[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Refractive Indices and Molar Refractions of Some Halogen Fluorides and Fluorocarbon Derivatives in the Vapor State[1]

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The refractive indices of a series of halogen fluorides, and of several fluorocarbon derivatives, have been measured in the vapor state by an interferometric method. The molar refraction of each substance has been calculated and compared with the value obtained by addition of atomic refractions. The atomic refractions of fluorine suitable for description of the fluorocarbon derivatives (1.10) and the halogen fluorides (1.35) are larger than the normal value (0.80). This has been interpreted as indicating a greater importance of π bonds in the polyfluorides studied here than in monofluorides.

Introduction

The refractive indices of bromine trifluoride and bromine pentafluoride have been measured in the liquid state.[2] No other refractive indices or molecular refractions have been reported for the halogen fluorides. Since values of these constants were required for calculations of electric moments, and are of interest in other connections, we have measured the refractive indices of several halogen fluorides in the vapor state and have calculated their molar refractions. Similar data for several fluorocarbon derivatives also are reported.

Experimental

Materials.—The preparation and purification of iodine pentafluoride, bromine pentafluoride, bromine trifluoride and chlorine trifluoride have been described.[1,3] Chlorine monofluoride was prepared from chlorine and chlorine trifluoride at 250° in a Monel reaction vessel and was purified by several trap-to-trap distillations.[4] Chlorotrifluoroethylene was obtained from the Oak Ridge National Laboratory and was purified by distillation. Purified samples of the remaining fluorocarbon derivatives were the gift of the Minnesota Mining and Mfg. Co.

Apparatus and Technique.—Refractive indices were measured by use of a Rayleigh-type interferometer constructed in this Laboratory. Details of the construction, operation and calibration of the instrument have been given.

The cells were copper-plated brass tubes, three-eighths of an inch square in cross-section and 102.08 cm. long. Inlet and outlet tubes were silver-soldered into the ends of the cells and provided with nickel diaphragm valves. A water jacket surrounded the tubes except for the ends, and for a space for the upper beam which provided the reference fringes. The windows were quartz plates ground and polished optically flat. A copper vacuum line with nickel traps and Monel valves was connected with the cells for handling the halogen fluorides. Pressures were measured with a Monel Bourdon gage read with a micrometer device[6] and calibrated against a mercury manometer.

The system was initially evacuated and the fringes from the evacuated cell aligned with the reference set. As the gas to be measured was slowly introduced the fringe system moved relative to the reference set and the number of fringes by which the system was shifted (Δm) for given pressure change (Δp) was observed. The fringes were counted either visually or automatically using a photoelectric cell and recorder. The refractive index of the gas was computed from the equation

$$\frac{760\lambda}{l}\,\frac{\Delta m}{\Delta p} = (n - 1)10^6$$

where λ is the wave length of the monochromatic light source, l is the path length and $\Delta m/\Delta p$ is the number of fringes shifted for a pressure change of one milimeter of mercury. The mean of several (five to fifty) determinations of $\Delta m/\Delta p$ was used to compute the refractive index. The precision was limited by the precision of pressure measurement (about 0.7%) and by the reactivity of the halogen fluorides. When measurements on the latter compounds were made fresh samples were introduced into the cell until constant values of $\Delta m/\Delta p$ were obtained after which the actual measurements were made. It is believed that appreciable contamination of the initially pure materials was avoided by this technique. The quartz windows were attacked only very slowly.

Results

The refractive indices of the vapors at one atmosphere pressure and the indicated temperatures are shown in Table I along with the molar refractions computed using the Lorenz–Lorentz equation. Densities were computed by the ideal gas law. The precision of the refractive index measurements is limited only by the precision of the pressure measurement and the purity of the material. The probable errors in refractive index and molar refraction listed take the latter factor into account only partially since the great reactivity of the halogen fluorides makes it difficult to prevent contamination in handling. The molar refractions of bromine trifluoride and bromine pentafluoride agree within the limits of error with those ob-

TABLE I

REFRACTIVE INDICES AND MOLAR REFRACTIONS OF HALOGEN FLUORIDES AND FLUOROCARBON DERIVATIVES

Compound	Temp., °C.	$(n - 1) \times 10^6$	*MR*, cc./mole Obsd.	Calcd.
Chlorine monofluoride	24.0	494[a]	7.62[b]	7.19[c]
Chlorine trifluoride	26.0	633	10.34	9.89
Bromine trifluoride	53.0	725	12.92	12.79
Bromine pentafluoride	25.0	951	15.48	15.49
Iodine pentafluoride	29.0	1156	19.17	20.70
Chlorotrifluoroethylene	20.0	962	15.77	15.90
Perfluoroethyl ether	25.0	1440	23.49	23.13
Perfluorotetramethylene oxide	25.0	1023	16.67	16.50
Perfluorotriethylamine	27.5	2126	34.96	34.79

[a] The refractive indices are at one atmosphere pressure and the stated temperature and are for the mercury green line (λ = 5461 Å.). The probable error is about 1% of the value listed. [b] The molar refractions were computed with the ideal gas law and are for λ = 5461 Å. The probable error in these values is about ±0.3 cc./mole. [c] The molar refractions of the halogen fluorides were computed using a value of 1.35 for the atomic refraction of fluorine whereas the values for the fluorocarbon derivatives were obtained using the value 1.10.

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(1) Physical properties of the halogen fluorides VI. For preceding article of this series see M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, THIS JOURNAL, **78**, 44 (1956).

(2) L. Stein, R. C. Vogel and W. H. Ludewig, *ibid.*, **76**, 4287 (1954).

(3) M. T. Rogers, J. L. Speirs, H. B. Thompson and M. B. Panish, *ibid.*, **76**, 4843 (1954).

(4) M. T. Rogers and J. Phelps, unpublished results.

(5) J. G. Malik, J. L. Speirs and M. T. Rogers, *J. Chem. Educ.*, **30**, 437 (1953); J. G. Malik, Doctoral Thesis, Michigan State University, 1954.

(6) M. T. Rogers, H. B. Thompson and J. G. Malik, *Rev. Sci. Instr.*, **26**, 730 (1955).

tained by Stein and Vogel[2] from measurements of the refractive indices (Na D line) and densities of the liquids.

No single value of the atomic refraction of fluorine will, when combined with the standard refractions of other atoms, produce good agreement with the observed molar refractions of all fluorine-containing compounds. It is usually possible to select a satisfactory value of this quantity suitable for use in any given series of compounds, but in the case of the halogen fluorides the refractions of the other halogen atoms in their higher valence states are also unknown. If we use the value 1.35 cc./mole for the atomic refraction of fluorine and make no correction for change of valence state then the calculated molar refractions of the halogen fluorides are as shown in Table I. The fair agreement with experiment is probably fortuitous since the refraction of the central atom should decrease with the increase in oxidation number. It is possible that an increasing use of d-orbitals in π-bond formation in the tri- and pentafluorides produces a compensating increase in polarizability.

A value of 1.10 cc./mole for the atomic refraction of fluorine when combined with standard refractions of other atoms[7] leads to the calculated values of the molar refractions of the fluorocarbon derivatives shown in Table I. Since an atom refraction of fluorine of about 0.8 cc./mole is found for the monofluorides there is an increase in polarizability of fluorine in the polyfluorides; this may be associated with the increase in double-bond character of the carbon–fluorine bonds in the polyfluorides.[8]

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(7) A. I. Vogel, *J. Chem. Soc.*, 1833 (1948). Although our values are for $\lambda = 5461$ they have been compared with literature values for $\lambda = 5893$ with no correction for dispersion since the latter would be less than our experimental error.

(8) See, for example, L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

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[CONTRIBUTION FROM KINETICS SECTION, DIVISION OF EXPLOSIVES TECHNOLOGY, BUREAU OF MINES]

The Oxygen-induced Hydrogen–Deuterium Exchange[1,2]

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Oxygen in concentrations as low as two parts per 1000 in a hydrogen–deuterium mixture increases the rate of exchange over that of oxygen-free mixtures by a factor of 100 or more. This induced exchange results from a chain mechanism in which initiation occurs at the wall and termination in the gas phase. It is postulated that, in the presence of oxygen, OH radicals are produced at the wall, leading to a higher steady-state H-atom concentration in the gas phase than for an oxygen-free system. The terminating step is $H + O_2 + M \rightarrow HO_2 + M$ and not the atom recombination reaction operative in the uninduced exchange.

Introduction

Farkas and Farkas[4] studied the hydrogen–deuterium exchange in fused silica vessels in the temperature region 575 to 750°. They showed that the exchange is predominantly homogeneous and proceeds *via* the atomic processes

$$H + D_2 \rightleftarrows HD + D$$

and

$$D + H_2 \rightleftarrows HD + H$$

Initiation and termination of these reaction chains were shown to occur *via* the continuously maintained equilibria

$$H_2 \rightleftarrows 2H;\ D_2 \rightleftarrows 2D;\ \text{and}\ HD \rightleftarrows H + D$$

Van Meersche[5] also studied this reaction and extended the lower portion of the temperature range to 450°. His results are in complete agreement with an Arrhenius extrapolation of the Farkas and Farkas data.

Mund, *et al.*,[6–8] investigated the α-particle-initiated hydrogen–deuterium exchange in the temperature range 12 to 60°. Even at these temperatures reaction proceeds by an atomic chain sequence. It was shown that chain termination by the processes

$$H + O_2 \longrightarrow HO_2 \text{ and } D + O_2 \longrightarrow DO_2$$

becomes important in the presence of small amounts of oxygen and the exchange is inhibited. The HO_2 and DO_2 may undergo further reactions but do not regenerate the chain carriers H and D.

We find that traces of oxygen accelerate the rate of the hydrogen–deuterium exchange in fused silica vessels in the neighborhood of 500°. As little as 2 or 3 parts per 1000 of oxygen in a hydrogen–deuterium mixture increase the initial rate of HD formation by a factor of 100 or more, depending on the pretreatment of the vessel walls. The experimental results can be explained on the basis of a chain mechanism with wall initiation and gas-phase termination.

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(2) Presented at 127th meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, March 29 to April 7, 1955, in Cincinnati, Ohio.

(3) (a) Olin Mathieson Chemical Corp., New Haven, Conn. (b) General Electric Co., Cincinnati, Ohio.

(4) (a) A. Farkas and L. Farkas, *Nature*, **132**, 894 (1933); (b) *Proc. Roy. Soc.* (*London*), **A152**, 124 (1935).

(5) M. Van Meersche, *Bull. soc. chim. Belg.*, **60**, 99 (1951).

(6) W. Mund, L. Kaertkemeyer, M. Vanpee and A. Van Tiggelen, *ibid.*, **49**, 187 (1940).

(7) W. Mund, Th. De Menten De Horne and M. Van Meersche, *ibid.*, **56**, 386 (1947).

(8) W. Mund and M. Van Meersche, *ibid.*, **57**, 88 (1948).