

Relations between CarbonCarbon Bond Energy, Order, and Interatomic Distance

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Citation: [The Journal of Chemical Physics](#) **15**, 77 (1947); doi: 10.1063/1.1746296

View online: <http://dx.doi.org/10.1063/1.1746296>

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Letters to the Editor

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Ultraviolet Absorption Spectrum of Nitric Oxide

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November 29, 1946

Mulliken¹ has predicted a stable ${}^4\Pi$ state for NO which should be approximately 4.5 volts above the normal ${}^2\Pi$ state. One might therefore expect a weak absorption band system to occur in the spectral region $\lambda\lambda 3500\text{--}2200\text{\AA}$ corresponding to a ${}^4\Pi\leftarrow{}^2\Pi$ transition. Since CO shows a somewhat similar transition (${}^3\Pi\leftarrow{}^1\Sigma$) with an absorbing path of 1 meter² it seems not unreasonable to expect that the ${}^4\Pi\leftarrow{}^2\Pi$ transition of NO would be observed under comparable conditions. Experiments by Mundie,³ however, with a path length of 6 meters, were not successful.

It was considered desirable to extend this investigation by using much longer paths of the absorbing gas. A path of 30 meters length was obtained by multiple reflection in a tube 1.5 meters long by using the method of White.⁴ Nitric oxide pressures of 700, 300, 150, and 75 mm of mercury were used; corresponding to 28, 12, 6, and 3 meter-atmosphere paths, respectively.

Extreme purity of the NO was necessary. The gas was prepared by the action of sulfuric acid on potassium nitrite in the presence of potassium iodide and purified by bubbling through a 60-cm column of 90 percent H_2SO_4 , a 120-cm column of 50 percent KOH, a dry ice trap, and a P_2O_5 tube. The resulting gas was then solidified in a liquid-air bath and the pure NO distilled off into the absorption tube. The purity of the gas can be judged from the fact that NO_2 absorption bands were absent from all spectra obtained with the above-mentioned path lengths (in spite of their considerable intrinsic intensity), and the HNO_2 absorption bands at $\lambda 3400$ described by Melvin and Wulf⁵ were observed very weakly only at the highest pressure used (700 mm i.e., a path length of 28 meter-atmospheres).

At pressures less than 150 mm the only NO absorption found down to $\lambda 2200$ was the 0-1 band of the γ system. This band could be readily photographed in a few minutes with a conventional hydrogen source and a Hilger medium quartz spectrograph (which were used throughout). At higher pressures a strong continuous absorption setting in at about $\lambda 2600$ made observation at shorter wave-lengths

impossible. No discrete NO absorption was observed above $\lambda 2600$ at 700-mm pressure, above $\lambda 2500$ at 300-mm pressure, and above $\lambda 2400$ at 150-mm pressure. These negative results show that either the ${}^4\Pi$ state has not the predicted energy or that the ${}^4\Pi\leftarrow{}^2\Pi$ transition is much weaker than expected. This latter alternative does not appear very likely since even the ${}^1\Sigma\leftarrow{}^3\Sigma$ transition of O_2 , which arises solely from magnetic dipole radiation, and is thus much more strictly forbidden than the ${}^4\Pi\leftarrow{}^2\Pi$ transition of NO,⁶ is readily observed under comparable conditions in an 18-meter path.⁷

The origin of the continuous absorption below $\lambda 2600$ is not clear. It cannot be due to NO since its dissociation energy is 5.29 eV and therefore a continuous absorption cannot occur above $\lambda 2340\text{\AA}$. The observed continuous absorption may be due to an impurity (perhaps HNO_2) or to N_2O_2 molecules which according to Johnston and Weimer⁸ are probably present in NO at atmospheric pressure.

The absorption spectrum of liquid NO was also obtained through a 3-cm path at -152°C , with a tungsten filament as source. A strong continuous absorption starting at $\lambda 4000$ and extending to shorter wave-lengths, and one at $\lambda 5600$ and extending to longer wave-lengths were observed. Maximum transmission occurs around $\lambda 4600$. These results agree with those obtained by Vodar.⁹

Since liquid NO is completely associated¹⁰ the strong violet and red cut-offs are very probably due to N_2O_2 molecules.

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Relations between Carbon-Carbon Bond Energy, Order, and Interatomic Distance

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December 13, 1946

It is well known that smooth curves can be drawn through the points of plot of bond-energy (and energy of dissociation), bond-order, and interatomic distance for carbon-carbon bonds. Several investigators¹⁻⁴ have derived empirical equations fitting such curves.

Inspection of the curve drawn through the points plotting the bond-order, N , of C-C, C=C, and C \equiv C bonds against the bond-energy, E (58.6, 100, 123 kcal./mole, respectively)⁵ indicate a curve of the type,

$$(N_0 - N)^p = k(E_0 - E) \quad (1)$$

where N_0 , E_0 , p , and k are constants. Making use of the point (0, 0), corresponding to $E = N = 0$, k can be eliminated from (1) giving

$$[1 - (N/N_0)]^p = 1 - (E/E_0). \quad (2)$$

The solution of Eq. (2) is facilitated by differentiating with respect to E or N and substituting for the derivative values of the slope measured from the curve. In this manner the constant p is found to be equal to 2 so that Eq. (2) becomes that of the parabola

$$[1 - (N/N_0)]^2 = 1 - (E/E_0) \quad (3)$$

with vertex at (N_0, E_0) . The solution of this equation, by using the known values of E and N , gives $N_0 = 4$, $E_0 = 133$. Equation (3) becomes

$$[1 - (N/4)]^2 = 1 - (E/133) \quad (4)$$

which fits the known points with an accuracy of 0.8 percent.

The value of the constant $N_0 = 4$ is, perhaps, significant since theoretically this is the maximum bond-order for carbon-carbon bonds as well as being the number of carbon valence electrons. The interesting result follows that, according to Eq. (4), the maximum value of E is 133 kcal./mole, namely that of the hypothetical carbon-carbon quadruple bond.

From Eq. (4) we can calculate the carbon-carbon bond-order for benzene. Substituting the benzene value of 85.9 kcal./mole ($1/6 [Qf(\text{benzene})^6 - 6E_{C-H}^6]$) for E in Eq. (4), one obtains $N = 1.62$. This is identical with the value obtained by Penney⁶ through quantum-mechanical considerations and compares well with the empirical values found by others.^{1,3,4}

A recent equation³ by the author relates bond-order and interatomic distance of covalent bonds. For carbon-carbon bonds this type takes the form

$$D = a + b(n - \frac{1}{2}/n + \frac{1}{2})^N, \quad (5)$$

where D is the interatomic distance in Å, n the principal quantum number of the valence electrons, a and b constants, and N the bond order. Eliminating N from (4) and (5) we have an equation

$$D = a + b(n - \frac{1}{2}/n + \frac{1}{2})^\gamma, \quad (6)$$

where $\gamma = 4 - 4(1 - E/133)^{1/2}$, relating bond-energy and interatomic distance. Substituting the numerical values³ of n , a , and b , we have

$$D = 1.015 + 0.875(3/5)^\gamma. \quad (7)$$

Cherton² has given a simple linear expression relating these same quantities. His equation has the form

$$E = (1.89 - D)m, \quad (8)$$

where m is a constant of proportionality. It is most interesting to observe that for $E = 0$ Cherton's equation gives the value $D = 1.89\text{Å}$, which is precisely the value obtained from D from (7) when $E = 0$ (or from (5) when $N = 0$, i.e., $a + b = 1.89\text{Å}$). Considering Eq. (5) we have by simultaneous solution of the three equations obtained in D_1 , D_2 , and D_3 by letting $N = 1, 2, 3$ the identity

$$a + b \equiv \frac{D_2(D_2 - D_1) + D_1(D_1 - D_3)}{D_2 - D_3} \equiv 1.89\text{Å}, \quad (9)$$

where D_1 , D_2 , and D_3 are the accepted values of C-C, C=C, and C≡C bonds (1.54Å, 1.33Å, 1.204Å, respectively³).

From the point of view of possible theoretical significance Eq. (7) has the advantage that it does not allow values of $D = 0$ in accordance with physical considerations, whereas this is not true in the case of Cherton's equation.

In papers by Douglas Clark¹ and Fox and Martin⁴ values of the energy of dissociation, E_D , are given for C-C, C=C, and C≡C bonds and the benzene carbon-carbon bond (71.8, 125.1, 161, and 105.3 kg cal., respectively). The modified form of Eq. (4)

$$[1 - (N/4)]^2 = 1 - (E_D/167) \quad (10)$$

fits the C-C, C=C, and C≡C values of E_D to within 1.5 percent. Using the benzene value of E_D in Eq. (10) we obtain a bond order of 1.62 for the benzene bond which again is identical with Penney's derivation.

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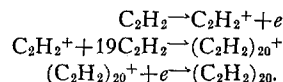
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On the Polymerization of Unsaturated Hydrocarbons by Ionizing Radiations

WARREN M. GARRISON

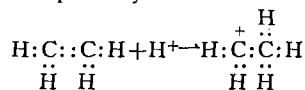
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December 16, 1946

It has been shown that α -particles^{1,2} polymerize acetylene to give solid polymer with a composition corresponding to $(C_2H_2)_n$. Approximately twenty acetylene molecules are removed from the gas phase per ion-pair formed. To explain these results Lind and Bardwell³ postulated an ion cluster theory involving twenty acetylene molecules condensed about a positive ion nucleus:



Although there is some theoretical evidence for clustering, it is of interest to note that the polymerization of acetylene by ionizing radiations can be explained in terms of both an ionic and free radical mechanism either of which may be initiated by $C_2H_2^+$ ions.

In an ionic or Friedel-Crafts polymerization aluminum chloride, boron trifluoride, protons, and other strong acids lower the activation energy by combining with the ionic activated state in which two electrons of the unsaturated bond occupy the same orbital.⁴ It has been shown, for example,⁵ that in the acid polymerization of ethylene the primary process is probably:



It is suggested here that in the polymerization of acetylene by ionizing radiations the $C_2H_2^+$ ions⁶ may act as the acid catalyst by combining with the negative carbon atom of