Crystal and Molecular Structure of N,N-Dimethylisopropylideniminium Perchlorate

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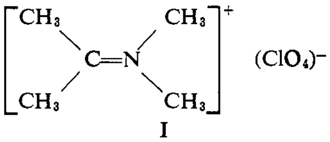
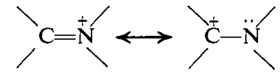
Abstract: The crystal and molecular structure of N,N-dimethylisopropylideniminium perchlorate has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in the tetragonal space group $I_{4/m}$ mm with two molecules in a unit cell of dimensions $a = 7.741 \pm 0.003$ and $c = 7.866 \pm 0.003$ A. The molecule is disordered in the crystalline state with the oxygen atoms in the perchlorate group occupying equivalent eightfold positions. The N,N-dimethylisopropylideniminium ion is planar with a $C{=}N^+$ distance of 1.30_2 A and a $C-CH_3$ (or $N-CH_3$) distance of 1.51_3 A. The $H_3C-N-CH_3$ angle is 125.4° and the H_3C-C-N angle is 117.3°. The perchlorate ion has a long Cl–O distance of 1.59_7 A with O–Cl–O angles of 114.7°. The 93 observed structure factors have been refined to an R value of 0.133 with all shifts in coordinates less than 0.001 A. SCF and VESCF calculations have been carried out on the $C{=}N^+$ to estimate net charges on these atoms and to assign a tentative bond order.

The structure determination of the compound N,N-dimethylisopropylideniminium perchlorate (I) was



I

undertaken for the following reasons: (a) it affords a comparatively simple compound in which one can find a value for a carbon–nitrogen double bond distance uncomplicated with other unsaturation or with an atom possessing π electrons; (b) an accurate determination of this distance would be of considerable interest in discussing the contribution of resonance structures



(c) it would provide molecular parameters (bond distances, bond angles, ionic distances) and the stereochemistry for this type of system.

Crystal Data

Crystalline samples of the compound were kindly furnished to us by Professor N. Leonard.[2]

The compound crystallizes in a body-centered tetragonal system with $a = 7.741$ and $c = 7.866 \pm 0.003$ A. The only extinctions were those for $h + k + l = 2n + 1$. The space group choices narrowed eventually to I_{42m} or $I_{4/m}$ mm. The data and equivalent positions will fit either space group equally well as was eventually confirmed by the completed structure determination. Since the space group $I_{4/m}$ mm presumes less about the actual geometry of the ordered molecules, it is to be preferred. The calculated density of 1.30_8 g/cc, based on two formula weights in the unit cell, agrees well with the measured density of 1.30 ± 0.02 g/cc (by flotation methods).

A precession camera using filtered molybdenum Kα radiation was used to obtain data for the ($h0l$), ($h1l$), ($h2l$), (hhl), ($h,h - 1,l$), and ($h,h - 2,l$) zones. A Weissenberg camera using filtered copper Kα radiation was used to obtain data for the ($hk0$), ($hk1$), and ($hk2$) zones. Since the crystal was very small, no absorption corrections were made. The intensities were read visually by comparison to a set of scales, corrected for camera factors, correlated, and put on a single relative scale.

Determination of the Structure

With only two molecules per unit cell, the chlorine must occupy one of the two twofold positions. The coordinates (0, 0, $^1/_2$) and ($^1/_2$, $^1/_2$, 0) were chosen for the chlorine atoms.

Chemically, the carbon and nitrogen atoms involved in the double bond should be unique and also occupy twofold positions. However, such twofold positions do not exist, and, consequently, these atoms must be equivalent with respect to X-rays and occupy at least fourfold positions. Since carbon and nitrogen (+1) are isoelectronic, this is plausible, although orientational disorder would also account for the equivalence of the carbon and nitrogen (+1). An average scattering factor curve[3] $(f_C + f_{N^+})/2$ was used for these atoms.

Of the fourfold positions allowed, only one (4e)[4] will allow these bonded atoms to be less than 3.0 A apart. However, this leads to further difficulties. If the $C{=}N^+$ groups are put into this fourfold position, packing considerations do not allow one to put both the four methyl groups and the four oxygens around the $C{=}N^+$ and the chlorine, respectively. Hence, the $C{=}N^+$ must be disordered further and be in at least an eightfold position. All of the eightfold positions were tried with only one (8h) leading to any reasonable agreement with the observed data.

The methyl groups were placed next. These could occupy either ordered eightfold positions (8i) or, in turn, be disordered and occupy 16-fold positions (16l). It is curious that if one does disorder the methyl

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[1] (a) Reprints available from this author; (b) Louisiana State University; (c) Texas A & M University.

[2] N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963).

[3] These and all subsequent scattering factor curves have been taken from the "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962.

[4] The notations used to identify the special positions are those found in ref 3, pp 241, 242.

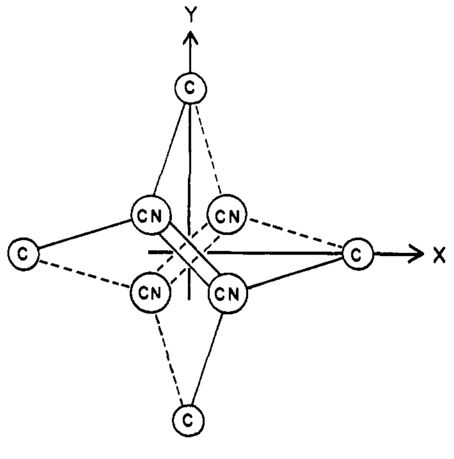

Figure 1. Disordered N,N-dimethylisopropylidenimium ion: ——, one bonding arrangement; --------, the other bonding arrangement.

carbons, they refine to positions differing from the ordered position by 0.06 A, but with a standard deviation of 0.12 A. Ultimately, when the structure was refined anisotropically, the disordered 16-fold position refined toward the ordered eightfold position, but also led to very large oscillating shifts in the temperature factor β_{yy}. On the other hand, the eightfold position refined without further difficulty. Thus, the planar dimethylisopropylideniminium ion can be viewed as possessing the orientational disorder indicated in Figure 1, where (CN) indicates that the position is occupied by an atom averaged as $(f_C + f_{N^+})/2$.

At this point, it was not necessarily obvious how to situate the oxygen atoms about the chlorine in the perchlorate ion, and so a preliminary structure factor calculation was made, excluding the four oxygens per molecule. The value of the "reliability index," $R = 0.283$, was quite promising, considering that the oxygens had not yet been included.

Attempts to put the oxygens in an eightfold position for the two perchlorate groups led to very close packing and did not help the structure refine. The best results led to $R = 0.275$. Hence, 16-fold positions were tried next with the best results obtained from isotropic least-squares refinements leading to $R = 0.214$.

To check the extent of disorder of the oxygen atom, a three-dimensional Fourier map was calculated omitting any oxygen contribution. Figure 2, which shows the vicinity about the chlorine in the xy plane, indicates a large degree of smearing-out of the oxygen positions about the chlorine atom. Since the oxygen positions are mirrored below the chlorine, there are, in fact, eight positions about each of the chlorine atoms where maxima in electron density are observed. The electron density is then smeared-out in a circular distribution about the chlorine.

Attempts were made to complete the refinement of this structure in two ways: (a) a spherical distribution function about the origin was used to approximate the oxygen positions;[5,6] (b) unique 16-fold positions were chosen for the oxygen and the structure was allowed to refine anisotropically.

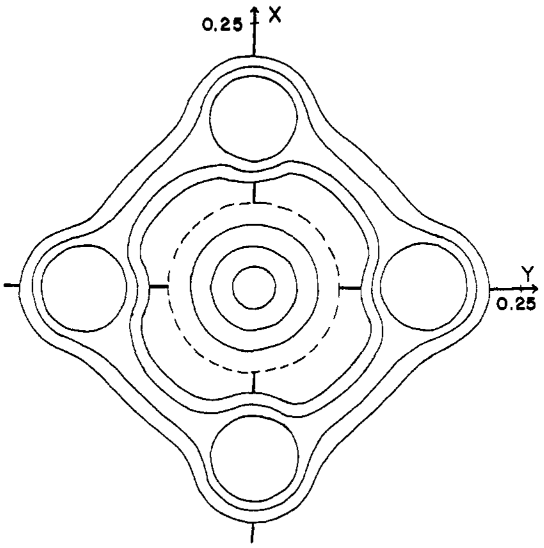

Figure 2. Chlorine at (0, 0, 1/2) with contours drawn at intervals of 5 electrons/A^3 beginning with zero contour (dotted); oxygen at $Z = 0.4$ and 0.6 with contours drawn at intervals of 0.5 electron/A^3 beginning with contour at 1.0 electron/A^3.

The use of the spherical distribution function turned out to be a poor approximation to the oxygen positions.

It is of interest, however, to note that in this treatment of the perchlorate group as a rigid body in which the only parameters are the chlorine–oxygen distance and the oxygen temperature factor, this distance refines to 1.50 A with $\beta_{\text{oxygen}} = 14$ A^2. At the same time, the structure refines only to a value of the weighted residual factor[7] of $r = 0.166$ with estimated standard deviations double those obtained using other weighting-factor schemes.

Table I

Weighting scheme	Final r	Parameters and their standard deviations Cl—O	C=N	C—CH$_3$
UW	0.128	1.681 ± 0.071	1.364 ± 0.064	1.531 ± 0.047
SCWI	0.167	1.613 ± 0.034	1.288 ± 0.046	1.510 ± 0.038
SCWA	0.137	1.597 ± 0.033	1.302 ± 0.043	1.513 ± 0.031
FW	0.147	1.579 ± 0.031	1.335 ± 0.061	1.516 ± 0.043
EW	0.157	Refinement oscillates and diverges at this point		

Anisotropic refinements have led to the solution of the structure. A final value of $R = 0.133$ and a weighted[7] value of $r = 0.137$ have been obtained. All coordinate shifts are less than 0.001 A, and the temperature factor shifts are 0.006 A^2 or less.[8]

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(5) W. H. Zachariasen, "Theory of X-ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945.

(6) R. F. Copeland, Thesis, Texas A & M University, 1963.

(7) The least-squares program uses a weighted reliability factor, r, where $r = (\Sigma[w(F_o - kF_c)^2]/(\Sigma w F_o^2))^{1/2}$. A variety of weighting schemes was used: (1) UW, unit weights, $w = 1$; (2) SCWI and SCWA, self-consistent weights (The weights are proportional to the reciprocal of the standard deviation of each reflection with the reflections taken in blocks of 19 each. This was done using both isotropic (SCWI) and anisotropic (SCWA) temperature factor); (3) FW, weights proportional to the reciprocal of the atomic scattering factor; (4) EW, weights proportional to the square root of the number of experimental readings of the intensity of a given reflection. The results are summarized in Table I.

(8) A listing of the values of the observed and calculated structure factors has been deposited as Document No. 8627 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

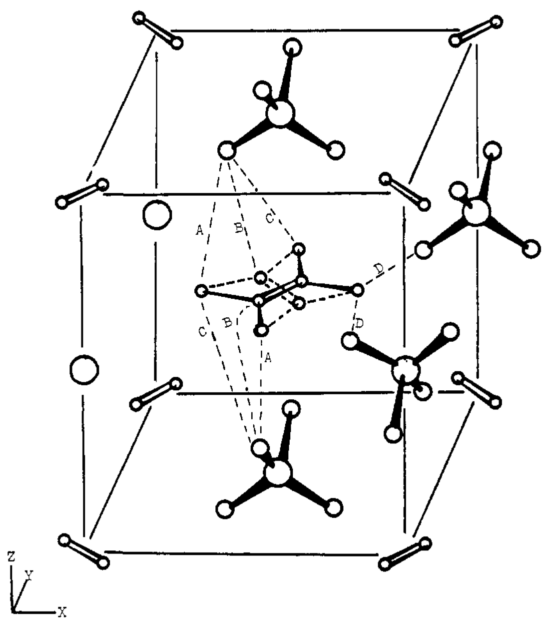

Figure 3. Projected view through unit cell showing interionic contact distances with each ion in both orientations: a = 3.12, b = 3.23, c = 3.23, d = 3.32 A.

Results and Discussion

Figure 3 shows a projected view through the unit cell in which the disordered perchlorate anion is shown in both orientations as is the disordered dimethylisopropylideniminium cation. Closest contact distances between the atoms in the various anions are indicated. Figure 4, the projection down the unique z axis, shows clearly that the ions in either orientational packing within the unit cell fill the available space equally well. Since this is the case, it is not surprising that orientational disorder exists within both ionic species.

The various distances, bond angles, and closest contact distances are summarized, together with their average deviations, in Table II. The final coordinates and anisotropic temperature factors are listed in Table III.

Table II. Bond Distances, Bond Angles, and Closest Contacts

Bond or angle	Distance, A[a]	Angle, deg	Estd std dev
C—CH (N—CH)	1.51_3		0.031
C=N	1.30_2		0.043[b]
Cl—O	1.59_7		0.033
O—Cl—O		114.7	2.3
C—C—C		125.4	1.6[b]
C—C=N		117.3	1.6[b]
C····O	3.12, 3.23, 3.32		
N·····O	3.23		

[a] Results obtained using anisotropic self-consistent weighting factors. [b] Related by mirror plane.

The tetrahedral perchlorate ion has an appreciably lengthened Cl-O distance (1.59_7 A) as compared to 1.42 A in perchloric acid[9] and 1.43 A in perchloric acid monohydrate.[10] Using a variety of weighting schemes and starting with the Cl-O distance at 1.40 A, many attempts were made to again refine this distance. All but one of these attempts[7] were at least internally consistent in ultimately refining this distance to a range from 1.58 to 1.61 A. Difference-Fourier techniques also led to the same range.

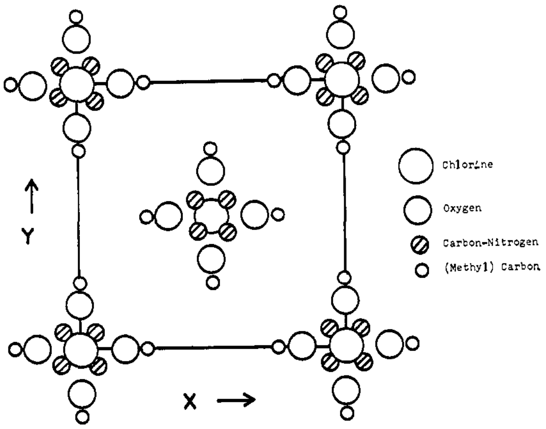

Figure 4. Packing in unit cell looking down the z axis (body-centered group at $z + 1/2$).

The dimethylisopropylideniminium cation is planar (D_{2h} crystallographic symmetry, C_{2v} molecular symmetry) with the entire molecule lying in the $z = 0$ plane. Since the carbon and nitrogen atoms involved in the C=N are symmetry equivalent, one cannot distinguish between the N-CH_3 and C-CH_3 distances nor the H_3C-N-CH_3 and the H_3C-C-CH_3 angles. The H_3C-N-CH_3 angle (and its equivalent H_3C-C-CH_3 angle) are opened up beyond the expected sp^2 angle to 125.4°. The packing of the perchlorate ion (in either orientation) about the dimethylisopropylideniminium ion accounts in part for this widening of the angle, for each methyl carbon has an oxygen within 3.12 A of it (Figure 3). In fact, even the C=N approaches within 3.23 A of the oxygen atoms. One can almost visualize linear infinite chains of alternating anions and cations in the z direction, approaching within 3.12 A of each other and separated from similar parallel chains by a distance of 3.32 A.

The carbon-nitrogen double bond in I is of theoretical interest since it is essentially a "pure" carbon-nitrogen double bond. There are no other centers of unsaturation or atoms possessing π electrons present as there are in other molecules having the C=N bond whose structures have been determined. With this fact in mind, self-consistent molecular orbital (SCMO) calculations have been performed on the π systems using both the molecular self-consistent field (SCF) formalism of Pople[11a] and the variable electronegativity SCF (VESCF) method of Brown.[11b] Table IV presents the bond orders and net positive charge on carbon calculated for the $C{=}N^+$ system using both methods of calculation and both the theoretical values of the interelectronic repulsion integrals and the Pariser and Parr values[12] for the integrals. It is seen that there is a large variation in properties, depending on the method of calculation and choice of parameters.

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(9) P. A. Akishin, L. V. Vilkov, and B. Y. Rosolovsky, *Krystallografiya*, 4, 353 (1959).

(10) F. S. Lee and G. B. Carpenter, *J. Phys. Chem.*, **63**, 279 (1959).

(11) (a) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); (b) R. D. Brown and M. L. Heffernan, *ibid.*, **54**, 757 (1958).

(12) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

Table III. Coordinates and Anisotropic Temperature Factors[a]

	x	y	z	11	22	33	12	13	23
Chlorine	(0)	(0)	(0.5)	[0.01703]	[0.01703]	0.01607	(0)	(0)	(0)
Oxygen	(0)	0.1737	0.6096	0.06696	0.07087	0.04471	(0)	(0)	−0.00666
(Carbon–nitrogen)/2	[0.0594]	[0.0594]	(0)	[0.01859]	[0.01859]	0.01261	−0.00483	(0)	(0)
Carbon (methyls)	0.2456	(0)	(0)	0.01417	0.02902	0.04198	(0)	(0)	(0)

[a] Value in parentheses indicates parameter fixed at this value; value in brackets indicates adjacent parameters have identical values.

There have been various attempts to relate the length of a bond to its π-bond order.[13] Gordy has suggested a relationship in which the bond order should vary linearly with the inverse square of the bond length.[14]

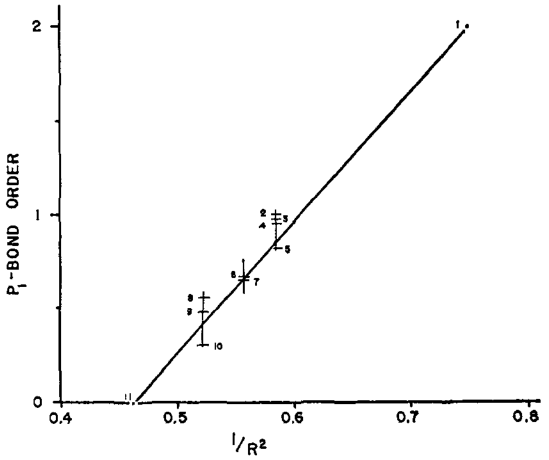

Figure 5. Plot of π-bond order *vs.* inverse square of bond length: (1) C≡N; (2) >C=N<$^+$, VESCF with theoretical repulsion integrals; (3) >C=N<$^+$, SCMO with theoretical repulsion integrals; (4) >C=N<$^+$, VESCF with Pariser and Parr integrals; (5) >C=N<$^+$, SCMO with Pariser and Parr integrals; (6) pyridine C-N, SCMO and VESCF with theoretical repulsion integrals; (7) pyridine C-N, SCMO with Pariser and Parr integrals; (8) pyrrole C-N, VESCF with theoretical integrals; (9) pyrrole C-N, SCMO with theoretical integrals; (10) pyrrole C-N, SCMO with Pariser and Parr integrals; (11) >C-N<.

Table IV. π-Bond Order and Net π Charge in the System >C=N<$^+$

Method of calcn	Integrals	Bond order	Net positive charge on C
SCMO	T[a]	0.9817	0.1902
SCMO	P and P[b]	0.8312	0.5560
VESCF	T[a]	0.9951	0.0989
VESCF	P and P[b]	0.9592	0.2827

[a] Theoretical. [b] Pariser and Parr.

Table V. π-Bond Orders and Bond Lengths

Molecule	Calcn	—π-Bond order— T[a]	P and P[b]	C-N bond length
C=N$^+$	SCMO	0.98	0.83	1.30
	VESCF	1.00	0.96	
Pyrrole	SCMO	0.49	0.30	1.383
	VESCF	0.56	...	
Pyridine	SCMO	0.67	0.66	1.340
	VESCF	0.67	...	

[a] For theoretical integrals. [b] For Pariser and Parr integrals.

In order to test the validity of the calculations on I and to choose between the various calculations, a check of the Gordy relationship was made with I and several other carbon–nitrogen bonds. A carbon–nitrogen single bond was assumed to have no π-bond character, while an unconjugated carbon–nitrogen triple bond was assumed to have a π-bond order of two. In addition, the calculated carbon–nitrogen bond order in pyridine was found to be essentially independent of the method of calculation (Table V); therefore, it was included with some confidence. Figure 5 shows a plot of π-bond order *vs.* the inverse square of the bond length for the carbon–nitrogen triple bond, single bond, and pyridine, along with the results of four calculations for the bond order of I and three calculations for the bond order of pyrrole (Table V). All experimental bond lengths except I were taken from the Chemical Society tabulation.[15] The expected linear relationship is obtained for the first three of these. The calculated values for I and pyrrole bracket the line.

Examination of Tables IV and V reveals that for the SCMO calculations the choice of integrals affects the bond order and charge distribution very greatly. If it is assumed that there is a linear relationship between the bond order and the value of the carbon one-center, two-electron integral, an estimate of this value can be obtained by reading an apparent bond order off the line in Figure 5. The apparent bond order so obtained is 0.851. This yields a value of 12.96 ev for the one-center carbon integral. This is remarkably close to the theoretical value of 12.72 ev derived by Orloff and Sinanoglu[16] when electron correlation energies are considered.

The molecular orbital calculations were performed on IBM 1620 and IBM 704 computers, employing the formalism of Pople[11a] for the SCMO calculations or of Brown[11b] for the VESCF calculations. The repulsion integrals were obtained by a Pariser and Parr type approximation.[12] The extrapolation was carried out to either the theoretical values of the one-center integrals, derived from modified Slater exponents (Z^{C}_{eff} = 3.18, Z^{N}_{eff} = 4.18), or the Pariser and Parr "empirical" values. The valence-state ionization potentials for carbon and nitrogen were taken from Pilcher and Skinner[17] (I^C = 11.22 ev, I^N = 27.31 ev for pyrrole and

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[13] For a summary, see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 165.

[14] W. Gordy, *J. Chem. Phys.*, **15**, 305 (1947).

[15] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958; supplement, 1964.

[16] M. K. Orloff and O. Sinanoglu, *J. Chem. Phys.*, **43**, 49 (1965).

[17] G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

I, $I^N = 14.49$ for pyridine). The core β terms were estimated by an empirical equation of the type $\beta_{xy} = A \exp[(B(Z^x_{\text{eff}} - Z^y_{\text{eff}})^2 - c)R_{xy}]$, where A, B, and C are empirical parameters and R_{xy} is the bond length.

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Preparation and Properties of Monocesium Xenate ($CsHXeO_4$)

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Abstract: Crystalline monocesium xenate has been prepared by the reaction of xenon trioxide with aqueous cesium hydroxide in the presence of fluoride ion. Good yields of cesium xenate are obtained from solutions which are approximately 0.1 *M* in xenon trioxide, 0.1 *M* in fluoride ion, and 2.5 *M* in cesium hydroxide. Cesium xenate, which has an apparent formula weight of 334, is stable in air and is considerably more stable than xenon trioxide. The existence of monocesium xenate has been confirmed by the determination of the oxidation equivalent by the "hi-lo" titration method, X-ray powder diffraction patterns, and infrared spectroscopy.

In a recent publication Spittler and Jaselskis[2] describe preparative methods for monosodium xenate and other alkali xenates by the reaction of equivalent amounts of alkali hydroxides and xenon trioxide followed by lyophilization of the mixtures. However, this method of preparation is not suitable for large-scale production. Thus further attempts to prepare alkali xenate salts from aqueous hydroxide solutions have been carried out.

Experimental Section

Chemicals and Apparatus. Xenon trioxide solutions were made by hydrolysis of xenon hexafluoride.[3] Xenon hexafluoride was made on heating xenon and fluorine for 16 hr at 300° with a total pressure of 40 atm, and a xenon-to-fluorine ratio of 1:20 in accord with Weinstock's equilibrium constants.[4] The reactants were heated in a welded container of Monel 400 fitted with an Autoclave Engineers 30 VM 6071 valve. Excess fluorine was removed from the container at Dry Ice temperature and after warming to room temperature the product was purified by distillation into a U-shaped Monel weighing can fitted with two Hoke A 431 valves, the can being cooled with Dry Ice.

To prevent a violent reaction when the xenon hexafluoride was hydrolyzed the reaction was carried out over a period of about 6 hr by sweeping the contents of the can through Kel-F tubing into water in a stream of nitrogen. To minimize possible metallic contamination the Hoke valve was removed from the exit of the can and the tubing connected directly to the can. The water was contained in a Teflon bottle in which the solution was afterwards stored. A bubbler had been constructed at the end of the Kel-F tubing by closing heated plastic into fine copper wires which were then removed with nitric acid. Quantitative character of the hydrolysis was shown by lack of a test for oxidizing power (starch iodide paper) in the nitrogen leaving the Teflon bottle.

The cesium and rubidium hydroxide solutions were prepared from the 99.9% purity hydroxide pellets supplied by K & K Laboratories. The insoluble residues in the 5 *M* cesium and rubidium hydroxide solutions were separated by centrifugation and the clear supernatant liquid used for the preparation of the crystalline cesium xenate.

Infrared spectra of the resulting precipitate were run in a silver chloride matrix using Perkin-Elmer 21, KBr Infracord, and Perkin-Elmer 521 recording spectrophotometers. The X-ray powder diffraction patterns were obtained on a Norelco instrument using a 114-mm camera and the copper Kα line with a nickel filter.

Preparation of Crystalline Monocesium Xenate. The monocesium xenate was prepared by mixing 1.0 ml of 0.25 *M* xenon trioxide hydrolysate with approximately 1.5 ml of 5.0 *M* cesium hydroxide. After mixing the solution was placed in a refrigerator and kept for about 6 hr. The supernatant liquid was decanted and the white crystals were washed with several portions of ice-cold water. Similar attempts to prepare rubidium xenate yielded a mixed salt of xenon (VI) and xenon (VIII).

The amounts of xenon(VI) and xenon(VIII) in the crystalline compound were determined by the "hi-lo" titration method as described by Appelman and Malm.[3] Cesium was determined gravimetrically as cesium perchlorate after the decomposition of the xenate with aqueous methanol solution. A test for fluoride ion was made, after the decomposition of xenate with aqueous methanol, using the zirconium–alizarin complex.

In addition, gases evolved by the cesium xenate on heating and on decomposition in concentrated sulfuric acid were analyzed in a time-of-flight mass spectrometer. On heating, carbon dioxide, water, and larger quantities of oxygen and xenon were observed. The same gases were observed from the sulfuric acid decomposition and in addition a small amount of HF was produced which could be detected after removal of xenon and oxygen and fractionation of the HF from a much larger quantity of carbon dioxide. The cesium xenate does not incorporate fluoride in any significantly stoichiometric amount even though the presence of fluoride ion in the xenic acid solution is essential for its formation.

No xenon compounds were observed in the gases in either case.

Results

Infrared Data. The infrared spectrum of monocesium xenate in silver chloride matrix shows, besides very weak bands at 3120 and 1430 cm^{-1}, two sets of four bands at 783, 740, 721, and 699 cm^{-1} and a 451,

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[1] On leave from Detroit University, Detroit, Mich.

[2] T. M. Spittler and B. Jaselskis, *J. Am. Chem. Soc.*, **87**, 3357 (1965).

[3] E. H. Appelman and J. G. Malm, *ibid.*, **86**, 2141 (1964).

[4] B. Weinstock, E. E. Weaver, and C. P. Knop, quoted by J. G. Malm, H. Selig, J. Fortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).