Raman Line of Cyanide Ion

George Glockler and H. T. Baker

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The Carbon–Hydrogen Bond Strengths in Methane and Ethane

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WE have determined, from the kinetics of the photochemical methane-bromine and ethane-bromine reactions, the activation energies of simple steps which can be used to calculate the upper limits of the binding energies of the systems CH_3–H and C_2H_5–H. Additional research, coupled with highly probable analogies, establishes the absolute bond strength with considerable certainty in the case of methane, and an uncertainty of not more than 2 kcal. for ethane.

The dependence of the photochemical rate of bromination of methane on concentrations, light intensity, and total pressure establishes the following mechanism:

(1) $Br_2 + h\nu = 2Br$
(2) $Br + CH_4 = CH_3 + HBr$
(3) $CH_3 + Br_2 = CH_3Br + Br$
(4) $CH_3 + HBr = CH_4 + Br$
(5) $Br + Br + M = Br_2 + M$.
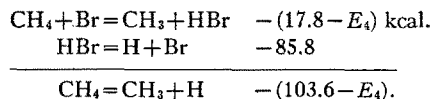
The over-all reaction rate derivable from this chain, and agreeing with the experimental facts, is

$$\frac{d(CH_3Br)}{dt} = \frac{k_2 k' I^{\frac{1}{2}}(CH_4)(Br_2)^{\frac{1}{2}}(1/C_{tot})^{\frac{1}{2}}}{1 + k_4(HBr)/k_3(Br_2)},$$

where I is the incident light intensity, k' a non-temperature-dependent apparatus constant, and C_{tot} the total concentration of all gases. The exact similarity with the hydrogen-bromine reactions, investigated by the Bodenstein school, will be noted; indeed, the bond strength derivation is modeled after that of the H − H bond, as described in detail by Bodenstein and Jung.[1]

The temperature dependence of the over-all rate, which is clearly ascribable to reaction (2), is such that E_2, the activation energy, is 17.8 kcal. Since the energy change in a simple reaction is equal to the difference in activation

energies, we have

$$CH_4 + Br = CH_3 + HBr \quad -(17.8 - E_4) \text{ kcal.}$$
$$HBr = H + Br \quad -85.8$$
$$\overline{CH_4 = CH_3 + H \quad -(103.6 - E_4).}$$

The energy of dissociation of hydrogen bromide is from the best available thermal and spectroscopic data.[2, 3]

The activation energy of (4) is believed to be very small, since it is similar to the reaction of hydrogen atoms with hydrogen bromide, whose activation energy is only about 1 kcal.[4] Its magnitude was nonetheless determined in two independent ways: (a) The temperature variation of inhibition by hydrogen bromide—through step (4)—showed that $E_4 - E_3$ was about 2 kcal., with some uncertainty because the rate is rather insensitive to changes in k_4/k_3. (b) The yield of methane in the photolysis of methyl iodide-hydrogen bromide mixtures, which is attributable to reaction (4), shows that E_4 is about 0.8 kcal. greater than the activation energy of

$$CH_3 + I_2 = CH_3I + I,$$
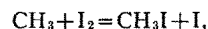
which a considerable body of evidence indicates as proceeding on practically every collision. We choose $E_4 = 1.5 \pm 1$ kcal. as a sufficiently conservative estimate from these experiments.

Combining this quantity with the maximum, the bond strength becomes 102 ± 1 kcal.

A similar study of the photochemical bromination of ethane gave an activation energy of 13.8 kcal., so that the maximum value here is $13.8 + 85.8 = 99.6$ kcal. The difference in the activation energies of the corresponding reactions (4) and (5) was zero in this case. No experiments of the type described under (b) were performed, but it is reasonable to assume that E_3 is not much more than 2 kcal. If this is done, the bond strength is, in round numbers, 98 ± 2 kcal. in ethane.

The experimental details, as well as additional theoretical aspects, will be published in a series of papers as soon as the pressure of other work permits.

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[1] Bodenstein and Jung, Zeits. f. physik. Chemie 121, 127 (1926).
[2] Beutler, Zeits. f. physik. Chemie B29, 315 (1935).
[3] A. R. Gordon and C. Barnes, J. Chem. Phys. 1, 692 (1933).
[4] J. C. Morris and R. N. Pease, J. Chem. Phys. 3, 796 (1935).

Raman Line of Cyanide Ion

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IN a study involving the force constant of the cyanide ion, we noticed incidentally two lines (838 and 2080 cm^{-1}) mentioned by Hibben.[1] The original experiments were carried out by Pal and Sen Gupta[2] on potassium cyanide solutions. For a diatomic ion only one Raman line should be found. From other compounds containing the cyanide group 2080 cm^{-1} evidently is its frequency. The lower vibration must, therefore, be spurious, either because of the use of an improper excitation line or because of the presence of an impurity. We determined the Raman spectrum of sodium cyanide solutions (Hilger E(2) spectro-

graph, Eastman I-J spectrographic plates, 4358A Hg lines for excitation). We find one line only corresponding to a frequency of 2086.7 ± 2.7 cm^{-1}, as the average of six different measurements. No trace of the lower frequency appears on any of our plates. Further study convinced us that the low vibration is caused by a line of the cyanate ion.[2] Its presence as an impurity in cyanide because of oxidation of the initial material by atmospheric oxygen is readily understood. The force constant of cyanide ion is 1.65 megadynes per cm.

[1] J. H. Hibben, *The Raman Effect and Its Chemical Applications* (Reinhold Publishing Corporation, New York, 1939), Table 90, p. 453.
[2] N. N. Pal and P. N. Sen Gupta, Ind. J. Phys. **5**, 13, (1930).

On the Heat of Sublimation of Carbon

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ON the basis of a theoretical interpretation of the absorption spectra of benzene, butadiene, and hexatriene, Kynch and Penney[1] in a recent paper come to the conclusion that "the weight of evidence in favor of L (heat of sublimation of carbon) = 170 kcal./mole is overwhelming." Accordingly, they conclude that there is no discrepancy between the dynamically and statically determined heat of sublimation and that the explanation of this discrepancy suggested by Herzberg, Herzfeld, and Teller[2] is unnecessary and unsound. Kynch and Penney have, however, overlooked important published work which, in the writer's opinion, eliminates definitely the value $L = 170$ kcal./mole and only permits values of $L \leqslant 135$ kcal./mole.

A value $L = 170$ kcal./mole would imply, as Kynch and Penney realize, that the heat of dissociation of carbon monoxide $D(CO)$ is 11.111 ev (256.1 kcal./mole).[3] However, Faltings, Groth, and Harteck[4] have shown that carbon monoxide is dissociated by absorption of light of wave-length 1295A (but not of light of wave-length 1470A) with a quantum yield one. This experiment seems to prove that $D(CO) \leqslant 9.57$ ev and therefore that $L \leqslant 135$ kcal./mole. It would at any rate require rather artificial assumptions to account for this photolysis on the basis of $D(CO) = 11.111$ ev. Accordingly, the apparent agreement obtained by Kynch and Penney between the long wavelength limits of the observed absorption spectra of benzene, butadiene, and hexatriene with those calculated on the basis of $L = 170$ kcal./mole seems to be due to a chance coincidence.

In addition to this apparent agreement, Kynch and Penney give some further evidence which, in their opinion, supports $L = 170$ kcal./mole. They say that the old Birge-Sponer extrapolation of the vibrational levels of the ground state of CO leads to 11.34 ev for $D(CO)$ in good agreement with their adopted value (11.054 ev). However, it is now well known that for almost all diatomic molecules in their ground states the linear extrapolation of the first vibrational quanta gives a value for D_0 that is 20–40 percent too high. If anything, therefore, the vibrational levels are in favor of the lower $D(CO)$ value.

Furthermore, Kynch and Penney refer to the work of

White[5] who found the heat of dissociation of C_2N_2 into 2CN to be 6.33 ev by measuring the equilibrium concentration of CN in C_2N_2. This value for $D(C_2N_2)$, on the basis of thermochemical equations and with $D(CO) = 11.111$ and 9.144 ev, leads to $D(CN) = 6.43$ and 4.46 ev, respectively. The smallness of the latter value is taken as evidence against $D(CO) = 9.144$ and $L = 170$ kcal./mole. However, White's $D(C_2N_2)$ value seems to be open to serious objection since it is about equal to or larger than $D(CN)$. Even considering the resonance between the single and triple bonds in C_2N_2 one would certainly expect that the energy required to break the C−C bond in C_2N_2 is appreciably smaller than the energy required to break the C≡N bond. If one accepts White's value for $D(C_2N_2)$, that is, admits a failure of valence theory for as simple a molecule as C_2N_2, it seems one could not expect a quantitative agreement of calculations based on this theory with experiment for such complicated molecules as butadiene, hexatriene, and benzene. If any such agreement is obtained it would appear to be fortuitous.

It may be mentioned that White's results disagree strongly with the earlier low dispersion work of Kistiakowsky and Gershinowitz[6] who obtained the very reasonable value $D(C_2N_2) = 77$ kcal./mole. At any rate it appears that White's determination of $D(C_2N_2)$ is much less direct and more subject to errors than the determination of an upper limit of $D(CO)$ by observing its photo-dissociation.

Finally, Kynch and Penney refer to the considerations of Baughan[7] who considers the difference between the heat of removal of the first H atom from CH$_4$ (103.6 kcal.) and the average C−H bond strength (87.3 kcal.), as obtained from $L = 124$ kcal. and the heat of formation of CH$_4$, as evidence against the low value of L. He finds that with $L = 169$ kcal. one obtains an average C−H bond energy of 98.6 kcal. which is almost equal to the heat of removal of the first H atom. However, the energy of dissociation of CH is known to be 80.0 kcal.[8] showing that considerable differences between the heats of removal exist (as it does also for H$_2$O). Hence there does not appear to be any difficulty from this angle in adopting a low value for L. Rather the opposite is the case.

The discussion of the mechanism of the sublimation of graphite by Herzfeld, Herzberg, and Teller[2] was meant as a possible explanation, not (as Kynch and Penney seem to think) as supporting evidence for the discrepancy between Marshall and Norton's L (obtained from rates of evaporation of carbon in vacuum) and the equilibrium L obtained from the spectrum. But later unpublished work by Johnston and Marshall[9] seems to confirm this explanation since an exceedingly small accommodation coefficient was found for carbon atoms on graphite. Johnston and Marshall have also shown that Bassett's[10] determination of the triple point of carbon is only compatible with a low (equilibrium) value for the heat of sublimation.

A great deal of work on the ionization and dissociation of CO, CH$_4$, and other molecules by Tate and his co-workers also seems to rule out $D(CO) = 11.144$ ev and favor $D(CO) \sim 9.6$ ev [see, for example, Hagstrum and Tate].[11]

From all this it seems to follow that the weight of