



Mass Spectrometric Test for an Intermediate in a Photochemical Reaction Involving Chlorine

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syndiotactic polyvinyl chloride shows that the 638 and 603 cm⁻¹ bands are assigned to the symmetric (A_1) and antisymmetric (B_1) C—Cl stretching vibrations, respectively, and both the 963 and 1255 cm⁻¹ bands belong to the B_1 -type vibration. This fact suggests that the initial orientation of the polyvinyl chloride chain is different from that obtained when the film is stretched to a great extent. The details of the results will be published later.

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S. Krimm (private communication). ⁵ M. Asahina and S. Enomoto, J. Chem. Soc. Japan, Pure Chem. Sect. 81, 1370 (1960).

M. Tasumi and T. Shimanouchi (to be published).

7 T. Shimanouchi and M. Tasumi, Bull. Chem. Soc. Japan (to be published).

Erratum: X-Ray Scattering by a Cell-Model Liquid

[J. Chem. Phys. 33, 1086 (1960)]

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N Figs. 2–5, the values of "a" in the legends in each . case should be the value of "a" indicated in the right top corner of each figure.

The expression for p(r) preceding Eq. (8) is Gaussian in r. In the paper the r^2 appears to be an exponent for the square bracket in the exponential.

Erratum: Oxygen Diffusion in Periclase Crystals

[J. Chem. Phys. 33, 905-6 (1960)]

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(Received December 7, 1960)

) N p. 906 incorrect numerical values are given by the activation entropy and activation energy for diffusion. Following Eq. (3), the correct values are $\Delta S^* = -21$ cal/deg and $\Delta H^* = 58$ kcal/mole.

Notes

Mass Spectrometric Test for an Intermediate in a Photochemical Reaction **Involving Chlorine**

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URING the course of studies aimed at developing techniques of direct application of a research mass spectrometer to problems in chemistry and radiation chemistry, a brief investigation was made of the photochemical reaction^{1,2} of formic acid with chlorine,

HCOOH (monomer or dimer) $+ Cl_2 \xrightarrow{\text{visible}} 2HCl + CO_2$.

The technique used was similar to that employed by Zemeny and Burton³ and in some respects like the technique used by Kistiakowsky and Kydd.⁴ The earlier investigators1 had reported evidence for the presence of measurable quantities of a reaction intermediate which, they suggested, was probably chloroformic acid (ClCOOH). However, chloroformic acid is unstable, presumably because its structure includes a chlorine atom and a hydroxyl group attached to the same carbon atom. For this reason it seemed improbable to the present investigators that chloroformic acid could have been present as an intermediate in sufficient concentration to explain the experimental data of West and Rollefson.¹

The reaction was therefore carried out in a 25-ml reaction chamber just before the gold foil leak leading into the ionization chamber of a research mass spectrometer.⁵ The expansion bulb and the exit tube leading to the reaction chamber were always kept dark. With the light on, the progress of the reaction was readily followed by the changes in the mass spectrometric peaks corresponding to reactants and products.6 Mass spectrometric peaks corresponding to chloroformic acid might have been expected if that compound had been formed during the reaction. Although chloroformic acid has not been isolated, a structurally similar chlorine compound, phosgene, yields the positive ion [COCl₂]⁺ upon electron bombardment in the mass spectrometer.7 However, no measurable concentration of the ions [(Cl35COOH)+ and (Cl37COOH)+, masses 80 and 82; (Cl35COO)- and (Cl37COO)-, masses 79 and 81] that would be expected, on the basis of previous studies of the positive spectrum of phosgene⁷ and the positive and negative spectra of formic acid,⁸ to arise from chloroformic acid was found. Instead a series of ions including (Cl³⁵HCOOH)⁻ and (Cl³⁷HCOOH)⁻,

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masses 81 and 83, $(Cl^{35}Cl^{35}HCOOH)^{-}$ and $(Cl^{35}Cl^{37}-HCOOH)^{-}$, masses 116 and 118, and $[Cl^{35}Cl^{35}-(HCOOH)_2]^{-}$ and $[Cl^{35}Cl^{37}(HCOOH)_2]^{-}$, masses 162 and 164, were observed with the light either on or off. These ions were very probably produced by negative ion-molecule reactions⁹ between ionized chlorine and monomeric and dimeric formic acid molecules.

The extreme sensitivity of the research mass spectrometer and its adaptability for studying both positive and negative ions make it highly unlikely that an intermediate present in sufficient concentration to be detected by the methods employed by West and Rollefson would be overlooked in the study described here.

The presently described technique could be useful in examining other photochemical reactions for intermediates. The only proviso is that the intermediate sought for be capable of passing through the gold foil leak and yielding, under electron bombardment, representative positive or negative ions stable enough to reach the collector. Any species detected only with the light on could reasonably be attributed to some molecule or radical resulting from a photochemical process. Since natural chlorine contains 75% chlorine-35 and 25% chlorine-37, an ion containing one atom of chlorine can be identified readily because it gives rise to twin peaks, two mass units apart, with heights in 3:1 ratio. A similar characteristic pattern is observed if the ion contains two or more chlorine atoms or if it contains one or more bromine atoms.⁵ Ions containing hydrogen can often be identified with the help of deuterium labeling.

The present method can also be applied in tests for intermediates in other types of reactions than those induced by visible light. The source of visible light can, for example, be replaced by a source of ultraviolet light, by a source of ionizing radiation, by a hot filament or by a catalytic surface in the reaction chamber, etc., with minor alterations of the apparatus. Recent work with a modified ion source has demonstrated that the research mass spectrometer can be operated with the pressure as high as 1 mm inside the ionization chamber.¹⁰ With such a modified ion source, it should be possible to carry out a photochemically-induced reaction inside the ionization chamber by using a light pipe. With this arrangement it should be possible to detect intermediates such as free radicals that might be too unstable to pass through the gold foil leak of an ordinary mass spectrometer.

The authors acknowledge helpful discussions with Milton Burton, P. H. Emmett, and Russell Baldock. ⁴G. B. Kistiakowsky and P. H. Kydd, J. Am. Chem. Soc. 79, 4825 (1957).

⁸ C. E. Melton, Gus A. Ropp, and P. S. Rudolph, J. Chem. Phys. **29**, 968 (1958).

⁶Under controlled conditions, relative reactions rates have been estimated by this method with sufficient precision to permit calculation of deuterium isotope effect ratios, $k_{\rm H}/k_{\rm D}$, when samples of formic acid and formic-*d* acid were used alternately. Details will be presented in a later communication.

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Infrared Spectrum of Crystalline Boron Trichloride*

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N OT long ago one of us concluded,¹ from a study of the infrared spectrum, that the crystal structure of BF_3 was not the same as that of the other boron trihalides, and that there existed strong interactions between adjacent molecules in the crystal. We have now made a study of the spectrum of $BCl_3(s)$ which is of interest in connection with the previous work.

Samples of normal BCl₃ were purified by vacuum distillation. Enriched (90–95% boron-10) samples were prepared by conversion of the enriched BF₃ used previously by heating with AlCl₃ at 110°C for 20 hours. Spectra were obtained of the fundamental vibrational transitions above 400 wave numbers; the solid films were at about 84° K.

The spectra obtained showed for each of ν_2 and ν_3 a doublet due to the two boron isotopes; they were quite similar to the analogous spectra for BF₃ except that no shoulders appeared on the components of the doublets.

TABLE I. Observed frequencies in the infrared spectrum of crystalline BCl₃.

80% B ¹¹	5–10% B ¹¹	Gasª	Assignment
447.1	445.0	460	$\nu_2(B^{11})$
466.0	469.0	480	$\nu_{2}(\mathbf{B}^{10})$
926	936	956	$\nu_{3}(B^{11})$
980	962	995	$\nu_{3}(\mathbf{B}^{10})$

^a See footnote 2.

No evidence was found for the appearance of the totally symmetric frequency ν_1 , which is almost coincident with ν_2 .² The other fundamental ν_4 lies below

^{*} Operated by the Union Carbide Corporation for the U. S. Atomic Energy Commission. ¹ H. L. West and G. K. Rollefson, J. Am. Chem. Soc. **58**, 2140

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