopy and intramolecular energy transfer in isocyanic acid \(HNCO\)](#)

J. Chem. Phys. **110**, 10850 (1999); 10.1063/1.479026

[Microwave spectra of molecules of astrophysical interest X. Isocyanic acid](#)

J. Phys. Chem. Ref. Data **5**, 79 (1976); 10.1063/1.555531

[The Molecular Structure of Isocyanic Acid from Microwave and InfraRed Absorption Spectra](#)

J. Chem. Phys. **18**, 990 (1950); 10.1063/1.1747827

[The Absorption Spectra and Dissociation Energies of Cyanic Acid and Some Isocyanates—A Correction](#)

J. Chem. Phys. **5**, 499 (1937); 10.1063/1.1750063



The Absorption Spectra and Dissociation Energies of Cyanic Acid and Some Isocyanates

SHO-CHOW WOO AND TA-KONG LIU, *National Research Institute of Chemistry, Academia Sinica, Shanghai, China*

(Received June 10, 1935)

The absorption spectra of gaseous isocyanic acid, methyl, ethyl and phenyl isocyanates have been observed in the ultraviolet. The long wavelength limits of the continuous absorption found were as follows: HNCO , $\lambda 2240$; CH_3NCO , $\lambda 2550$; $\text{C}_2\text{H}_5\text{NCO}$, $\lambda 2480$; $\text{C}_6\text{H}_5\text{NCO}$, $\lambda 2420\text{A}$. In the case of isocyanic acid, diffuse bands were also found in the region $\lambda 2570$ – 2250A . Characteristic

absorption bands due to an excitation in the benzene ring were found in phenyl isocyanate. The structures are probably represented by the formulae $\text{H}-\text{N}=\text{C}=\text{O}$, $\text{CH}_3-\text{N}=\text{C}=\text{O}$, $\text{C}_2\text{H}_5-\text{N}=\text{C}=\text{O}$, $\text{C}_6\text{H}_5-\text{N}=\text{C}=\text{O}$. The products and energies of dissociation have been described. The absence of the characteristic absorption due to $>\text{C}=\text{O}$ has also been discussed.

THE structure of cyanides and cyanates has long been a subject of numerous investigations. Most of the classical studies were, however, limited to solutions. Recently a great deal of interesting results have been obtained through spectroscopic investigations on simple cyanides. Quite lately, the Raman spectra of isocyanates have been investigated by Kohlrausch and others.¹ It seemed probable that a study of the ultraviolet absorption spectra might yield some interesting information regarding the nature and strength of binding and the structure in some organic cyanates.

EXPERIMENTAL

The chemicals employed for preparation of the substances used in this investigation were of c. p. grade, unless otherwise stated.

Cyanic acid was prepared by heating cyanuric acid (Technical, Eastman Kodak Co.). The gas obtained was condensed in a trap cooled by freezing mixture. On account of the rapid polymerization of liquid cyanic acid, purification was effected by distillation under vacuum between freezing mixture and liquid air temperatures. The middle portions only were taken for the experiment. Under such conditions, no appreciable polymerization was observed and the product thus obtained was a colorless liquid.

Methyl isocyanate was prepared according to Slotta and Lorenz² by heating a mixture of freshly distilled dimethyl sulfate (Kahlbaum, "for scientific purpose") and potassium cyanate

in the presence of anhydrous sodium carbonate. The product was purified by repeated distillations and finally the portion of B. P. 42 – 42.5°C was collected. As shown by the spectrum, traces of sulfur dioxide ($<0.5\%$) probably from the decomposition of the sulfate were found present. Since the spectrum of sulfur dioxide is well known and no convenient method is available for its separation when present in such a small quantity, no further purification was applied.

Ethyl isocyanate was prepared by the same method as for methyl isocyanate, Kahlbaum technical dimethyl sulfate being used in this case. After repeated distillations, the middle portion of B. P. 60°C was collected for use. Traces of sulfur dioxide were also found present.

Phenyl isocyanate used was a Kahlbaum scientific preparation. Preliminary experiments showed that the freshly redistilled product gave the same spectrum as the original material, which was then used without further purification.

The spectra were taken with a small Hilger quartz spectrograph, a hydrogen discharge tube being used as the continuous light source. The time of exposure was generally one hour. Absorption cells of 10 cm, 130 cm and 285 cm length were employed. The pressure of phenyl isocyanate was its vapor pressure at room temperature, while those of methyl and ethyl isocyanate varied from 1 mm up to 274 mm and 131 mm, respectively. On account of the violent polymerization of the liquid above 0°C , the highest pressure of cyanic acid used was its vapor pressure at this temperature. One experiment was carried out with a pressure of 373 mm by leading the gas generated from the decomposition of

¹ K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (1931), pp. 246–247, 321, 332.

² K. H. Slotta and L. Lorenz, *Ber. D. Chem. Ges.* **58**, 1320 (1925).

cyanuric acid directly into the absorption cell. No difference in the spectrum was observed. But polymerization was considerable. Experiments with different amounts of the absorbing gas were considered necessary for the following reasons. In the case of continuous absorption, bands may sometimes be found at low pressures, if the continuum at moderate pressures is only apparent; while with increasing pressure the continuous absorption may be displaced toward the red side so that the upper limit of dissociation energy may be estimated more nearly to the true value. In the case of discrete absorption, the system of bands may be more completely developed with varying amounts of the absorbing gas. Actually this was found true here as is usually the case.

RESULTS AND DISCUSSION

In the cases of methyl and ethyl isocyanates only continuous absorption was found, and a careful search failed to detect any discrete bands.* For phenyl isocyanate, bands corresponding to the characteristic absorption of the phenyl group were found in the region $\lambda\lambda 2770$ – 2550\AA in addition to the continuum. The long wavelength limits of the continuous absorption of methyl and ethyl isocyanates were found to shift toward greater wavelength with increasing amounts of the absorbing gas, finally approaching a value which remained almost constant with further increase of the absorbing gas. In the case of cyanic acid, very diffuse bands immediately followed by a continuum appeared in the region $\lambda\lambda 2570$ – 2250\AA . With varying amounts of the absorbing gas, the extension of the band system and the long wavelength limit varied considerably. These bands were so diffuse and broad that only their approximate wavelengths could be given. Moreover, because of the low dispersion used, it was not possible to determine which of the bands are really without fine structure. The long wavelength limit of the continuum in this case was estimated when the amount of the absorbing gas was at such an optimum value that the bands of shortest wavelength just began to appear. The results of the measurements are presented in Table I.

* A group of faint bands was found in the region $\lambda\lambda 3100$ – 2500 at highest pressure of the absorbing gases (130 cm absorption length). This was finally proved to be due to sulfur dioxide.

TABLE I.

MOLECULES	CONTINUA $\lambda(\text{\AA})$	ENERGIES OF DISSOCIATION (KCAL./MOLE)
HNCO	> 2240	< 126.9
CH ₃ NCO	> 2550	< 111.5
C ₂ H ₅ NCO	> 2480	< 112.4
C ₆ H ₅ NCO*	> 2420	< 117.5
Approximate wavelength of HNCO bands:		
2565, 2545, 2528, 2513, 2505, 2495, 2477, 2465,		
2445, 2434, 2415, 2400, 2385, 2370, 2357, 2345.		

* Bands due to phenyl group are not given.

As a result of the light absorption, the molecules are either excited when discrete absorption appears or directly decompose where a continuum results. The absorption bands of phenyl isocyanate are certainly due to an electronic excitation in the benzene ring for they are similar to the phenyl bands of aniline with respect both to the spectral region, the band spacings and the intensity distribution. The discrete absorption of cyanic acid appears in about the same region as in the cases of primary, secondary and tertiary amines.³ They are thus probably due to an electronic excitation of the $\text{H}-\text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}=\text{O}$ bond. The differences in band spacings and intensity distribution in these two cases may be what we should expect for the asymmetry of the cyanic acid molecule ($\text{H}-\text{N}=\text{C}=\text{O}$) in comparison with the molecules of the amines. Thus the structure of gaseous cyanic acid may be represented by $\text{H}-\text{N}=\text{C}=\text{O}$. A comparison of the spectral regions where the continua set in will show that the methyl, ethyl and phenyl compounds have probably a similar structure $\text{R}-\text{N}=\text{C}=\text{O}$.

The results obtained by Kohlrausch and others¹ from Raman spectrum investigations also indicate the structure $\text{R}-\text{N}=\text{C}=\text{O}$ for the molecules of methyl, ethyl and phenyl isocyanates[†] in the liquid state.

It will be seen that in all these cases there was found no absorption characteristic of the carbonyl group $\text{>C}=\text{O}$, which has been observed for aldehydes and ketones. The characteristic ab-

³ G. Herzberg and R. Kölsch, *Zeits. f. Elektrochemie* 39, 572 (1933).

[†] New results on the Raman spectra of methyl and ethyl isocyanates have been obtained by H. Kopper and A. Pongratz (*Monatsh.* 62, 78–89 (1933)). Unfortunately this original paper is not available here.

sorption of >C=O may, however, be influenced to a certain extent by the nature of the group or groups attached to the carbon atom. Thus in the case of aldehydes and ketones, this absorption appears, generally in the region $\lambda\lambda 3400\text{--}2500\text{\AA}$, while in the case of carboxylic acids and esters, it is displaced considerably to the shorter wavelength.⁴ It will be further noticed that isocyanic acid HNCO is isosteric with carbon dioxide and ketene and all of them contain the >C=O group. The absorption bands of ketene set in at 3850\AA ⁵ while no absorption of carbon dioxide has been observed until 1850\AA .⁶ Hence the absence of absorption $\sim 3000\text{\AA}$ in the case of the isocyanates may not be an evidence for the absence of >C=O group in these molecules. Recently Herzberg³ has also failed to find the absorption characteristic of >C=O and NH in gaseous formamide and seemed to incline to the revision of the classical formula $\text{H}-\text{C}=\text{O}$. On the other hand, the



existence of the carbonyl group as well as the

amino group seems to have been definitely proved in the liquid formamide by Raman spectrum investigations.⁷ It will be interesting in this connection to investigate the absorption spectrum of liquid formamide.

In each of these cases the long wavelength limit of the continuum is taken as the upper limit of the dissociation energy of the molecule. In the case of cyanic acid, predissociation might have started at longer wavelength and thus the value given here is probably somewhat too high. If a structure of the isoform $\text{R}-\text{N}=\text{C}=\text{O}$ is assumed for each of these molecules, photochemical dissociation may take place at one of the three bonds, $\text{R}-\text{N}$ ($\text{H}-\text{N}$, $\text{C}_{\text{al}}-\text{N}$, $\text{C}_{\text{ar}}-\text{N}$), $\text{N}=\text{C}$ and $\text{C}=\text{O}$. The bond energy of $\text{N}=\text{C}$ amounts to about 125 Kcal.,⁸ while that of $\text{C}=\text{O}$ about 180 Kcal. The bond energies for $\text{H}-\text{N}$ and $\text{C}-\text{N}$ may be taken approximately as 87 Kcal. and 60 Kcal., respectively. It will be seen that the optical dissociation energies are only sufficient to account for the splitting of the $\text{R}-\text{N}$ bonds. The excess of energy for each case is as follows: $\text{H}-\text{NCO}$ 39.9 Kcal., CH_3-NCO 51.5 Kcal., $\text{C}_2\text{H}_5-\text{NCO}$ 52.4 Kcal., and $\text{C}_6\text{H}_5-\text{NCO}$ 57.5 Kcal. Unfortunately neither is any thermochemical datum available nor are the energies of activation for NCO, CH_3 , C_2H_5 and C_6H_5 definitely known for a direct comparison.

⁷ K. W. F. Kohlrausch, reference 1, p. 313.

⁸ N. V. Sidgwick, *The Covalent Link in Chemistry* (1933), p. 119.

Errata: Experimental Investigation of the Effect of Pressure on Phase Equilibria of Sodium Tungstate and of Related Thermodynamic Properties

R. W. GORANSON AND F. C. KRACEK, *Geophysical Laboratory, Carnegie Institution of Washington*
(J. Chem. Phys. 3, 87, 1935)

IN Table 4, column 3, on page 91, read dt/dp instead of dp/dt .

The first equation in the second column on page 92 should be

$$v - v_{20} = v_{20}[53.194(t-20)10^{-6} + 41.5(t-20)^2 10^{-9}]$$

instead of

$$v - v_{20} = v_{20}[53.194(t-20)10^{-6} + 41.5(t-20)^2 10^{-8}].$$