

The Coordinate Scheme in Crystalline Boron

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Citation: *The Journal of Chemical Physics* **18**, 1121 (1950); doi: 10.1063/1.1747888

View online: <http://dx.doi.org/10.1063/1.1747888>

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that reactivity is conditioned by another factor than electronic density of the molecule in its equilibrium position.

A detailed analysis of this problem has convinced us that the only simple way to solve the present contradiction between the accepted ideas and the facts was to abandon the static pattern and to adopt a dynamic one involving the molecular vibrations.

It is indeed well known that one of the out-of-plane fundamental vibrations of ethylene is a twisting vibration [$\delta \leq 1015 \text{ cm}^{-1}$].⁴ This gives rise to a torsion of the CH_2 groups with respect to one another through an angle amounting to several degrees in the first excited state ($v=1$). According to our knowledge of the electronic structure of a double bond it is to be expected, therefore, that the overlapping of the π -orbitals decreases in the course of such a motion, which means that the strength of the π -bond also decreases. In other words, one might say that several percent of the electrons forming the bond become effectively free and are responsible for the nucleophilic reaction of addition with the halogenated acids.

In the case of acetylene, on the other hand, such a dissociating twisting vibration does not appear among the fundamental movements on account of the linearity of the molecule. This has the important consequence of decreasing to a great extent its relative reactivity.

This specific vibrational effect not only provides a way out of an important particular difficulty of reactivity, but is furthermore able to furnish a unifying principle embracing any additional reaction. For instance, we should mention that it is easy to show that the reactions between benzene and the halogens, and the very peculiar 1.4 addition of the halogens to butadiene, can now be explained by making use of appropriate out-plane vibrations, which characterize the symmetry of these molecules. We therefore suggest identifying as addition-vibrations those twisting vibrations which are able to dissociate π -bonds.

Let us now turn our interest to another fundamental type of reaction, i.e., substitution reactions. It is well known⁵ that, above 350°C , substitution of ethylene by halogens starts to predominate over addition, giving such products as $\text{C}_2\text{H}_5\text{Cl}$. This change of reactivity cannot be reconciled with the current ideas based on a static pattern. Indeed, in such a case the distribution of the electronic density in the molecule is not expected to be changed by a rise of temperature. Furthermore, the static dipole moment bound to the CH bond being practically zero for ethylene,⁶ no electrophilic point of attack is available on the hydrogens to react with Cl^- of the supposed Cl^+Cl^- chlorine molecule. As for the addition reaction, it is possible, if we adopt a dynamic system, to recognize ethylene vibrations, especially valency and bending vibrations ν_{CH} (1343 cm^{-1}) and δ_{CH} (3107 cm^{-1}), required by our accepted scheme of reaction. These vibrations indeed are able to bring a negative charge on the carbons and a positive charge on the hydrogens. This possibility arises from a discussion of changes of hybridization at the carbon atom when the molecule is distorted in a certain way from its equilibrium position.⁷ That the magnitude of these charges appearing on the atoms as a consequence of their motion is not negligible is strongly supported by a recent work⁸ which shows that the correct intensity of infra-red absorption in ethylene can only be interpreted on the assumption that a rather important dipole moment bound to the CH vibrating bonds does exist. Therefore, it is quite permissible to admit that positive charges at least as large as $e/50$ could be brought up to, and then taken away from a hydrogen atom in the course of the vibration. It is to be noticed that the σ -electrons and consequently only planar vibrations are involved in the substitution process, whereas the π -electrons alone, i.e., out-of-plane vibrations, are responsible of the addition reaction. This specific character of vibrations toward reactivity is also of great significance in explaining the influence of temperature on the orientation of the reaction. Indeed, out-of-plane vibrations are small with respect to planar ones, which means that by increasing temperature, we produce a relative increase in the proportion of molecules in states such as ν_{CH} and δ_{CH} with respect to δ . This is not in disagreement with the experimental fact that the substitution reaction predominates at

higher temperatures. On the other hand, arguments can be put forward in favor of the idea that the π -electrons tend to lose their normal properties when, at high temperature, the amplitude of the twisting frequency becomes large. This would tend to support the observed fact that addition reactivity even decreases in these conditions.

It is now to be strongly presumed that the specific properties of vibrations should be considered in the field of reactivity. This new factor, which seems of a very general importance, opens the road to a development of a theory through which we could envisage the possibility of determining *a priori* the best conditions to orient a chemical reaction in the direction desired. Of course, these considerations do not destroy the importance of the part played by effects connected with the static pattern, such as inductive and mesomeric effects. These last phenomena have, on the contrary, to be considered, as well as the vibrational effect, in order to reach a satisfactory representation of the facts. It follows from the present developments that infra-red photo-activation should be possible.

A full account of this preliminary note will appear elsewhere.

My best thanks are due Professors C. A. Coulson and C. K. Ingold for a helpful and stimulating correspondence.

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The Coordinate Scheme in Crystalline Boron

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June 7, 1950

PRELIMINARY x-ray diffraction studies of crystalline boron have been reported,¹ but as yet it has not been possible to index the powder pattern, or to get satisfactory crystals for single

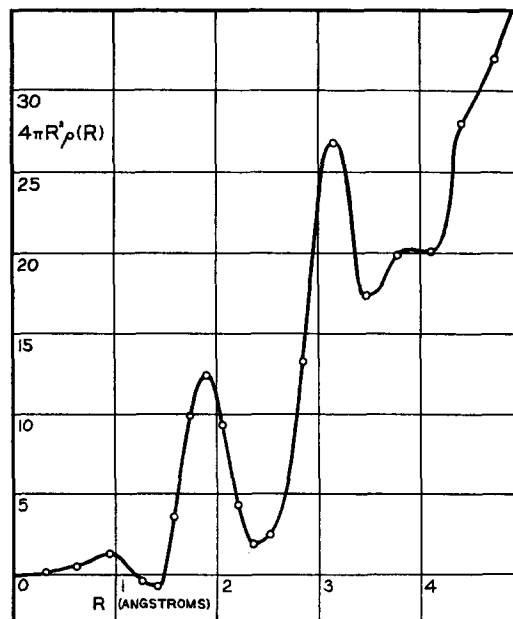


FIG. 1. Radial distribution curve for crystalline boron.

crystal patterns. The coordination scheme (number of nearest neighbors and interatomic distances) can be determined by a Fourier integral analysis² of the powder pattern, even when the pattern cannot be indexed and a complete structure determination is not possible.

The sample used in this investigation was boron of density 2.30 g/cm³ and of purity presumably greater than 99 percent. The crystalline form can be partially characterized by the prominent "*d*" values: 7.99, 5.52, 5.05, 4.69, 4.48, 3.57, 2.94, 2.86Å. The Fourier analysis was made from the microphotometer record of a powder pattern made with crystal monochromated MoK α -radiation in a camera of diameter 8.93 cm. The area of the first peak of the radial distribution curve (Fig. 1) corresponds to 6.15 atoms. The area and position of this peak indicate six nearest neighbors at an average distance of 1.89Å in crystalline boron.

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² Hultgren, Gingrich, and Warren, *J. Chem. Phys.* **3**, 351 (1935).

The Absorption Spectrum and the Dissociation Energy of Fluorine

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May 29, 1950

RECENT spectroscopic and thermal data on the heats of formation and dissociation of ClF¹ have cast doubt upon the value of 60 kcal. of the heat of dissociation, D_0 , of F₂. The indications are that D_0 =30–40 kcal. Pitzer² more or less arbitrarily assumed a tentative value of 50 kcal.

Wicke³ has questioned the interpretation of the absorption spectrum of ClF, suggesting that the low intensity of the bands are not in agreement with the Franck-Condon principle. He also measured the thermal conductivity of fluorine as a function of the temperature and found it to agree with the conductivity of nitrogen. Since his calculated curves for F₂ and N₂ almost coincide if no dissociation occurs, Wicke concluded that his experiments supported a high dissociation energy. Finally, a low D_0 of F₂ would correspond to an electron affinity of fluorine which would be below that of chlorine.

These arguments are not conclusive.

1. If the interpretation of the absorption spectrum of ClF is wrong, the true D_0 of ClF could only be lower than the one obtained from spectroscopic data. This would lower the dissociation energy of fluorine, rather than increase it.

2. In the calculations of the heat conductivity a value for the collision cross section and for the vibrational frequency occurring in the specific heat had to be assumed. For the latter the value 856 cm⁻¹ was calculated by Murphy and Vance with Badger's rule and the values for the other halogens and the interatomic distance.⁴ Recently Andrychuk⁵ obtained the Raman spectrum of fluorine and found the value 892 cm⁻¹. The difference with the assumed value will have only a small effect on the calculated heat conductivity.

More serious is the assumption that the collision cross section of F₂ lies between that of O₂ and of N₂, although the interatomic distance is larger than either of the two, *viz.*, 1.48Å as compared to 1.10Å for N₂ and 1.21 for O₂. Using the values given by Pauling,⁶ for the van der Waals radii of oxygen, nitrogen and fluorine, one finds the largest dimension of the diatomic molecules to be: 4.01Å for O₂, 4.10Å for N₂ and 4.18Å for F₂. The collision cross section at $T = \infty$ may be several percent, probably five-ten percent higher than assumed by Wicke. This would cause the calculated curve for F₂ to be ten percent or more below the curve for N₂. Since the experimental results for N₂ and F₂ coincide to within ± 10 percent, the heat conductivity experiments conducted by Wicke are not at all conclusive.

The probability of a low D_0 for F₂ was reason to investigate the absorption spectrum of F₂ in the photographic infra-red. The visible region was investigated by Gale and Monk⁷ who could not detect any absorption. The region covered by the present work extended from 7000Å to 9600Å.

The spectra were obtained in a Baird spectrograph with a 3m concave grating and photographed on Eastman I-N and (hyper-sensitized) I-M plates. The light source was a tungsten ribbon lamp. A Corning-3480 filter was placed in the light beam in order to cut out the blue, which would otherwise have shown up as a second-order spectrum. A 185-cm Pyrex tube was used as the absorption cell. The fluorine was introduced into the cell under a pressure of approximately one atmos.

The only absorption that could be detected was the forbidden oxygen band at 7600Å and water absorption around 9000Å, due to the long light path through air (7m). The detection of the oxygen band is evidence of the sensitivity of the method, and it may be concluded that there is no allowed transition for F₂ from the ground state to an attractive upper state in the region 7000–9600Å. The sensitivity of the instrument toward detection of a possible weak continuous absorption resulting from a transition to a repulsive state is not as high, however, as that toward the detection of discrete absorption lines, because of the large dispersion (5.55Å/mm). No definite conclusions can, therefore, be drawn about the dissociation energy of fluorine from this work.

The thermochemical work on ClF, however, as well as the large interatomic distance of fluorine presumably caused by outer shell repulsion, and the doubtfulness of the interpretation by Wicke of his thermal conductivity measurement, favor the low value of the dissociation energy of fluorine.

I would like to thank Professor L. Brewer for the many discussions on the subject and also for providing the fluorine; Professor F. A. Jenkins for the discussions, and Dr. C. Thurmond for his aid in building the transferring system for the fluorine.

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¹ See, e.g., R. L. Potter, *J. Chem. Phys.* **17**, 957 (1949).

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The Ionization Potential of Cyclopropane of Electron Impact

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May 29, 1950

WE have determined the ionization potential of cyclopropane by electron impact and find its value to be 10.14 ± 0.05 volts.

The measurements were made with a Westinghouse Type LV mass spectrometer using the vanishing current method.¹ The calibrating gas of known ionization potential and the cyclopropane were introduced simultaneously. The potential normally used to move the ions from the region in which they are formed through the slit in the first ion-accelerating electrode (the ion-drawout or pusher potential) was maintained at zero in order to obtain a satisfactory degree of reproducibility of results. The sensitivity of the instrument was thus diminished, but the energy spread of the ionizing electrons was also diminished. The voltage of the ionizing electrons was measured by means of a voltage divider placed across the electrodes of the electron gun and a Leeds and Northrup Type K-2 potentiometer. The accuracy of the voltage