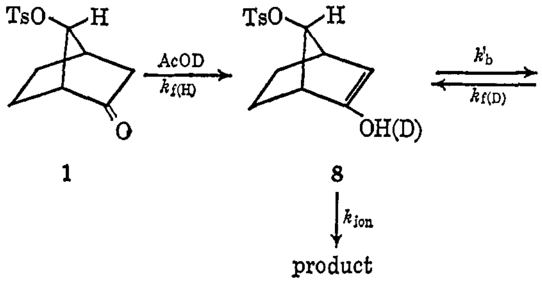
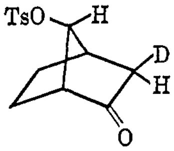
enolization is the removal of the α-hydrogen subsequent to proton addition to the carbonyl,[9,10] it would be anticipated that a primary isotope effect would be noted in the solvolysis of **11**. Since the preparation of **11** presented certain problems, the solvolysis of **1** was carried out in acetic acid-O-*d*. If k_b and k_{ion} were of the same order, a deuterium isotope effect should be noted. Table II lists the results of acetolysis in acetic acid-O-*d*. Whereas **1** gave excellent pseudo-first-order kinetics throughout 72% reaction in regular acetic acid, in acetic acid-O-*d* buffered with sodium acetate the rate decreased almost sevenfold before a constant pseudo-first-order rate was observed. This demonstrated that there was return of the enol **8** to **11**, followed by enolization of **11** at a slower rate, $k_{f(D)}$. The over-all sevenfold decrease of rate in going from **1** to **11** was in excellent agreement with the primary deuterium isotope effect of eight observed for the acid-catalyzed enolization of perdeuterioacetone.[11] By comparison, **4** showed good pseudo-first-order kinetics on solvolysis in acetic acid-O-*d* buffered with sodium acetate. In addition to the kinetic data for deuterium incorporation *via* enolization, mass spectral analysis for the presence of deuterium in a sample of **1** recovered after 39% solvolysis showed 34% deuterium incorporation. This data firmly established the importance of enolization in the solvolysis of **1** and further indicated the significant role which enolization can play in "carbonyl participation" especially when the substrate molecule does not allow direct interaction by the carbonyl oxygen.



1 **8**



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Acknowledgment. This investigation was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. We wish to thank Dr. Rodger Foltz of Battelle Memorial Institute for the mass spectral analysis.

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Received February 21, 1966

Geometry of the Bichloride Ion. Preparation and Crystal Structure of Cesium Chloride · $^1/_3$ Hydronium Bichloride[1]

Sir:

West's[2] initial report of the preparation of cesium bichloride, $\mathrm{CsHCl_2}$, by the reaction of anhydrous hydrogen chloride with a saturated aqueous solution of cesium chloride, stimulated interest in this system and led ultimately[3,4] to chemical and spectroscopic evidence that West had actually prepared $\mathrm{CsCl}\cdot{}^3/_4\mathrm{H_3OCl}$. We have studied the system further, making use of single-crystal X-ray techniques, and we find two distinct crystalline phases. We report here on the composition and structure of the hexagonal phase; the compound is cesium chloride·$^1/_3$ hydronium bichloride, $\mathrm{CsCl}\cdot{}^1/_3\mathrm{H_3OHCl_2}$.

As West reported, crystalline material is readily obtained when hydrogen chloride gas is bubbled through a saturated cesium chloride solution. The material is unstable except in the presence of HCl. Suitable crystals were transferred from the reaction vessel to X-ray capillary tubes in the presence of HCl gas, and the tubes were then sealed. Under these conditions the crystals are stable. Our initial preparation yielded an orthorhombic phase; subsequent preparations have yielded the hexagonal phase reported upon here.[5] On the basis of Weissenberg and precession photographs, taken with Mo Kα radiation, we find this phase to have Laue symmetry 6/m with lattice constants $a = 10.28$ and $c = 6.78$ A. The only systematic absences observed are for 00l for $l \neq 2n$; thus the most probable space groups are $P6_3/m$ and $P6_3$.

Intensity data were collected by the equiinclination Weissenberg technique for successive layers *hk*0 through *hk*8, using Mo Kα radiation. The intensities were estimated visually against a calibrated strip. After the composition of the material had been established from the structure determination, the absorption coefficient was computed and an absorption correction applied. This correction is necessarily approximate, owing to the difficulty of measuring accurately an irregularly shaped crystal which is inside a capillary tube. The data were reduced in the usual way and a three-dimensional Patterson function was computed. This function provided support that space group $P6_3/m$ is to be preferred to $P6_3$. The structure was solved by a succession of least-squares and Fourier calculations. The Cs was located in the sixfold positions (6h), and Cl atoms Cl(1) and Cl(2) were located in the six- and fourfold positions 6h and 4f, respectively. Hence the Cl/Cs ratio is 5/3. A difference Fourier computed at this point showed as its only significant feature a large peak (11 e/A^3) at position 4e, 0, 0, z, with z approximately $^1/_8$. This position is equidistant from three Cl(1) atoms, at the apex of a relatively flat pyramid. Such a position is one expected for the hydronium ion, $\mathrm{H_3O^+}$, entering into three O–H–Cl bonds, an arrange-

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[1] This research was supported by ARPA through the Northwestern University Materials Research Center.

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[5] West[2] presented evidence that his initial material belonged to the orthorhombic system. It is not clear whether subsequent studies[3,4] were carried out on the orthorhombic phase, on the hexagonal phase, or on a mixture of the two.

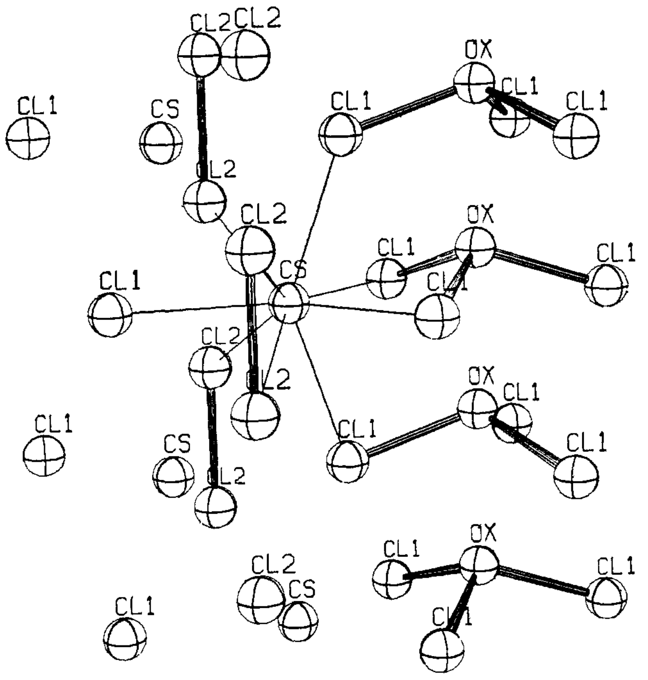

Figure 1. Part of the structure of $CsCl \cdot {}^1/_3H_3OHCl_2$. The *c* axis is vertical in the figure. The disorder of the oxygen positions is not shown, nor are the hydrogen positions. The shaded lines represent probable hydrogen bonds.

ment found in H_3OCl.[6] Yet in $P6_3/m$ an atom at 0, 0, z is related by symmetry to an atom at 0, 0, $^1/_2 - z$, and this leads to an O–O distance of 1.8 A. Thus we believe that the strings of hydronium ions along the *c* axis are disordered in the sense that there is no common origin for these strings; in effect each oxygen position is a half-position since there is equal probability that a given oxygen will be above or below its chlorine plane. Precisely this type of disorder is found in H_3OCl.[6] The usual R and weighted R factors (for least-squares refinement on F_o) that had been 0.126 and 0.150 before inclusion of the half-oxygen dropped to 0.093 and 0.103, respectively, after its inclusion. A final difference Fourier showed no features higher than 3 e/A^3 and provided some evidence for anisotropy in the cesium position. However, since the data were collected around only one axis (there being no choice in this case) and since the absorption correction is an approximate one, we felt that the anisotropic thermal parameters that could have been obtained would reflect systematic errors in our data rather than physical reality. Thus the calculations were terminated at the isotropic refinement.

Upon location of the half-oxygen positions, the composition of the material becomes $CsCl \cdot {}^2/_3HCl \cdot {}^1/_3H_2O$, where the hydrogen atoms have been added to balance charge. No direct evidence for the hydrogen atoms has been obtained from the present data. However, as we remarked above, the geometrical arrangement strongly suggests the presence of the hydronium ion. In fact, the geometry here is remarkably similar to that in H_3OCl.[6] The comparative values between the present study and that one are O–Cl distance: 2.92 ± 02, 2.95 ± 0.01 A; Cl–O–Cl angle: 110.1, 110.4°. (The hydrogen atom positions were located, albeit inexactly, in H_3OCl.[6]) Thus the composition of our material at this point becomes $CsCl \cdot {}^1/_3H_3O^+ \cdot {}^1/_3H^+ \cdot {}^2/_3Cl^-$ and there is the implication that the compound contains the bichloride ion, HCl_2^-. This is readily supported in more direct fashion by the Cl–Cl distances. All of these are 3.6 A (the normal van der Waals distance) or greater with the exception of one Cl(2)–Cl(2) contact which is 3.14 A, some 0.50 A shorter than that reported in any compounds where there are only van der Waals interactions. Clearly, then, this is strong evidence for a chemical bond between the two chlorines and hence for the existence of the bichloride ion in this compound. Thus we believe that we have prepared the remarkable compound $CsCl \cdot {}^1/_3H_3O^+ \cdot HCl_2^-$. The Cl–Cl distance in the bichloride ion in this compound, the first such distance to be determined, is 3.14 ± 0.02 A. This distance is reasonable on the basis of the 0.5-A shortening between F···F (2.8 A) and F–F in the bifluoride ion (2.26 A).

Part of the structure is shown in Figure 1. Both strings of bichloride ions and of hydronium ions run parallel to the *c* axis. The Cs atom is nine-coordinated with the Cs–Cl distance ranging from 3.44 to 3.70 A. The Cl(2)–Cl(2) distances alternate between 3.14 and 3.64 A; all other Cl–Cl contacts exceed 4.07 A. The Cl(1) atoms which enter into hydrogen bonds with the hydronium ion may be thought of as being arranged at the corners of octahedra which are contracted along their threefold axis. These octahedra share faces.

Infrared studies of our material have been largely inconclusive, owing to the rapid decomposition of the material in Nujol or perfluorocarbon mulls, although we have obtained some indications of band positions corresponding to those expected for the hydronium ion. Further studies are in progress.

A neutron-diffraction study is planned on this compound since it contains both the hydronium ion and the bichloride ion and since detailed geometries of both of these ions are of interest.

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Received March 16, 1966

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The Photochemical Reaction of Pummerer's Ketone[1]

Sir:

The photochemical reaction of 2-cyclohexenones in various organic solvents has been shown to result in the formation of several types of products[2-5] and has been explained in terms of triplet biradical intermediates by Zimmerman, *et al.*[5] We wish to report on a new type of the reaction of a 2-cyclohexenone, *i.e.*,

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