Comments and Communications

A Simple Microfilm Reader and the Microfilm Process

As an aid in research the use of microfilm copies of inaccessible references is steadily increasing. A serious drawback to the more extended use of microfilming has been the expense and unsatisfactory performance of the reading equipment. The usual form of reader is a cumbersome camera obscura, where the film is projected on a reading screen. For those lacking a reading machine, enlarged prints from microfilm can be bought, but they cost more.

A simple, inexpensive, and practical reader is available in the common box-type substage lamp used with a low power microscope. A piece of glass the size of the top, fastened at the ends with adhesive tape and raised so as just to permit the film to slide through, will hold the film steadily in focus. A magnification of about 10 × affords a visual impression slightly smaller than the printed original, and with wide-field oculars will accommodate a page at a time. With the substage viewer, perfect processing of the film is not important, because underexposed or overdeveloped films are still legible. The viewer may be used for perforated or nonperforated film as well as for 16-mm strips, which is not the case with some commercial readers.

Library equipment for microfilming is elaborate and expensive. For personal use a 35-mm camera has proved satisfactory when provided with a supplementary lens to shorten the focus and with a focusing attachment for centering the field.

It has been expertly estimated that more than 25 billion records have been microfilmed during the twenty years that this process has been used. Most of these microfilms have been utilized in industry, where the saving of space is important in keeping records. But it is obvious that hundreds of thousands of pages of copyrighted material have been photographed for the use of research workers, a technical infringement of the copyright law, which explicitly provides that the owner of a copyright "shall have the exclusive right: to print, reprint, publish, copy and vend the copyrighted work" in whole or in any part. The fact that the copying is for research and not profit does not enter into the statute.

While microfilming excerpts of a copyrighted article may constitute a technical legal infringement, it is now so universally done that courts would be reluctant to impose penalties on individual scientists who in good faith are dependent on the process. It is the custom of libraries not to sell but only to lend the microfilm, though for an indeterminate period, the charge being only for the service and based on actual cost to the institution. Libraries also require a release from the applicant, who must assume full responsibility for possible misuse of the copyright. While these restrictions may seem formidable, it is generally conceded that research workers may rely with safety on a "fair-dealing" agreement, constituted in 1935 and confirmed in 1946, between a committee on research and representatives of book publishers. In effect, this agreement approves microfilming extracts of copyrighted scientific works for research purposes. Heretofore, there has been no legal interference with copying by hand for scholarly use, and photoduplication is now regarded as a modern timesaving substitute.

A useful directory of microfilm services in the United States and Canada is available from the Special Libraries Association, 31 East 10th Street, New York City, which lists institutions, commercial firms, costs, stipulations and conditions concerning this important process.

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The Mechanism of Ionization in Solution

According to L. Pauling's calculations from data on bond energies (*The Nature of the Chemical Bond*, Ithaca, New York: Cornell Univ. Press, 1941), the relative ionic contributions in the series HI, HBr, HCl, and HF amount to 5%, 11%, 17%, and 60% respectively, despite the fact that the first three in aqueous solutions are strong acids. He emphasized the fact that "the amount of ionic character of a bond in a molecule must not be confused with the tendency of the molecule to ionize in a suitable solvent." The mechanism of ionization in solution is not simple because transformation of bond type, deformation of structure, and solvation are all involved. The purpose of this note is to summarize current ideas in order to form a preliminary general picture of the process of ionization. When the hydrogen halides HI, HBr, and HCl are brought into solution from the gas phase, their covalent contributions decrease and seem to disappear in water, which possesses the same leveling effect on each of these acids. It would therefore be of interest to know the extent to which their ionic contributions increase in other solvents. This procedure may reveal the transition from the covalent to the ionic binding.

F. Fairbrother (*Trans. Faraday Soc.*, 1932, 30, 862) suggested that measurements of the dipole moments of hydrogen halides in nonpolar solvents would yield some information on change in bond type. His measurements, as well as those of Mizuschima (Mizuschima, S., Suenaga, K., and Kojima, K. *Bull. chem. Soc. Japan.*, 1935, 10, 167), show moments which are distinctly higher than those obtained in the gas phase. Table 1 summarizes these results. From their data the amount of relative ionic character of the H-X bond in solution is estimated in the last column as the ratio of the dipole moment measured in solution to the product of charge and interatomic distance. F. C. Frank (*Proc. roy. Soc.*, 1935, **A152**, 171) explained Fairbrother's data on the basis of a large moment induced on solution. Further evidence is obtained from the work of Ulich (Ulich, H., Hertel, E., and Nespital, W. *Z. phys. Chem.*, 1932, **B17**, 21), who studied the deformation of inorganic halides in solution

TABLE 1

CALCULATION OF IONIC CONTRIBUTION IN SOLUTION

HX	Solvent	μ* Gas	μ* Solution	μ* Solution/ex†
HCl	C_6H_6	1.03	1.22	0.20
	CCl_4		1.32	0.217
	$c-C_6H_{12}$		1.32	0.217
	$n-C_6H_{14}$		1.04	0.17
	$CH_3 \cdot C_6H_5$		1.24	0.204
	$CHCl_3$		1.03	0.17
	$(C_2H_5)_2O$		2.22	0.365
HBr	C_6H_6	0.79	1.01	0.15
	CCl_4		.96	0.143
HI	C_6H_6	0.38	.58	0.076
	CCl_4		.50	0.065

* μ = Dipole moment.

† e = Electronic charge ; x = distance of separation of atom.

by dipole moment measurements. They showed that the symmetry of stannic chloride is changed by attachment to a polar molecule such as ether or acetone, from a regular tetrahedron with no dipole moment to a pyramid with a moment of 2.46 D (Debye units—1D = 10^{-18} electrostatic units). The measurements of these authors showed that metal halides suffer not only deformation by association with polar molecules, but also with nonpolar molecules such as hydrocarbons. Thus, aluminum chloride in solution undergoes a certain deformation which might lead to false conclusions in the case of anisotropic hydrocarbons. Aluminum bromide in benzene has a moment of 5.5 D and zero moment in carbon disulphide. The measurements show that angular deformation takes place by the attachment of other molecules, resulting in an increase in dipole moment.

G. Briegleb and W. Lauppe (*Z. phys. Chem.*, 1935, **B28**, 154) proposed that acetone deforms the beryllium chloride molecule by changing the valence spring force, producing a distorted molecule with a moment of 5.7 D. They also obtained evidence for this symmetry deformation by measuring the shift of the Raman lines when stannic chloride was dissolved in alcohol. Six lines, characteristic of a triangular pyramid, appeared. Aluminum chloride shows similar behavior.

This picture of deformation of inorganic halides finds application in visualizing the mechanism of Friedel-Craft's reaction. Aromatic hydrocarbons (ArH) may be alkylated by means of mixed ethers R_1OR_2. The relative amounts of ArR_1 or ArR_2 in the product will depend largely upon the mechanism of the interaction of aluminum chloride with the ether used. The separation of either R_1^+ or R_2^+ from the coordination complex will depend on the extent of the deformation in the C-O-C angle by the attachment of aluminum chloride to the lone pair of electrons on the oxygen atom. The more positively charged the alkyl group, the greater its tendency to separate as an ion. Considerable infrared (Williams, D., *Phys. Rev.*, 1936, 50, 719) and Raman spectroscopic work (West, W. and Arthur, P. *J. chem. Phys.*, 1937, 5, 10) on solutions of hydrogen halides show that their vibration characteristics change when the halides form hydrogen bonds with oxygenated solvents. Gross and co-workers (Weith, A. M., Hobbs, M. E., and Gross, P. M. *J. Amer. chem. Soc.*, 1948, 70, 805) find that hydrogen chloride in dioxane exhibits absorption bands in a region which can be ascribed to the perturbed hydrogen chloride molecule. This result indicates that the solute has not gone over into an ion pair in dioxane.

From the calculations of Table 1 and the optical evidence obtained for hydrogen halides in solution, it becomes apparent that an increase in the amount of ionic character of the bond is accompanied by a shift in the absorption bands. This leads to the suggestion that in solution the nuclei are vibrating over an equilibrium distance which is greater than that of the gaseous molecule. As the dielectric constant of the solvent increases, the ionic character of the bond increases and a high dipole moment should be observed. This results in a deformation of the molecule, the nuclei of which will vibrate over a greater equilibrium distance. An increase in the vibrational energy should require a decrease in the potential energy, and the latter goes to a minimum when the former goes to a maximum. Beyond this limit, a new potential energy of the system $H^+ X^-$ is required. A deformation in the H-Cl bond has been reported by P. D. Bartlett and H. J. Dauben, Jr. (*J. Amer. chem. Soc.*, 1940, 62, 1339) and is accompanied by an increase in the acid strength of hydrogen chloride due to hydrogen bond formation with phenols in dioxane as a solvent. The HCl-phenol complex can be looked upon as similar to the beryllium chloride-acetone complex.

Very recently C. G. Swain and R. W. Eddy (*J. Amer. chem. Soc.*, 1948, **70**, 2989) investigated termolecular displacement reactions of methyl halides in benzene solution. Methyl bromide was allowed to react with pyridine in benzene solution at 100° C. They found that added methanol, phenol, or mercuric chloride facilitates the reaction, apparently by solvating the bromine atom of methyl bromide in front, while pyridine simultaneously attacks from the back. Their push-pull mechanism finds a simple explanation in the light of deformation theory. The amount of ionic character of the C-Br bond in methyl bromide would be expected to increase in the presence of benzene or alcohol, due to the deformation occurring in the tetrahedral structure. This deformation would be accompanied by a larger dipole moment, which results in the formation of a more positively charged carbon atom. Pyridine then would attack readily with its lone pair of electrons on the more positively charged carbon atom. Aluminum bromide, which is deformed in benzene and acquires a dipole moment of 5.5 D, has been reported by these authors to accelerate the reaction by 20% ± 8% in a .045 M solution.

The above examples suggest that solvation by one of several mechanisms occurs in general on solution of a polar substance, leading to a change in the relative ionic character of the bond with respect to the state of the gas molecule. The ionizing tendency of the solute is in turn determined by the ionic character of the resulting complex.

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