obtained are very close to Luft's estimation (110° and 135–160°, respectively).[8] It is of interest to see that the tetrahedral structure of valence angle is almost preserved in the ground state of the radical as in the ammonia molecule. The calculated value of a $^2B_1 \rightarrow ^2A_1$ transition (1.8 ev) is in fairly good agreement with the experimental data, in which the observed absorption spectrum is in the region of 4500–7400A.[1] The $^2B_2$ state is, however, calculated to locate higher than in Mulliken's prediction.[1] This is mainly due to the facts that the present calculation ignores configuration interaction and that the variational procedure is carried out for the $^2B_1$ state only. Especially, the second $^2B_2$ state $K(1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^1$ is very close to the lowest $^2B_2$ state, and then the effect of configuration interaction may be probably large. The experimental results will be explained more clearly if configuration interaction is included.

The complete details of the calculation will be published later.

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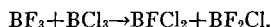[8] N. W. Luft, Discussions Faraday Soc. No. 14, 114 (1952).

An Infrared Study of the BF_3-BCl_3 Reaction*

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A PRELIMINARY kinetic study has been made of the gas-phase reaction,

$$BF_3+BCl_3 \rightarrow BFCl_2+BF_2Cl.$$

A fast-scanning infrared spectrometer[1] was used to follow the changes in intensity of the appropriate absorption bands.

The reaction was carried out in apparatus similar to that used in previous studies of rapid gas-phase reactions.[2] An 11.4-cm absorption cell with rocksalt windows was employed. The reacting gases were admitted to the evacuated cell from storage bulbs through jet tips insuring rapid mixing of the reacting gases.

Matheson BF_3 was used without purification except that a quantity of the gas was condensed and redistilled into a storage bulb, the middle third of the distillate being taken. The BF_3 was
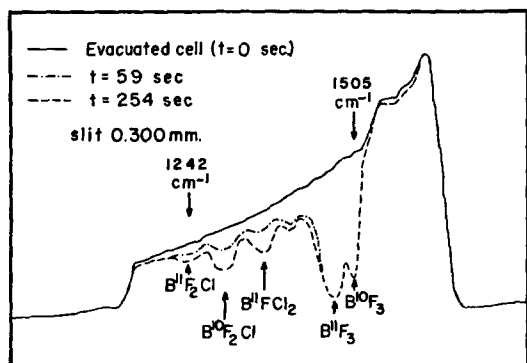

FIG. 1. Infrared spectra of the BF_3-BCl_3 reaction.

pressurized with dry nitrogen. The other jet storage bulb was filled with Matheson Technical BCl_3 which had been redistilled in the same way as the BF_3 and was pressurized to the same total pressure. Halocarbon grease was used on the stopcocks and ground joints of the vacuum system since Apiezon stopcock grease was rapidly attacked by these gases. Pressures were read with a mercury manometer without any noticeable attack of the mercury.

With the spectrometer running, the stopcocks leading to the absorption cell were opened simultaneously and absorption bands of BF_3, $BFCl_2$, and BF_2Cl were recorded. Figure 1 shows the results of a typical experiment in which the spectral region was scanned about 3 times a second. In this case the initial pressure of BF_3 and BCl_3 was 6.6 mm Hg and the total pressure was 342 mm Hg at 23°C.

This reaction does not go to completion and so the back reaction would have to be considered in a detailed kinetic study. However, from the data early in the reaction the half-life for the forward rate is estimated to be on the order of 10 minutes. This would call for a second-order rate constant of about 5×10^3 cc (mole)$^{-1}$ (sec)$^{-1}$. Garvin and Kistiakowsky[3] have studied the reaction of BF_3 with tri-, di-, and monomethyl amine and found these reactions to be extremely rapid. In this reaction a complex $R_3N:BF_3$ is formed with a very small energy of activation. One might expect the BF_3-BCl_3 reaction to be very rapid if it goes through a bridged intermediate similar to B_2H_6 or Al_2Cl_6. In view of the rather slow rate this does not seem to be the case; at least, the reaction must involve a significant activation energy.

We would like to thank Professor R. A. Ogg, Jr., of Stanford University for calling this interesting reaction to our attention. We are also very grateful to Professor M. K. Wilson of Harvard University for supplying us with spectra of the molecules, BF_3, BCl_3, $BFCl_2$, and BF_2Cl and their vibrational assignments.

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Selection Rules and Frequencies of the Skeletal Vibrations of Long Chain Polymers in the Crystalline State

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IN the interpretation of the infrared spectra of long chain polymers attention has hitherto been concentrated almost exclusively on the identification of nonskeletal frequencies, such as those characteristic of CH, OH, NH, and carbon-halogen groups, and the majority of the bands occurring below 1300 cm^{-1} are either unassigned or vaguely referred to as skeletal vibrations. In the course of a systematic study of the spectra of a variety of polymers between 2.5μ and 100μ we have found that the following method of dealing with the skeletal frequencies offers considerable promise.

The skeletal frequencies of long chain paraffins have been discussed by Kirkwood,[1] Pitzer,[2] Mizushima and Simanouti,[3] and others.[4-6] Kirkwood and Pitzer used a modification of the Born-Karman treatment[7] of a one-dimensional lattice and arrived at equations of the form

$$\nu_\pm^2(k_1,k_2,\lambda)=0 \quad \text{(for in plane frequencies)} \tag{1}$$

and

$$\nu^2(k_3,\lambda)=0 \quad \text{(for out of plane frequencies),} \tag{2}$$

where λ is the phase difference between successive carbon atoms in the chain, which is assumed to be a planar zig-zag, and the

k's are force constants. We have found this method very useful although we would suggest that the possible values of λ should be governed by the equation

$$\lambda = \pi 1/(N-1) \quad \text{with} \quad 1=0, 1, 2 \cdots N-1, \qquad (3)$$

instead of

$$\lambda = \pi 1/N \quad \text{with} \quad 1=1, 2 \cdots N-1, \qquad (4)$$

where N is the total number of atoms in the finite chain.

However, out of all of these $3N$ skeletal frequencies (which include the translation and rotation of the molecule as a whole), only a very small number can give rise to infrared absorption if the molecule is in the crystalline state. The fundamentals which can be strong in absorption are only those in which corresponding atoms in each unit cell move in phase. For a finite chain, the intensity of those vibrations in which unit cells do not move in phase can be shown to be very much weaker; for an infinite chain they will have zero intensity. Thus, if there are p atoms of a single chain within the unit cell then, according to the above criterion, only those modes for which

$$\lambda = 2\pi r/p \quad (\text{where } r=0, 1, \cdots p-1) \qquad (5)$$

can be potentially active in absorption. Whether even those will be active depends on the change of dipole moment associated with them. This gives a maximum of $3p$ potentially active skeletal vibrations, of which 4 are of zero frequency and correspond to 3 translational motions and the rotational motion of the molecule about the chain axis. The computation of these $3p-4$ fundamentals from Eqs. (1) and (2) is a relatively simple matter and the vibration patterns can also be derived so that the dichroism can be predicted.

For instance in polyethylene, where x-ray investigations indicate that $p=2$, there should therefore be two potentially active fundamentals. Taking $\lambda=0$ and $\lambda=\pi$ [the possible values from Eq. (5)], we calculate the respective frequencies of these potentially active fundamentals as $\nu_+(0) = 1070$ cm^{-1} and $\nu_+(\pi) = 1137$ cm^{-1}. The vibration patterns of these and the other four zero frequencies are shown in Fig. 1. Thus, the higher frequency should exhibit parallel dichroism with respect to the chain direction while the opposite should be true for the lower frequency. It should be noted that interactions between neighboring chains are neglected in this case.

For, $p=4$, six new frequencies are possible, corresponding to the additional values of λ, viz., $\pi/2$ and $3\pi/2$. Their vibration
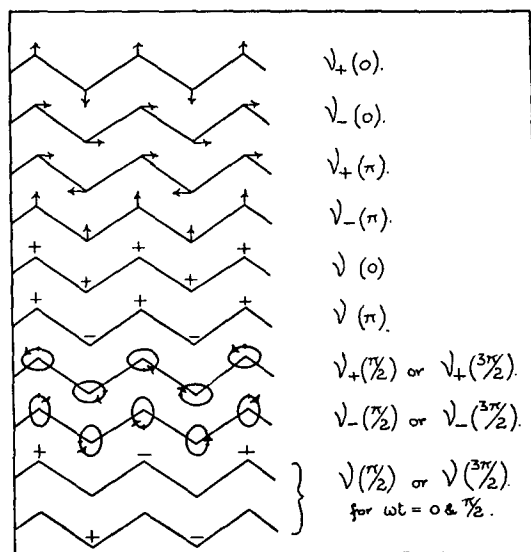

Fig. 1. Fundamental skeletal modes of long chain molecules. The modes for $p=2$ are $\nu_+(0)$, $\nu_-(0)$, $\nu_+(\pi)$, $\nu_-(\pi)$, $\nu(0)$, and $\nu(\pi)$. The remaining modes are the additional ones obtained for $p=4$.

patterns are also given in Fig. 1. It will be observed that they really consist of 3 doubly degenerate vibrations, which are computed to be $\nu_+(\pi/2) = \nu_+(3\pi/2) = 980$ cm^{-1}, $\nu_-(\pi/2) = \nu_-(3\pi/2) = 438$ cm^{-1}, and $\nu(\pi/2) = \nu(3\pi/2) = 198$ cm^{-1}. Bands are observed near these positions for many vinyl polymers such as polyvinyl chloride.

A full discussion of this method and its applications will be given later in conjunction with the publication of our new experimental work on the spectra of high polymers.

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Conduction by Oxide Ion in the Solid State

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IN 1943 Wagner[1] postulated O$^-$ transport as the means of conduction in the Nernst glower. He pointed out that Nernst had observed qualitatively the evolution of oxygen at the anode. Evidence regarding the structure of this ceramic was obtained by Hund who studied the density and x-ray diffraction of mixed oxides.[2] He showed that in the composition region corresponding to the Nernst glower the lower valent cation substituted in the lattice which resulted in oxide ion (O$^-$) vacancies. These, in turn, provided a path for diffusing O$^-$ ions which, because of their size, would have had to be stationary in the absence of vacancies. These were permissive hypotheses but not positive experimental proof.

We have been able to demonstrate that the O$^-$ ion is a carrier by observing quantitatively the evolution of oxygen on passing current through a Nernst glower (obtained from the Stupakoff Company).

The glower was a cylindrical piece of ceramic (0.5 inch long, 0.05 inch diameter) of the type used as a light source on infrared spectrometers. This material has a normal composition of 85 mole percent ZrO_2 and 15 mole percent Y_2O_3. Our x-ray emission spectrography showed several percent hafnium and minor amounts of some rare earths. These glowers were suspended in a quartz tube by their own platinum leads. The tube was sealed to the sample inlet of a mass spectrometer and located in a furnace which could be heated to 1100°C. Only the ceramic, platinum leads, and quartz were located in the heated zone so that any gas evolved could not be readsorbed.

The rate of evolution of gases from the glower could be determined as a function of temperature and current flowing through the glower. These rates were found to be dependent on the history of the material. The rate of oxygen production was measured with the spectrometer and accounted for 7 to 80 percent of the current by Faraday's laws. The efficiency decreased with increasing temperature and age. Carbon dioxide was also evolved as a function of current. Other gases (CO, H_2S, SO_2, HCl) were desorbed on heating the glower initially but their rates were independent of the passage of current through the glower. We assume that CO_2 arose from the reaction of oxygen with residue of an organic binder used in the manufacture of the ceramic. Thus the oxide ion conductivity may be considerably larger than the values given.

For the purpose of illustration Fig. 1 presents the rate of evolution of oxygen as a function of current through the glower under different conditions. The equation of line 5 is $\Delta O_2/\Delta t = 40\,000\ I$ where $\Delta O_2/\Delta t$ is the rate of oxygen evolution and I, the current in milliamperes. The value of the constant applies when the rate of