of the reaction, based on approximate equations for the change of activity coefficient with concentration.

By use of Brönsted's theory of reaction mechanism, the method is applied to the oxidation of ammonia by persulfate ion in the presence of silver ion.

The principles by which the activity coefficients in non-electrolyte mixtures may be approximately evaluated are given, and illustrated by their application to the reaction of *p*-nitrobenzoyl chloride with certain alcohols.

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THE PHOTOCHEMICAL DISSOCIATION OF TRIATOMIC MOLECULES. HYDROGEN CYANIDE

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The remarkable success of Franck, Kuhn and Rollefson[1] in explaining the absorption spectra of the Group I halides leads one to the query whether the same mechanism does not hold also in the case of polyatomic molecules. Its importance to photochemistry cannot be neglected, especially in view of the attempt of Franck and Scheibe[2] to explain in a reasonable manner the photolysis of hydrogen iodide in aqueous and hexane solutions. According to Franck and Kuhn[3] an "atomic"[4] molecule may be dissociated photochemically into a normal atom plus an excited atom. Only two continuous absorption regions in the near ultraviolet should result, depending on which is the one excited. On the other hand, an "ionic"[5] molecule may be dissociated photochemically into two normal atoms, one way in addition to those in which the "atomic" molecule may dissociate. In this case an extra absorption region is to be found to the red side of the spectrum and at a distance corresponding to the energy difference $^2P_{1/2} - {}^2P_{1 1/2}$ of the halogen ground doublet. The first step toward the application of their theory to polyatomic molecules is the consideration of triatomic molecules. When several of these have been investigated it will be time to take up the more complicated ones. Terenin[6] has already studied triatomic molecules, two atoms of which are similar. As this is likely to lead to degeneracy complications in the analysis of the spectra, it was thought desirable to choose

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[1] Franck, Kuhn and Rollefson, *Z. Physik*, **43**, 155 (1927).

[2] Franck and Scheibe, *Z. physik. Chem.*, **139A**, 22 (1928).

[3] Franck and Kuhn, *Z. Physik*, **43**, 164 (1927).

[4] An atomic molecule may be defined as one which when given sufficient vibrational energy will dissociate into atoms.

[5] An ionic molecule may be defined as one which when given sufficient vibrational energy will dissociate into ions.

[6] Terenin, *Z. Physik*, **44**, 713 (1927); **49**, 882 (1928); *Nature*, **118**, 843 (1926).

a triatomic molecule all three atoms of which are different. For this purpose hydrogen cyanide seemed ideal. It possesses the unique advantage (over Terenin's diatomic halides) that the spectra of its partial decomposition products are well known. Thus if hydrogen cyanide will dissociate in any of the four modes

$$\mathrm{HCN} + E_1 = \mathrm{H} + \mathrm{C} + \mathrm{N} \tag{1}$$
$$\mathrm{HCN} + E_2 = \mathrm{H} + \mathrm{CN} \tag{2}$$
$$\mathrm{HCN} + E_3 = \mathrm{C} + \mathrm{NH} \tag{3}$$
$$\mathrm{HCN} + E_4 = \mathrm{N} + \mathrm{CH} \tag{4}$$

we should be able to identify by its fluorescence any excited decomposition molecule which was not in a metastable state. The investigation of hydrogen cyanide seems to have an advantage over the original one of Franck and Kuhn in that we are not likely to be disappointed by getting metastable products. In this work a calculation was first made of these different dissociation energies and this was then checked by trying to locate experimentally the predicted absorption spectra of hydrogen cyanide.

The Heat of Dissociation of Normal Hydrogen Cyanide.—The heat of dissociation of normal hydrogen cyanide may be calculated from the equation

$$\begin{array}{llllll} \mathrm{HCN} + Q & + \tfrac{1}{2}D_{\mathrm{H_2}} & + \tfrac{1}{2}D_{\mathrm{N_2}} & + S_{\mathrm{C}} & = \mathrm{H} + \mathrm{C} + \mathrm{N} \\ \quad -1.39^{7} & + \tfrac{1}{2}4.38^{8} & + \tfrac{1}{2}9.5^{9} & + 6.10^{10} & = 11.65\ \mathrm{v.} \end{array}$$

where Q is the heat of formation from the element molecules (values given in volts; 1 v. = 23 kilo cal.), D the heat of dissociation of the element molecules and S_{C} the heat of sublimation of diamond.

In order to calculate the heats of dissociation for Reactions 2, 3 and 4 we must know the heats of dissociation of the respective dissociation products. Two of these have been calculated elsewhere.[11] Heitler and Herzberg[12] have found the heat of dissociation of CN to be 9.7 v., the products being, according to Mulliken,[13] a normal ^3P C atom and an excited ^2D N atom. The dissociation of CN into two normal atoms then should be $9.7 - 2.4 = 7.3$ v. The probable error in this value may amount to as much as +0.8 v. by mistaking the excitation energy of the excited atom.[14]

With these values we get for the heats of dissociation of normal hydrogen cyanide

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[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 591.

[8] Witmer, *Proc. Nat. Acad. Sci.*, **12**, 238 (1926).

[9] Mulliken and Birge, *Nature*, **122**, 842 (1928).

[10] Kohn and Guckel, *Naturwissenschaften*, **12**, 139 (1924).

[11] Villars, This Journal, **51**, 2374 (1929); $D_{\mathrm{NH}} = 4.65$ v.; $D_{\mathrm{CH}} = 3.55$ v.

[12] Heitler and Herzberg, *Z. Physik*, **53**, 52 (1929).

[13] Mulliken, *Phys. Rev.*, **32**, 761 (1928).

[14] Heitler and Herzberg believe the excited atom to be a 1.6 v. ^5S C atom instead of a 2.4 v. ^2D N atom.

$$\begin{array}{llll}
E_1 = 11.65\text{ v.} & (\mathrm{H + C + N}) & E_3 \fallingdotseq 7.0 & (\mathrm{C + NH}) \\
E_2 = 4.35 & (\mathrm{H + CN}) & E_4 \fallingdotseq 8.1 & (\mathrm{N + CH})
\end{array}$$

These figures show that in a thermal collision process Reaction 2 should greatly outweigh the other three. The velocity of such a dissociation should be represented by an activation energy equal to or less than 4.35 × 23 = 100 kilo cal. A rough calculation[15] was made to see what the speed of decomposition according to (2) would be if the heat of activation were 3.1 v. At 1000°K. there should be a 0.2% change per second at 1 atm. It was a very surprising experimental observation that hydrogen cyanide gas at one atmosphere pressure did not take on any visible change when heated in a furnace at 1000°. The liquid which was condensed in the tube protruding outside the furnace, however, turned brown, showing that a slow reaction was taking place, the products probably condensing out as rapidly as they were formed.

The Photochemical Dissociation of Hydrogen Cyanide.—That hydrogen cyanide is most likely not an "ionic"[16] molecule even though it has an electric moment (it has an infra-red absorption spectrum) is attested by the fact that its ionization constant in water is 10^{-9}. If this is true, then, according to Franck's theory, a photochemical dissociation in an elementary act should not be possible unless one of the products comes off in an excited state. The excitation energies of the different products of dissociation are as follows (doubtful values given in parentheses)

$$\begin{array}{rll}
\mathrm{H} & + 10.15\text{ v.} & = \mathrm{H}^* \\
\mathrm{N}(2s)^2(2p)^3\ {}^4S & + 2.35 & = \mathrm{N}^*(2s)^2(2p)^3\ {}^2D \\
 & + 10.38 & = \mathrm{N}'(2s)^2(2p)^2(3s)\ {}^4P \\
\mathrm{C}(2s)^2(2p)^2\ {}^3P & + (2.0)^{17} & = \mathrm{C}^*(2s)^2(2p)^2\ {}^1D \\
 & + (3.2)^{17} & = \mathrm{C}'(2s)^2(2p)^2\ {}^1S \\
\mathrm{NH}\ {}^3\Sigma & + 3.7 & = \mathrm{NH}^*\ {}^3\Pi^{18} \\
\mathrm{CH}\ {}^2\Pi_n & + 2.9 & = \mathrm{CH}^*\ {}^2\Delta_i \\
 & + 3.2 & = \mathrm{CH}'\ {}^2\Sigma \\
\mathrm{CN}\ {}^2\Sigma & + 1.8 & = \mathrm{CN}^*\ {}^2\Pi \\
 & + 3.2 & = \mathrm{CN}'\ {}^2\Sigma
\end{array}$$

The energies necessary for the different photochemical dissociation possibilities are then as follows

$$\begin{array}{rrlll}
4.35 & + 1.8 = & 6.2\text{ v.} & \mathrm{H + CN^*}\ {}^2\Pi & \text{(2a)} \\
 & + 3.2 = & 7.6 & \mathrm{H + CN'}\ {}^2\Sigma & \text{(2b)} \\
7.0 & + 2.0 = & 9.0 & \mathrm{C^*}\ {}^1D + \mathrm{NH} & \text{(3a)} \\
 & + 3.2 = & 10.2 & \mathrm{C'}\ {}^1D + \mathrm{NH} & \text{(3b)} \\
 & + 3.7 = & 10.7 & \mathrm{C + NH^*}\ {}^3\Pi & \text{(3c)} \\
8.1 & + 2.4 = & 10.5 & \mathrm{N^*}\ {}^2D + \mathrm{CH} & \text{(4a)} \\
 & + 2.9 = & 11.0 & \mathrm{N + CH^*}\ {}^2\Delta_i & \text{(4b)} \\
 & + 3.2 = & 11.3 & \mathrm{N + CH'}\ {}^2\Sigma & \text{(4c)}
\end{array}$$

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[15] *Cf.* Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, **1926**, p. 91.

[16] If we may be permitted to extend the sense of Franck's definition to the case where one of the ions is diatomic.

[17] Rough estimates by Mulliken (private communication) who used Turner's method, *Phys. Rev.*, **32**, 727 (1928).

[18] *Cf.* Mulliken, *Phys. Rev.*, **33**, 730 (1929).

Thus it is seen that the photochemical dissociation which takes the least amount of light energy is also that which would give a hydrogen atom and a CN molecule (this time in an excited state). Unfortunately, the only spectrograph at my disposal was an E_1 Hilger which takes photographs of wave lengths down to 2100 Å. (5.9 v.). A check over this range nevertheless seems of use to make sure we have not gone astray in the above calculations. An error of 0.8 v. in the dissociation products of CN would lower the above expected convergence limit from 6.2 to 5.4 v. (=2280 Å.), a point where we might have hopes of detecting absorption if it occurred. The presence or absence of an absorption spectrum at wave lengths below 2800 Å. (4.35 v.) should also throw light on our conclusions as to the type of binding between the H and CN part of the molecule.

Apparatus

The hydrogen cyanide used was prepared by dropping 1-1 sulfuric acid on solid potassium cyanide.[19] The evolved gas was at first dried by passing it over a tube of phosphorus pentoxide 130 cm. long and condensed by an ice–salt (−14°) mixture surrounding the first tube of a distilling train. The yield was not good and at a later date when the gas was being prepared a second time the yield was only a few per cent. This was found to be caused by the substitution of a phosphorus pentoxide drying tube 2 meters long, a close examination revealing a sirupy combination product of $P_2O_5 \cdot xHCN$. In the final apparatus no drying was attempted and the gas was purified from water by five fractional distillations. After the distillation and before sealing off, the hydrogen cyanide would be frozen in both tubes to prevent its decomposition by heat and the apparatus evacuated.[20] As it was discovered that hydrogen cyanide has marked solvent action on De Khotinsky cement, the last distillation from pyrex to the quartz absorption cell was made through a quartz–pyrex glass joint. The liquid was quite stable and did not turn brown until after its subjection to an electric discharge or to a high temperature and pressure.

By supporting the cell proper in a furnace and controlling the temperature of the ice condensed in the tube leading from the cell to a point outside the furnace, both temperature and pressure could be regulated easily. This tube dipped into a Dewar filled with a mixture of alcohol and dry ice. The temperature in the Dewar was controlled by a toluene thermometer and that in the furnace by a Chromel–Alumel thermocouple.

The furnace consisted of a specially molded porcelain core with two side tubes sticking out of its center at right angles, the smaller one to house the thermocouple leads, the larger one to introduce light for a fluorescence experiment. The core was wound with 50 feet of No. 12 Chromel wire and surrounded by a packing of Sil-o-cel. The openings were closed by fused quartz windows to prevent convection. This furnace when drawing 19 amperes from a 110-volt main would reach the temperature of 1000° in an hour and a half.

The light source used was a hydrogen discharge tube built according to the specifica-

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[19] The method recommended in "Organic Syntheses," Vol. VII, **1927**, p. 50, had the great disadvantage that the sodium cyanide solution cakes and plugs up the apparatus, after which it has to be dismantled before the preparation can be continued.

[20] The hydrogen cyanide was found to gum up the mercury badly in a mercury vapor pump, so only the supporting Hi-Vac pump was used.

tions of Bay and Steiner.[21] It was found that the spectrum of such a tube cleaned itself up after several hours of running and that it was not necessary to run the discharge beforehand at a higher load in a continuous stream of hydrogen as has been recommended by other authors.

An E_1 Hilger quartz spectrograph was used. Owing to its high dispersion and the twelve quartz reflecting surfaces through which the light from the lamp had to pass, a period of thirty minutes was required to give a satisfactory exposure.

In some of the photographs the light source used was an iron arc. This was because at the crucial moment a leak had developed in the hydrogen lamp, putting it out of commission.

Results and Discussion

Absorption.—The transmission spectrum of hydrogen cyanide at 741 mm. and 25° is exactly that of the lamp for wave lengths between 2240 and 6593 Å. To investigate the region below 2240 Å., Schumann plates were used. In this case the spectrum of the iron arc is identical with that transmitted through the hydrogen cyanide (atmospheric pressure) as far as the limit of the spectrograph (2094 Å.).

In order to increase the probability of absorption at the wave lengths accessible to the quartz spectrograph, the expedient was used of raising the molecules to higher initial vibrational quantum levels by increasing the temperature of the gas. Thus, assuming the distribution law, $N = N_0 e^{-E/kT}$, at room temperature (300°K.), 2% of the molecules have an energy 0.1 v. greater than average. At 1000°K. this number has increased to 32%, while the percentage of those having 1 v. excess energy has increased from the negligible amount of 10^{-15} to 0.001%. At 1273°K. the number having 1 v. excess energy should be about 0.01%. We might, therefore, hope to increase our absorption some 10^{13} times by raising the temperature to 1000°. Of course, there are reasons why this attempt should fail. The number of absorbing molecules may still be so small as to be negligible. Moreover, in the photochemical dissociation of hydrogen chloride, absorption sets in 1.1 v. *beyond* the convergence limit, the distance beyond depending on the loss in stability of the molecule in the excited state. If the stability of hydrogen cyanide changed on excitation by the same amount as in hydrogen chloride, so that its absorption maximum is 1.1 v. beyond its convergence limit, then we should not be able to detect absorption until well down in the Schumann region (1700 Å.).

Our attempt was, indeed, unsuccessful. The continuous spectrum of the hydrogen discharge was photographed after passing through hydrogen cyanide at 1000° at a pressure of 1 mm. No absorption could be observed. The investigation of hydrogen cyanide in a vacuum spectrograph should prove very fruitful, but first of all the difficulties introduced by its solvent action on cements and on mercury must be overcome.

As a final resort, the hydrogen cyanide was allowed to reach atmospheric

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[21] Bay and Steiner, *Z. Physik*, **45**, 337 (1927).

pressure at 1000° and the spectrum photographed from 2240 to 2800 Å. The spectrograms were run through a microphotometer but no detectable absorption was evident. Contrary to expectation, the hydrogen cyanide did not decompose rapidly under this treatment. The vapor remained perfectly colorless to the eye, but the liquid started to turn brown, and thereafter was completely changed to a brown solid within a couple of weeks. The liquid had been prepared six weeks before being used, during which time it remained perfectly clear and colorless.

The fact that hydrogen cyanide gas shows no absorption between 2800 and 2240 Å. falls in line with the assumption that it is not an "ionic" molecule. As it certainly does not show an ionic character in aqueous solution, it seems extremely doubtful that the results reported by Andant and Rousseau[22] concerning its photolysis in light of wave lengths 3650, 3130 Å. and below could have been caused by pure hydrocyanic acid.

Fluorescence.—On the chance that the sought continuous absorption might set in immediately after the calculated convergence limit, the pressure in the cell (room temperature) was reduced to about 1 mm. by freezing the hydrogen cyanide in carbon dioxide snow and the cell was illuminated with light from a silver arc, which should furnish quite a few wave lengths in the region 1967 to 1802 Å. There was no visible fluorescence (1.8 v. excitation of CN) nor ultraviolet fluorescence (3.2 v. excitation of CN). The lines appearing were the silver lines. Neither could one observe at the temperature of 1000° a visible fluorescence of the red CN bands against the background of the relatively cold window. It is not at all surprising that we have failed to excite fluorescence by the silver arc, for the intensity of its short wave lengths (1967–1802 Å.) must have been considerably reduced in the passage of the light through the air and the quartz cell wall.

Polymerization.—Either the treatment of the hydrogen cyanide gas with light of these extremely short wave lengths or else an extremely slow chemical reaction (two months) had initiated, by the time the first absorption measurements had been completed, a decomposition or a polymerization of the hydrogen cyanide liquid in the cell. This was at first indicated by a yellowish color in the liquid, which became darker and darker. I am inclined to favor the former hypothesis for the following reasons. The polymerization of hydrogen cyanide to colorless plates of $(HCN)_3$ occurs after a long period of heating of the pure substance at 100°, or after a long irradiation with sunlight in the presence of epichlorohydrin.[23] A trace of potassium cyanide or of an alkali carbonate catalyzes the polymerization of hydrogen cyanide to a black substance, out of which can be crystallized the $(HCN)_3$. Cyanogen, on the other hand, polymerizes to black or dark brown

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[22] Andant and Rousseau, *Compt. rend.*, **184**, 1553 (1927).

[23] Abegg, "Handbuch der anorganischen Chemie," Leipzig, **1909**, Vol. III, Part 2, p. 236.

paracyanogen. If our hypothesis is correct, it is quite reasonable that the steps should be the following

$$\begin{aligned} \mathrm{HCN} &\longrightarrow \mathrm{H} + \mathrm{CN} \\ 2\mathrm{CN} &\longrightarrow (\mathrm{CN})_2 \longrightarrow (\mathrm{CN})_x \end{aligned}$$

Further evidence that the decomposition products of hydrogen cyanide most readily obtained are H and CN is that when a faint emission spectrum was induced in the cell which contained the brown deposit, the 0,0(3), 1,1(1) and 2,2(0) CN($^2\Sigma - {}^2\Sigma$) bands were the most intense (intensities in parentheses). Two other bands were observed, the 0,0(1) N_2^+ band and the 0,1(1) of the second positive nitrogen group. All bands were very thin and were shaded toward the violet. Still further evidence that we have here a decomposition of hydrogen cyanide rather than a direct polymerization lies in the micro-analysis of the residual gas in the cell after opening it up under water and dissolving out the hydrogen cyanide left. A small bubble of insoluble gas remained, which was introduced into the top of a tube 6.25 mm. in diameter and mixed with an approximately equal volume of oxygen gas. A platinum resistance spiral in the top of the tube was then made to glow, and after the gases were cooled, a decrease in volume of 0.053 ± 0.008 cc. had occurred. This is an indication that hydrogen was the residual gas.

Summary

Summarizing, it may be stated that our calculations of the minimum energy required to dissociate hydrogen cyanide by a photochemical act are not contradicted by any experimental results. The supposition that hydrogen cyanide is not an "ionic" molecule is supported by the fact that it has no absorption spectrum between 4.35 and 5.9 v. (2800 and 2100 Å.). The dissociation into H and CN should require the least energy thermally (4.35 v. = 100 kilo cal.) as well as photochemically (6.2 v. = 1990 Å.), compared with dissociations into CH plus N and NH plus C. Evidence has been adduced to support the hypothesis that the brown coloration which hydrogen cyanide acquires comes from an initial decomposition into H and CN and a subsequent polymerization of cyanogen to paracyanogen, rather than that it is due to a direct polymerization of the hydrogen cyanide to $(HCN)_3$.

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