Acknowledgment. The authors wish to thank Drs. W. F. Brown and W. E. Crockett for the development of the computer program used in the normal coordinate analysis. We are also indebted to Mr. G. H. Post for his help with the experimental portion of the work.

Matrix Infrared Spectra of HOBr and HOCl[1]

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Abstract: The photolysis of mixtures of Ar–HX–O_3 at 4°K has produced the species HOBr (ν_1 3590, ν_2 1164, ν_3 626.0 cm^{-1}) and HOCl (ν_1 3581, ν_2 1239, ν_3 729 cm^{-1}). The use of the isotopic starting materials HX, DX, and $O^{16,18}{}_3$ produced data which have been used to calculate potential functions of these molecules.

The infrared spectrum of hypobromous acid, HOBr, has not been observed previously. That of hypochlorous acid was observed in the gas phase by Hedberg and Badger.[2] In this paper we present infrared studies of various isotopically substituted HOX species synthesized by photolysis of Ar–HX–O_3 mixtures at 4°K.

Experimental Section

The low-temperature infrared cell and its associated equipment have been described elsewhere.[3] Sample irradiations of up to 40 min were made using a high-pressure mercury arc (General Electric BH6). An elliptical spun aluminum reflector was used to focus the light from the arc onto the sample through an aqueous $NiSO_4$ solution filter (2200–3500 and 4500–5900 A). The filter (5-cm quartz cell) contained 100 g of $NiSO_4 \cdot 6H_2O$/l. of water. The infrared spectra were recorded from 4000 to 400 cm^{-1} on a Beckman IR-9 spectrometer. The estimated resolution and frequency accuracy was ±1 cm^{-1} for runs using isotopic substitution and ±2 cm^{-1} for all others.

All gas blends were prepared by standard manometric procedure using matrix to reactant ratios (M/R) of 40 for blends of HX (DX) in argon. Gas mixtures with ozone were produced by simultaneous deposition from two manifolds. Flow rates were adjusted to give M/R values between 25 and 40 for ozone in argon. The two reactant gas streams were not permitted to converge until just prior to deposition on the liquid helium cooled CsBr window. No unusual reactivity between the hydrogen halides and the CsBr window was observed. The HX (DX) blends were made up and deposited from a glass manifold covered with aluminum foil. Fluorolube grease was used on all stopcocks, and gas pressures were monitored by use of a pressure transducer gauge, the diaphragm of which was coated with Teflon. Ozone was deposited from an all metal manifold. In a typical run about 4.5 mmoles of blended material was deposited in 40 min at 4°K.

The following chemicals were used without further purification: argon (Airco, minimum purity 99.997%), H_2 and Cl_2 (Airco, research grade), O_2 (Matheson, research grade), D_2 (Matheson, 99.5% minimum isotopic purity), HCl (Matheson, 99% minimum purity), HBr (Matheson, 99.8% minimum purity), $O_2{}^{18}$ (Bio-Rad Laboratories, 99.5% O^{18}), and D_2O (General Dynamics Corp., 99.7%). Deuterium bromide was synthesized by the reaction of Br_2 and red phosphorus moistened with D_2O. The products were passed through a tower of red phosphorus and trapped in a liquid nitrogen cooled trap. The DBr was degassed and a midfraction used in making up blends. Deuterium chloride was synthesized by photolyzing mixtures of Cl_2 with excess D_2. The noncondensable gases at liquid nitrogen temperature were pumped off, and the DCl was separated from any unreacted Cl_2 by distillation from a −140° trap to a −196° trap. A midfraction of this material was used in matrix runs. Ozone and isotopically labeled O_3 were made by discharging O_2, with a Tesla coil, in a liquid nitrogen cooled Pyrex tube.

Results and Discussion

All the vibrational frequencies produced in the 4000–400-cm^{-1} range after photolysis of various mixtures of isotopically substituted reactants except those assigned to the various isomers of water are presented in Tables I and II. Figure 1 shows all bands produced in a typical run with an Ar:HBr:O_3 (50% O^{18}) ratio of 40:1:1. The spectrum, after deposition (B), contains bands assignable to the various isomers of ozone and those as-

Table I. Observed and Calculated[a] Vibrational Frequencies (cm^{-1}) of Hypobromous Acid from Ar–O_3–HBr Experiments Employing Isotopic Substitution

Ar–$O^{16}{}_3$–HBr	Ar–O_3 (50% O^{18})–HBr	Ar–$O^{16}{}_3$–DBr	Ar–O_3 (50% O^{18})–DBr
...	(3579) 3580	...	(2636) 2637
3589	(3591) 3590	2652	(2653) 2652
...	(1162) 1162	...	(848.6) 848.5
1164	(1165) 1162	854.0	(853.8) 853.9
...	(598.0) 597.8	...	(593.9) 593.8
626.0	(625.8) 626.0	621.8	(621.4) 621.5

[a] Values in parentheses calculated from force constants given in Table III.

Table II. Observed and Calculated[a] Vibrational Frequencies (cm^{-1}) of Hypochlorous Acid[b] from Ar–O_3–HCl Experiments Employing Isotopic Substitution

Ar–$O^{16}{}_3$–HCl^{35} [c]	Ar–O_3 (50% O^{18})–HCl^{35}	Ar–$O^{16}{}_3$–DCl^{35}	Ar–$O^{16}{}_3$–DCl^{35}
...	(3570) 3570	...	(2630) 2630
3578	(3581) 3581	2647	(2647) ...
...	(1236) 1237	...	(906) 906
1239	(1240) 1239	911	(911) ...
...	(702) 701	...	(702) 702
728	(728) 729	728	(728) ...

[a] Values in parentheses calculated from force constants given in Table III. [d] Gas-phase vibrational frequencies for HOCl at 3626, 1242, and 739 cm^{-1} and DOCl at 2674, 911, and 739 cm^{-1} are reported in ref 2. [c] Bands assignable to O–Cl^{37} were observed in only two cases: $HO^{16}Cl^{37}$, 723 cm^{-1}, and $HO^{16}Cl^{37}$, 695 cm^{-1} (calculated 723 and 696 cm^{-1}).

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[1] This work was supported by the AFRPL, Research and Technology Division, AFSC, Edwards, Calif., under Contract AF 04(611)-11389.

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[3] A. Arkell, R. R. Reinhard, and L. P. Larson, *J. Am. Chem. Soc.*, 87, 1016 (1965).

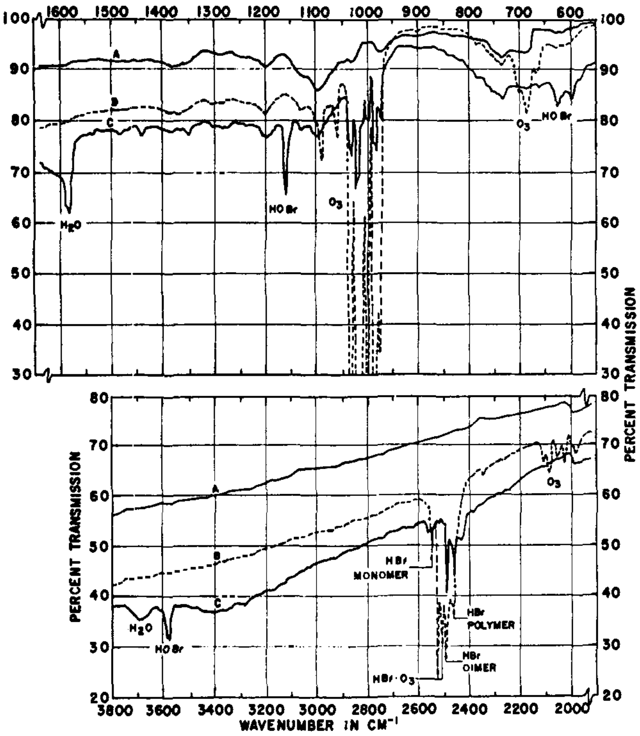

Figure 1. Absorptions produced by ultraviolet irradiation of $Ar:HBr:O_3$ (50% O^{16}) = 40:1:1 at 4°K: (A) background, (B) deposition, (C) photolysis (15 min, BH6 through $NiSO_4$ filter).

signable to the monomeric, dimeric, and polymeric species of HBr.[4,5] Two additional bands, not observed in reference runs, were also observed in the HBr region. These large bands at 2526 and 2509 cm^{-1} had counterparts at 1814 and 1801 cm^{-1} in the $Ar-DBr-O_3$ system. In the $Ar-HCl-O_3$ and $Ar-DCl-O_3$ systems only one "new band" at 2830 and 2047 cm^{-1}, respectively, was observed. These "new bands" are believed to be associated with $HX-O_3$ complexes. After photolysis with a BH6 lamp through a $NiSO_4$ filter (curve C, Figure 1) almost all of the O_3 and the $HX-O_3$ bands disappeared, the bands belonging to HX species decreased, and new bands assignable to the various isotopes of water appeared. In addition, photolysis led to the appearance of new bands (shown in Figure 1 for $HO^{16,18}Br$, and presented in Tables I and II for all HOX and DOX species observed) which may be assigned to the various isotopically substituted HOX species. In some experiments irradiations were continued after loss of excess starting materials, and small parallel decreases in the absorbances of the bands assigned to HOX fundamentals were observed. Similar experiments in the $Ar-HF-O_3$ system did not lead to the production of new bands assignable to the species HOF.

Warm-up studies were conducted in both the HOBr and HOCl systems. The absorptions assigned to the OH stretch and HOX bending mode begin to broaden and decrease as the temperature of the maxtrix is raised above 25°K and disappear between this temperature and 40°K, near which point diffusion becomes possible in an argon matrix. The bands assigned to the O–X stretches of HOCl and HOBr are less drastically affected by warm-up. They decrease less rapidly than the others, but survive diffusion. This type of behavior, in which one band in a molecule is broadened on diffusion while others are only slightly affected, has been reported to be typical of aggregation.[6]

The calculation of force constants and isotopic frequencies was made by using the observed frequencies reported in Tables I and II. The assumed molecular parameters used in the HOCl (DOCl) calculations were those previously estimated by Hedberg and Badger.[2] For the HOBr (DOBr) system the values used were estimated on the basis of the covalent radii of H, O, and Br. The molecular angle was estimated as 110° by analogy with the bond angles for the pair ClNO (116°) and BrNO (114°). A program based on equations derived by Cross and Van Vleck[7] was written for use with an IBM 1620 computer. The program permitted an iterative procedure to be used to minimize the squares of the differences between the observed and calculated frequencies. Attempts to use the combined HOBr–DOBr or HOCl–DOCl data to calculate one set of force constants for each molecule gave poor results. Therefore, the technique of solving the HOX and DOX sets separately omitting anharmonicity corrections was used. This technique affords better results because it increases the parametric freedom by reducing the number of independent observables. Calculations were carried out until successive iterations did not significantly alter the results. The calculated vibrational frequencies are presented in Tables I and II, and the calculated force constants are given in Table III. The program was set up so that all six force constants of the general valance force field could be calculated. However, the k_{OX-OH} and k_{HOX-OH} interaction constants were found to be small and to have only a minor effect on minimizing the differences between the observed and calculated frequencies. Therefore, the final calculations were made with the addition of only the k_{HOX-OX} interaction constant. The agreement between observed and calculated frequencies within each of the HOX and DOX sets is excellent; the average deviation between observed and calculated frequencies is less than ±0.7 cm^{-1} for each set. These results support the band assignments to the various HOX and DOX species.

Table III. Calculated Force Constants[a] for HOBr, DOBr, HOCl, and DOCl

Force constants	HOBr	DOBr	HOCl[b]	DOCl[b]
$k_{OH,OD}$, mdynes/A	7.143	7.357	7.104	7.321
k_{OX}, mdynes/A	3.594	3.372	3.980	3.763
k_{HOX}, mdyne A/rad^2	0.702	0.707	0.775	0.779
k_{HOX-OX}, mdyne/rad	0.638	0.446	0.677	0.473

[a] Assuming r_{OH} = 0.96 A, r_{OBr} = 1.85 A, r_{OCl} = 1.70 A, α_{HOBr} = 110°, α_{HOCl} = 113°, M_{Cl} = 35, M_{Br} = 80. [b] Force constants calculated from gas-phase data in ref 2: from HOCl, k_{OH} = 7.35, k_{OCl} = 3.86, k_{HOX} = 0.77, k_{HOX-OX} = 0.45; from DOCl, k_{OD} = 7.54, k_{OCl} = 4.02, k_{HOX} = 0.77, k_{HOX-OX} = 0.58.

The above results indicate that HOBr and HOCl have been produced in a low-temperature matrix after photolysis of $Ar-HX-O_3$ mixtures by the reaction

$$O_3 + HX + h\nu \longrightarrow HOX + O_2 \qquad (1)$$

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If it is assumed that the primary reactive species produced on photolysis of O_3 is atomic oxygen[8]

$$O_3 + h\nu \longrightarrow O + O_2 \qquad (2)$$

then two different detailed mechanisms may be proposed to explain the HOX formation

$$\text{(A)} \qquad O + HX \longrightarrow HOX \qquad (3)$$

$$\text{(B)} \qquad O + HX \longrightarrow HO + X \qquad (4)$$

$$HO + X \longrightarrow HOX \qquad (5)$$

A second product, H_2O, is probably produced by the competing reaction

$$HO + HX \longrightarrow HOH + X \qquad (6)$$

It is interesting to note that no bands assignable to the OH (OD) radical were observed despite the probable formation of this species as an intermediate in the production of H_2O (D_2O). Those bands which Ogilvie[9] suggested might belong to matrix isolated OH and OD at 3574 and 2635 cm^{-1} were sought but not found.

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Nuclear Magnetic Resonance Solvent Effects and Molecular Interactions

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Abstract: Certain solvent shifts in nmr spectroscopy have previously been explained by reaction field theory, with somewhat poor results. The authors attempt a different approach in this paper by explaining the shift in terms of collision complexes. Calculations with this model match observed shifts to within experimental error. Derived values for K, ΔH, and ΔS of the collision complexes are reasonable, K's being of order 10^{-1} l./mole, $\Delta H \sim -1.5$ kcal/mole, and $\Delta S = -6$–12 eu/mole.

It is well known that the chemical shifts of the hydrogens in a solute molecule are dependent upon the solvent used.[1,2] This solvent shift, δ_{obsd}, can be defined as the change in chemical shift for a given proton resonance on passing from a reference phase to an infinitely dilute solution in a solvent.

$$\delta_{\text{obsd}} = \delta_{\text{ref}} - \delta_{\text{soln}} \qquad (1)$$

It is generally accepted that such a solvent shift has many components.[2,3]

$$\delta_{\text{obsd}} = \delta_{\text{b}} + \delta_{\text{w}} + \delta_{\text{a}} + \delta_{\text{E}} + \delta_{\text{s}} \qquad (2)$$

Each of these contributions has been the subject of several investigations. A brief summary is given below. δ_{b} arises if an external reference is used, and is due to the bulk susceptibility differences of the solution and reference samples. In principle the effect is precisely calculable.[4,5] It can be separated from the other contributions to the solvent shift by a simple experiment outlined by Frei and Bernstein,[5,6] or by use of an internal reference.

δ_{w} is a downfield shift thought to arise from dispersion interactions,[2] calculations based on this model leading to better than order-of-magnitude agreement.[7] The effect is measured by use of nonpolar, isotropic solutes (*e.g.*, methane) and an external reference. A susceptibility correction is required; the separation from magnetic anisotropic effects (see below) is not necessarily obvious. The measurement or calculation of δ_{w} for anisotropic or polar solutes is quite difficult.

The importance of magnetic anisotropy contributions (δ_{a}) has been recognized for some time, particularly for aromatic solvents. Several quantitative calculations of *inter-* and *intra*molecular effects have been made for aromatic hydrocarbons.[8-10] Other important magnetic anisotropy shifts have been found in molecules containing carbonyl, nitro, and nitrile substituents.[3,11] δ_{a} has been detected experimentally by major deviations from expected behavior of methane based on δ_{b} and δ_{w}.[3] Thus precise measurements are limited by the uncertainties in these two values, as well as by possible "polar effects" if the solute has a dipole moment.

The solvent shifts experienced by polar molecules include all the terms described so far and, in addition, a "polar solvent shift."[3] A widely accepted explanation

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