[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE PHOTOCHEMICAL DISSOCIATION OF TRIATOMIC MOLECULES. II. POTASSIUM CYANIDE

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In a previous article[1] the dissociation energetics of hydrogen cyanide were investigated and it was found that if this molecule were of an atomic binding, as are the corresponding hydrogen halides, one should not expect it to have a continuous absorption spectrum in an energy region less than 6.2 volts ($\lambda > 1990$ Å.). This was verified experimentally. The next molecule chosen for investigation was potassium cyanide. This should be more amenable to experimentation, if one may infer an analogy between the corresponding cyanides and halides.

The Heat of Dissociation of Normal Potassium Cyanide.—The *atomic* heat of formation (Q_A) of potassium cyanide (the heat of formation from the gaseous atoms) may almost be estimated from data in the "International Critical Tables."

$$\begin{aligned} \text{KCN (c)} + Q + L_{S_K} + L_{S_C} + {}^1/_2\, D_{N_2} &= \text{K} + \text{C} + \text{N} \qquad (1) \\ 1.2 + 0.9 + 6.4 + 4.8 &= 13.3\ \text{v} = Q_{A-\text{KCN(c)}} \end{aligned}$$

From this value must be subtracted the heat of sublimation, L_S, to get the *atomic* heat of formation of gaseous potassium cyanide. This is not known but an estimate may be obtained by a method to be described below.

$$Q_{A-\text{KCN(g)}} = 13.3\ \text{v.} - L_S = E_1 \qquad (2)$$

When we consider the four possible dissociation combinations as in the previous work, we find we have the heat of formation of CN but not that of either KN or KC. However, we shall assume that the stability of such unsatisfied (as to valence) molecules is quite small, especially as their band spectra are not known, and, if this is so, such modes of dissociation should occur relatively infrequently when compared with the process

$$\text{KCN (g)} + E_2 \longrightarrow \text{K} + \text{CN} \qquad (3)$$

The energy, E_2, then is

$$\begin{aligned} E_2 &= 13.3 - L_S - 7.3\ \text{v.} \\ &= 6.0 - L_S \qquad (4) \end{aligned}$$

Experimental

The apparatus was of the same type as that used in the investigation of hydrogen cyanide, with the exception of a small Gaertner quartz spectrograph which was used instead of an E_1 Hilger. Although the dispersion of this instrument is much less (the whole spectrum of visible and ultraviolet is spread over a distance of about 105 mm.), nevertheless, this proves to be an advantage as the light strength of the instrument is so much the

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[1] Villars, THIS JOURNAL, **52,** 61 (1930), hereafter designated as I.

greater. The hydrogen arc (initial pressure of hydrogen 1.45 mm.) was run at about 0.55 ampere and 3500 volts and exposures of five and ten minutes were made. The potassium cyanide (Baker's 96–98% pure; SO_2, 0.05%; Cl, 0.25; org. matter, trace) was placed in the quartz tube adjacent to the constriction leading to the quartz absorption cell and after evacuating and outgassing the latter the cyanide was heated to distil it over into the cell. It melted quite readily and the liquid boiled (pressure 10^{-4} mm.), at the same time turning black. The distillation did not take place very readily, but several drops of the melt were pushed bodily across the constriction. The cell was sealed off and the isolated product had a clear transparent appearance with a reddish tint. No liquid–air trap was used during the evacuation process. The potassium compound was quite ruinous to the cell at high temperatures (1050°) as it caused such a rapid devitrification of the quartz that it fell to pieces shortly after cooling to room temperature.

A possible objection which might be made to the present work is that the spectra observed do not come from potassium cyanide, but from potassium hydroxide which might have been left behind as an hydrolysis product after the evacuation. Before the cyanide was sealed off, it had absorbed an appreciable amount of water during the glass blowing. This objection is overthrown by two considerations. First, an analysis of the residue showed that, within titration errors, there was no potassium hydroxide present. Second, it has been shown in a subsequent research, which will be reported later, that potassium hydroxide has to be heated to a much higher temperature before it will reach a vapor pressure great enough to absorb.

Results

Figure 1 gives the microphotometer record of the hydrogen source transmitted by the cell at room temperature (no absorption). The banded structure is due to the impurities in the lamp, the latter being only newly broken in. Figure 2 gives the record of the absorption at about 830° and Fig. 3 that at 875°. It is seen that, at this latter temperature, there are two regions of absorption. A visual study of the original plate indicated that the long wave length limits of these two regions are 2175 and 2900 Å., which correspond, respectively, to 5.7 and 4.3 volts, the difference being 1.4 v.

Since the difference of 1.4 v. is, within the errors of measurement, equal to the excitation energy of CN (1.8 v.) or K (1.6 v.), it is indicated that the photochemical dissociation process requiring least energy is the one resulting in *normal* products. This conclusion is not yet inescapable for the following reasons. If the longest wave length limit of continuous absorption should be at an energy corresponding to dissociation into a normal and an excited product, the next continuous absorption region should correspond to dissociation into a product in the next higher excited state. These energies would be in the following steps: K′ (1.6), CN′ (1.8), K″ (2.7), CN″ (3.2), K′ + CN′ (3.4), etc. Granting that in the roughness of the measurement the two expected regions spaced by 0.2 v. (K′ and CN′) are indistinguishable and that the one 1 v. farther on (K″) has too low an intensity, the next one (CN″) is at the experimentally observed distance from the first two (1.5 v.). One could decide for or against this possibility if he knew the heat of sublimation of potassium cyanide. For, if the first photochemical act were a dissociation into two *normal* products the energy, E_2, should exactly equal the energy corresponding to the convergence limit of continuous absorption (4.3 v.).

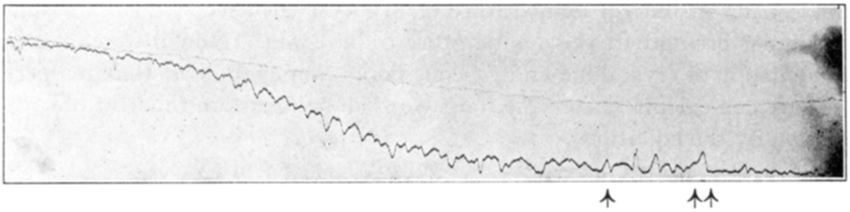

Fig. 1.—Plate M8, H_2 lamp, five minutes, cell at room temperature.

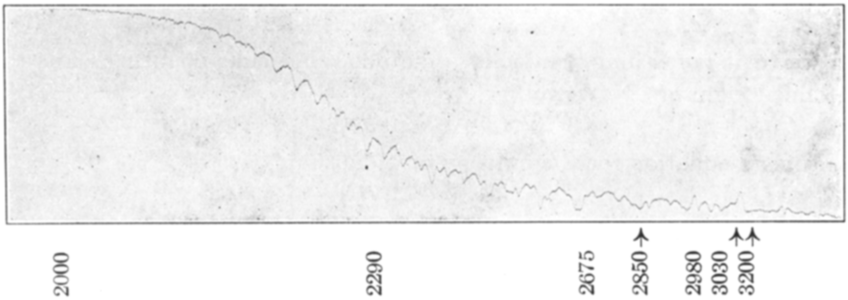

Fig. 2.—Plate M8 KCN, 790–870°.

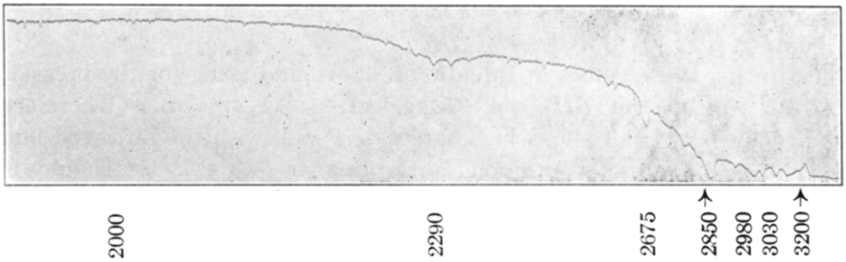

Fig. 3.—Plate M8 KCN above 875°.

If the act were a dissociation into a normal and an excited product, the longest wave length limit should correspond to E_2 + 1.6 v. (or + 1.8).

Although there are no measurements given of the heat of sublimation of potassium cyanide, an estimate may be obtained by making use of the third law. We know that, in order to absorb light, the vapor pressure must reach a value of the order of magnitude of 1–10 mm. Absorption not setting in until a temperature of 870° was reached, we shall assume the vapor pressure at this temperature to be 1 mm. Now if we can know the entropy of crystalline and gaseous potassium cyanide at that temperature we can calculate from the free energy of sublimation the heat of sublimation by the equation

$$\Delta F = \Delta H - T\Delta S = -RT \ln K = -RT \ln p \text{ vapor} \qquad (5)$$

$$\log p_{\text{atm.}} = -\Delta H/4.575T + \Delta S/4.575 \qquad (6)$$

Latimer[2] has shown that the entropy of diatomic solids may be well represented by the sum of "atomic" entropies

$$S^\circ_{298\text{ solid}} = (3/2)R \ln A - 0.94 \qquad (7)$$

If we treat potassium cyanide as a diatomic molecule, counting 26 as the atomic weight of CN, we get

$$S^\circ_{298\text{ KCN (c)}} = 18.73 \text{ E. U.}$$

Latimer's equation for the entropy of a diatomic gas

$$S^\circ_{298\text{ gas}} = R \ln (w^{3/2} A_1{}^{1/2} A_2{}^{1/2}) + 30.22 \qquad (8)$$

gives

$$S_{298\text{ KCN (g)}} = 49.58$$

and

$$\Delta S_{298} = 30.85$$

Correcting for temperature, we have

$$\begin{aligned}\Delta S_{1143} &= 30.85 + 3\,R \ln T/298 - (5/2)\,R \ln T/298 \\ &= 29.51 \qquad (9)\end{aligned}$$

Substituting these values in Equation 6 above and using for the pressure 0.00132 atm. we get ΔH = 48.75 kg. cal. = 2.1 v. = L_S. Therefore, $E_2 = 5.9 - 2.1 = 3.8$ v., which agrees very well with the observed long wave length limit of continuous absorption of (4.3 v.). It should be emphasized here, before passing on, that our estimate of the entropies of solid and gaseous potassium cyanide is extremely crude and for that reason the calculated value of E_2 is subject to considerable error.

From the above we see that, on the one hand, if the first photochemical act were dissociation into a normal and an excited product, the heat of dissociation into normal products would be approximately $4.3 - 1.6 = 2.7$ v., which corresponds to a heat of sublimation of $L_S = 6.0 - 2.7 = 3.3$ v. (= 74 kg. cal.). This requires, if our ΔS is correct, a vapor pressure of 10^{-5} mm., which is not enough for absorption. On the other hand, if the first act is a dissociation into normal products and we go to the

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[2] Latimer, THIS JOURNAL, **43**, 818 (1921).

extreme of taking the observed value of 4.3 v. for E_2 (a value which does not necessarily follow as the convergence limit of the absorption series was not actually observed), this gives a heat of sublimation of $L_S = 6.0 - 4.3 = 1.7$ v. (= 37 kg. cal.), which corresponds to a vapor pressure of 170 mm., much nearer the correct order of magnitude to account for light absorption in a cell only some 77 mm. in length.

Validity of the Franck–Kuhn[3] Criterion of Atomic and Ionic Binding.—It has been pointed out recently by Sommermeyer[4] that the test proposed by Franck and Kuhn[3] as a distinction between an ionic and an atomic binding is not definitive and is rigorous only when an atomic binding is indicated. This is because of the discovery by Herzberg[5] and Heitler[6] of a *second class* of atomic molecules, the *normal* state of which dissociates on vibration into a normal and an excited product. Thus, the thermal dissociation of normal CN (convergence limit at 9.5 v.) is supposed by Mulliken[7] to result in a normal ^3P carbon atom and an excited ^2D nitrogen atom. CN excited 1.8 v., however, dissociates into two normal atoms (convergence limit 8.6 v. above normal state of molecule). The potential energy curves of the *first class* of atomic molecules are represented in Fig. 4, while those of the new *second class* are represented by Fig. 5. Rigorously, when the longest wave length convergence limit is at an energy equal to the heat of dissociation into *normal* products, it means that the molecular state which dissociates into atoms on vibration (atomic binding) is an excited state of the molecule. Our data show that this obtains in potassium cyanide vapor, but are not sufficient to define whether it is a second-class molecule of atomic binding or a molecule of ionic binding. We may be reasonably certain, however, that it is an ionic molecule, first because the only second-class atomic molecules known are those having unsatisfied

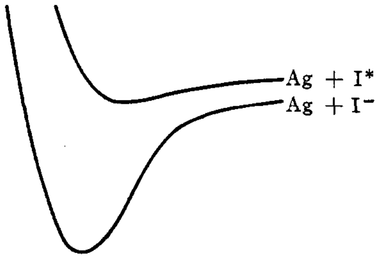

Fig. 4.—Potential energy curves for first-class atomic binding.

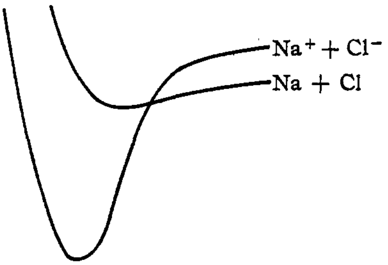

Fig. 5.—Potential energy curves for second-class atomic binding and ionic binding.

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

[4] Sommermeyer, *ibid.*, **56**, 548 (1929).

[5] Herzberg, *Ann. Physik*, **86**, 189 (1928).

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

[7] I, Refs. 13 and 14.

free valences, and second because the crystal structure[8] of potassium cyanide is the same as that of rock salt and presumably of an ionic nature. In general, the potential energy curves of ionic molecules cross in the same way as do those of second class atomic molecules (Fig. 5). This must be so if the data on electron affinities of the halogens are correct, for they are usually less (~ 3.5–4.5 v.) than the ionization potential of the metal (5.12, Na; 7.5, Ag; 4.3, K; etc.). This is not a necessary condition for validity of the principle that the first photochemical dissociation act (the one requiring least energy) of an ionic molecule will result in *normal* products. It makes no difference whether the ionic binding curve crosses the atomic binding one or not. Although at the end of the curve for NaCl (Fig. 5) the dissociated state, $Na^+ + Cl^-$, is higher than the one, Na + Cl, still we cannot expect to find an extra continuous absorption region corresponding to dissociation into the former products, because it belongs to the same potential energy curve as the initial (absorption) state and such large changes in vibrational quantum number with no change in electronic quantum number not only are not known, but they violate the Franck–Condon principle.

The change with temperature in the relative stability of the ionic and atomic forms of silver iodide postulated by Franck and Kuhn[3] is due, we should like to suggest, not to a variation in shape of the curves for different temperatures (they must necessarily be independent of temperature) but to the variation of the free energy of the reaction

$$\text{Ionic} \rightleftharpoons \text{Atomic} \qquad (10)$$

From Equation 5 may be obtained[9]

$$\Delta F = D_0 - T\Delta S' \qquad (11)$$

where D_0 is the heat of reaction (absorbed heat) at the absolute zero and[10]

$$S'_{\text{rot.}} = R \ln\ 8\pi^2 IkT/h^2 \qquad (12)$$

$$S'_{\text{vibr.}} = -R \ln\ (1 - e^{-\epsilon/kT}) \qquad (13)$$

Thus

$$\begin{aligned} \Delta S' &= R \ln I_A\,(1 - e^{-\epsilon_I/kT})/I_I(1 - e^{-\epsilon_A/kT}) \qquad (14)\\ &\longrightarrow R \ln I_A\,\epsilon_I/I_I\epsilon_A \text{ for } \epsilon << kT\\ &\longrightarrow R \ln I_A/I_I \qquad \text{for } \epsilon >> kT \end{aligned}$$

Since the moment of inertia in the atomic bound molecule is presumably larger and the vibrational quantum smaller, $\Delta S'$ is positive and therefore ΔF will vary from a positive quantity at 0°K. ($= D_0$) to a negative quantity at very high temperatures. This corresponds to the behavior postulated by Franck and Kuhn of the ionic and atomic forms of silver iodide. If this suggestion is valid, it seems that it should be possible, by going to still higher temperatures, to find one above which the atomic form of sodium chloride is in greater abundance than the ionic form.

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[8] Bozorth, This Journal, **44**, 317 (1922); Cooper, *Nature*, **110**, 544 (1922).

[9] Villars, *Proc. Nat. Acad. Sci.*, **15**, 705 (1929); **16**, 396 (1930).

[10] Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

Summary

Potassium cyanide vapor at 875° absorbs light in two regions, the long wave length boundaries of which are approximately 2175 (5.7 v.) and 2900 Å. (4.3 v.). The latter absorption region is interpreted, according to Franck, Kuhn and Rollefson, as representing dissociation of the *ionic* molecule into a normal potassium atom and a normal CN radical and agrees within 0.5 v. with the calorimetric data, supplemented by an estimate of the heat of sublimation (48.8 k. cal.). The former absorption act takes place at an energy 1.4 v. greater and represents dissociation into a normal and an excited dissociation product (K excitation 1.6; CN, 1.8 v.). The change with temperature in stability of the two molecular forms postulated by Franck and Kuhn is explained in the light of the free energy.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES.[1] III. THE DESIGN OF CELLS

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Historical Introduction

In 1923 H. C. Parker[2] published two papers which challenge a fundamental postulate of the Kohlrausch method for the measurement of the conductance of electrolytes, by the observation that "cell constants" are apparently not really constant but vary with the resistance being measured. If a solution of specific conductance, κ, is placed in a cell, A, whose length is l and whose cross section is a, then the fundamental premise of the Kohlrausch method is that the resistance, R_A, is given by the equation

$$R_A = \left(\frac{l}{a}\right)_A \frac{1}{\kappa} \tag{1}$$

$(l/a)_A$ is designated as the "cell constant"[3] and has been assumed to have a fixed value for any given cell at a given temperature, and this assumption is vital for the Kohlrausch method.

If we have two different cells, A and B, and fill them with the same solution and designate the corresponding resistances and cell constants by

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[1] The first two papers in this series are: Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and Giles M. Bollinger, *ibid.*, **51**, 2407 (1929).

[2] H. C. Parker, *ibid.*, **45**, 1366, 2017 (1923).

[3] If the cross section is not uniform the cell constant is $\int_0^l \frac{dl}{a}$.