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Structure-Optical Studies

I. X-Ray Diffraction by Addition Compounds of Halogens with Hydrophilic Organic Polymers

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July 14, 1947

IODINE, bromine, and iodine bromide can be incorporated in high concentrations in films or fibers of many hydrophilic organic high polymers, crystalline and amorphous, natural and artificial. Examples are starch, cellulose, polyvinyl alcohol (PVA), the polyamides called Nylon (not previously reported), and many of their derivatives. These polymers are all transparent in the visible, while the halogens by themselves absorb light in this region. It is easy to show that an increase in the absorption coefficient of the halogen generally accompanies its incorporation into the polymer, indeed a well-defined new, strong band often appears in the visible (blue starch-iodine). By a high concentration of, e.g., iodine on PVA, is meant about 30 percent by weight of free iodine, accompanied by an amount of hydrogen or alkali iodine which may be varied between wide limits. The presence of halogen in these preparations in the known orthorhombic, or any other three-dimensional crystal form, is readily excluded by x-ray diffraction study.

The polymers named (save starch), including such substantially amorphous PVA derivatives as the borate and the commercial butyral can be put into well-oriented uniaxial states by methods involving unidirectional stretching, if they do not naturally occur in this state. When the halogen is incorporated into such well-oriented preparations, then strong uniaxial positive dichroism accompanies the enhanced light absorption.[1]

We have photographed, by monochromatic x-ray diffraction under widely varying conditions, many such dichroic preparations and find, nearly without exception, a single constant characteristic feature on the pictures: a pair of diffuse continuous layer lines, which are also observable in the second and third orders under favorable conditions. This can only indicate diffraction by independent line gratings, which are here extended straight chains of halogen atoms all lying parallel to the orientation or absorption direction. The periodicities of the halogen chains are substantially independent of the original periodicity of the oriented organic polymer (if any) and are for iodine 3.10, for bromine 2.70, for iodine bromide 2.90A, with individual values possibly varying up to 0.15A from these figures. Besides these characteristic diffractions, accessory diffractions in other directions and varying to some extent with the mode of preparation are not uncommon, e.g., with PVA-iodine; these, however, need not affect the present arguments. Only rarely are the characteristic diffractions absent when they would be expected, such exceptions could be accounted for by picturing the halogen chains as short, or crooked, or both. With *unoriented* preparations, including those of starch-iodine, a diffuse halo corresponding in position to the first characteristic continuous layer line can usually be seen; by themselves such haloes can prove little in the present problem, but they do have a certain confirmatory interest.

The foregoing periodicities are much shorter than the unbonded separations of halogen atoms (4.3A for $I-I$, etc.) and are somewhat greater than the single bond separations (2.7A for $I-I$, etc.). Shortened distances between known atom pairs, AB, usually mean either a hydrogen bond between A and B, or the bonding of both A and B to a central atom C, or a direct bond of some kind between A and B. The foregoing data suggest that only the third possibility comes into question here; the halogens in these preparations form bonds with each other at 180°, weaker than single covalent bonds but much stronger than van der Waals attractions, they are therefore properly called linear polymeric halogens or polyhalogens for short. Such a picture is consistent with the observed small fugacity of halogen in these preparations, and with the observed optical properties. Concerning the probable mode of interaction (if any) between halogens and oxygen or nitrogen atoms in the organic polymer, which confer hydrophilic properties on the latter, one can for the present only speculate within two limitations: first, such interaction cannot depend on any crystalline or long-range order of the ligher atoms; second, the incorporation of the halogen does not affect the infra-red absorption spectrum of the organic polymer over the range 3–15 mu, so far as we are able to determine.

The several previous explanations for these addition compounds, of which the latest was made by Rundle and co-workers,[2] require revision to account for the characteristic x-ray diffractions which we consider to be the single most important clue to their structure.

[1] E. H. Land and C. D. West in J. Alexander, *Colloid Chemistry* (Reinhold Publishing Corporation, New York, 1946), Volume 6, Chapter 6, pp. 160–90.

[2] R. Rundle, J. Foster, and R. Baldwin, J. Am. Chem. Soc. 66, 2116 (1944).


Activation in Unimolecular Reactions*, **

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July 9, 1947

THE decomposition of nitrogen pentoxide remains first order to extremely low pressures, of the order of 0.01 mm. Kassel[2] has shown that to account for this it is necessary, using the most probable model for the system of oscillators comprising the molecule, to suppose that the diameter for collisional activation and deactivation is about 20×10^{-8} cm. Recently Ogg** has made an ingenious suggestion which appears to account for this characteristic of the reaction, as well as a number of other features, without any excessive collision diameters. It is supposed that the equilibrium

$$N_2O_5 \rightleftarrows NO_3 + NO_2$$

is established, and that the dissociated products of this equilibrium can occasionally react

$$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO$$
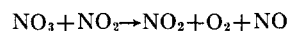
to give the decomposition. Working out this mechanism shows that the reaction should be first order to arbitrarily low pressures; the apparent observed falling off in the

rate constant at very low pressures presumably indicates that an appreciable fraction of the N_2O_5 is dissociated.

A brief historical note, which will indicate where this explanation stands in relation to the theory of unimolecular reactions, may be in order. In the early days of the discussion of these reactions it was supposed that the equilibrium fraction of activated molecules would be given by the simple exponential $e^{-Q/RT}$, where Q is the activation energy. The rate of activation could not be faster than the rate of deactivation which would occur if there were no reaction and consequently no draining away of activated molecules. This in turn would be equal to the number of collisions made by the activated fraction of molecules, $e^{-Q/RT}$, with other molecules. It was in general impossible, on this basis, to account for a sufficiently rapid rate of activation to maintain the reaction. It was soon pointed out,[3] however, that in the case of a molecule with many internal degrees of freedom, the fraction of molecules with energy greater than Q is much greater than $e^{-Q/RT}$. All this energy may be considered as activation energy if the molecule is capable of transferring energy between the internal degrees of freedom, and in particular to the bond which is to break in the reaction. Thus it is possible to account for much larger rates of activation. This comes about because there are many ways in which the excess energy necessary for activation can be distributed among the various oscillators of the molecule, thus increasing the probability, or the

entropy, of the activated molecules. Anything which increases this entropy may increase the rate of activation. For example, if the energy levels of an activated molecule are much closer together on the average than those in the normal state of the molecule, the rate of activation is increased. This can be important when the number of degrees of freedom is small.[4]

It is now apparent how Ogg's suggested mechanism fits into the scheme. The activated state of the molecule is actually the separated pair NO_2+NO_3 which has an extremely high entropy. The rate of activation can, therefore, be large. In fact, the difference in entropy between the activated and normal states increases with decreasing pressure in such a way as to render the rate of activation independent of the pressure. But the assumption that activation occurs while the parts of the molecule are separated is essentially a device for increasing the rate of activation.

* This document is based on work performed under Contract No. W–35–058–eng–71 for the Atomic Energy Project at the Clinton Laboratories.
** A remark on the note, "The Mechanism of Nitrogen Pentoxide Decomposition," by R. A. Ogg, Jr., J. Chem. Phys. **15**, 337 (1947).
1 On leave 1946–47 from the University of North Carolina.
2 L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions* (Reinhold Publishing Corporation, New York, 1932) p. 182.
3 G. N. Lewis and D. F. Smith, J. Am. Chem. Soc. **47**, 1514 (1925); J. A. Christiansen, Proc. Camb. Phil. Soc. **23**, 438 (1926); C. N. Hinshelwood, Proc. Roy. Soc. London **113A**, 230 (1926); O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927); see also Kassel, reference 3, p. 94.
4 O. K. Rice, J. Chem. Phys. **9**, 258 (1941).