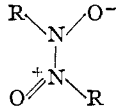
a twofold axis but not a center of symmetry and can be represented



plus other resonance forms. The absence of a center of symmetry agrees with the observation that the methyl analog, presumably of the same structure, possesses a permanent dipole moment.

The space group of the crystalline methyl analog, nitrosomesitylene, has been determined (Pbca; *a*, *b*, *c* = 10.82, 35.1, 8.82; eight dimers/unit cell).

ABERDEEN PROVING GROUND, MD.
RECEIVED MARCH 2, 1949

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Reaction Heats of Organic Fluorine Compounds. III. The Vapor Phase Heats of Hydrobromination of Some Simple Fluoroölefins[1]

BY J. R. LACHER, K. R. LEA, C. H. WALDEN,[2] G. G. OLSON AND J. D. PARK

The first two papers[3,4] of this series described the calorimeter and its performance, and presented the vapor phase heats of chlorination of tetrafluoroethylene, trifluorochloroethylene, 1,1-dichloro-2,2-difluoroethylene, perfluoropropene and perfluorocyclobutene. The present paper deals with the vapor phase heats of hydrobromination of the first three olefins listed above.

Experimental Details.—The olefins[5] were purified as described in papers I and II.[3,4] A sample of purified tetrafluoroethylene was submitted to Dr. F. L. Mohler of the National Bureau of Standards for mass spectrographic analysis. Aside from traces of mercury and water vapor (due to the method used in preparing the sample for shipment) nothing but the olefin could be detected. Hydrogen bromide obtained from the Matheson Company was used without further purification. The catalyst consisted of "Columbia" activated carbon which was sized to pass a number 6 and be retained on a number 20 screen. It was activated by heating to 250° *in vacuo* for two hours. After being transferred to the reaction chamber of the calorimeter, the catalyst was again evacuated for one hour at 94°. Hydrogen bromide was then passed into the catalyst chamber.

The procedure in making a run was similar to that used for the chlorination reactions described in papers I and II. The hydrogen bromide was mixed in the catalyst chamber with excess olefin. The product gases were then tested for unreacted hydrogen bromide. The reaction was quantitative in the case of tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene. An attempt was made to measure the heat of addition of hydrogen bromide to perfluorocyclobutene. However, at the temperature of the calorimeter, the reaction was far from quantitative and a steady state could not be attained. The incomplete reaction is presumed to be due to a small heat of reaction leading to an unfavorable equilibrium.

When hydrogen bromide adds to the three simple olefins, the bromine goes to the CF_2– group in accordance with Markownikoff's rule.[6] In order to test the calorimeter product for the presence of substances produced by a possible reverse addition or disproportionation reactions, samples of the effluent gases from the calorimeter were trapped at −80°. They were analyzed by taking infrared spectra in a manner similar to that previously described.[3,4] If any side reactions took place, they were less than 0.2%. Using auxiliary apparatus and a catalyst identical to that in the calorimeter, a considerable quantity of each of the hydrogen bromide adducts was prepared. The products were carefully distilled using a 36-inch Hypercal Podbielniak fractionating column. The distillation was followed by taking infrared spectra of the various fractions and again no evidence for reverse addition was found for the unsymmetrical olefins. The spectra of the carefully purified products are presented in Figs. 1, 2 and 3. A further attempt was made to detect the presence of the reverse addition product in case of the trifluorochloroethylene. The reaction was carried out at 200° with a little air in the hydrogen bromide stream. A careful distillation of the product and infrared analysis again indicated that the reaction takes place quantitatively in accordance with Markownikoff's rule.

TABLE I

VAPOR PHASE HEATS OF HYDROBROMINATION AT 94°

Run	Olefin flow, mole/min. × 10^4	HBr flow, mole/min. × 10^4	Energy input, cal./min.	$-\Delta H_{367°K.}$ cal./mole
		Tetrafluoroethylene		
1	5.0	3.5532	11.6245	32,746
3	6.6	1.9235	6.3442	32,982
4	4.8	1.9230	6.3288	32,910
6	5.1	2.4394	8.0624	33,050
			Average 32, 922 ± 180 cal./mole	
		Trifluorochloroethylene		
2	5.7	1.9766	5.1506	26,057
4	5.9	2.4338	6.2910	25,848
6	5.6	2.1860	5.7430	26,271
7	5.5	2.0996	5.4711	26,057
8	5.6	1.9726	5.1572	26,144
			Average 26,074 ± 226 cal./mole	
		1,1-Dichloro-2,2-difluoroethylene		
1	7.3	1.9241	4.4497	23,126
2	7.1	2.1505	4.9317	22,932
3	9.4	2.1505	4.9583	23,056
4	7.0	2.7239	6.2850	23,073
			Average 23,047 ± 115 cal./mole	

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[1] Presented before the Symposium on Fluorine Chemistry, 116th Meeting of the American Chemical Society, Atlantic City, N. J.

[2] American Cyanamid Fellow, 1948.

[3] J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson and J. D. Park, THIS JOURNAL, **71**, 1330 (1949).

[4] J. R. Lacher, J. J. McKinley, C. H. Walden, K. R. Lea and J. D. Park, *ibid.*, **71**, 1334 (1949).

[5] Samples of tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene were supplied us through the courtesy of Jackson Laboratory, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

[6] W. B. Markownikoff, *Ann.*, **153**, 256 (1870).

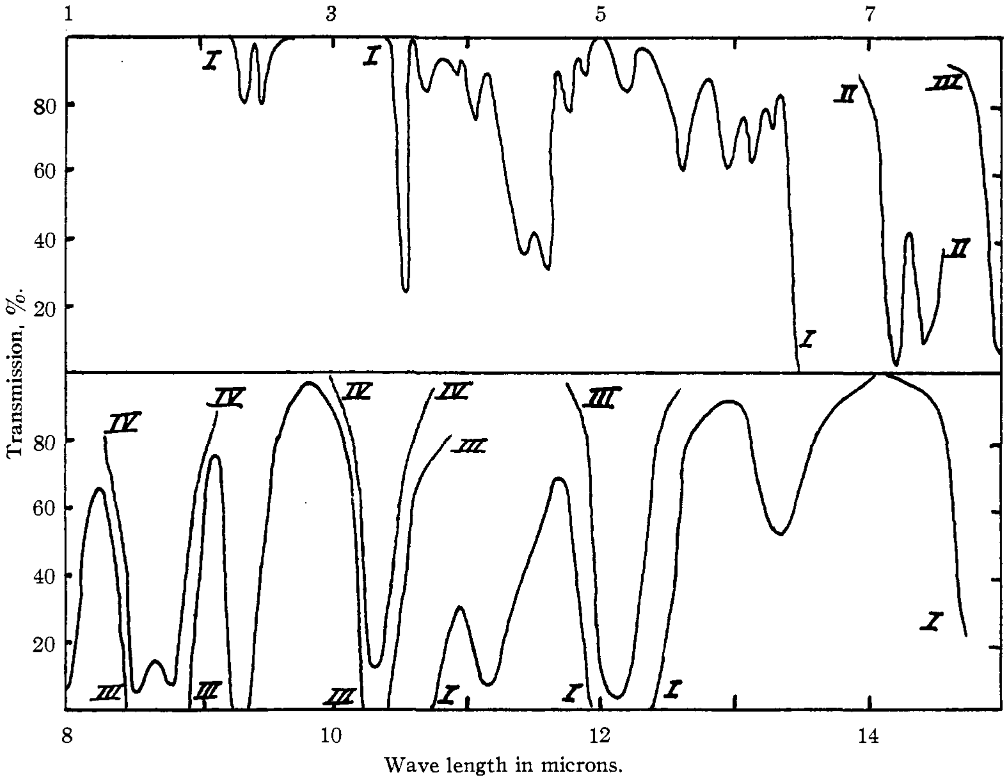

Fig. 1.—Infrared spectrum of CF_2Br-CF_2H in 10-cm. cell: I, 608 mm.; II, 100 mm.; III, 32 mm.; IV, 32 mm.

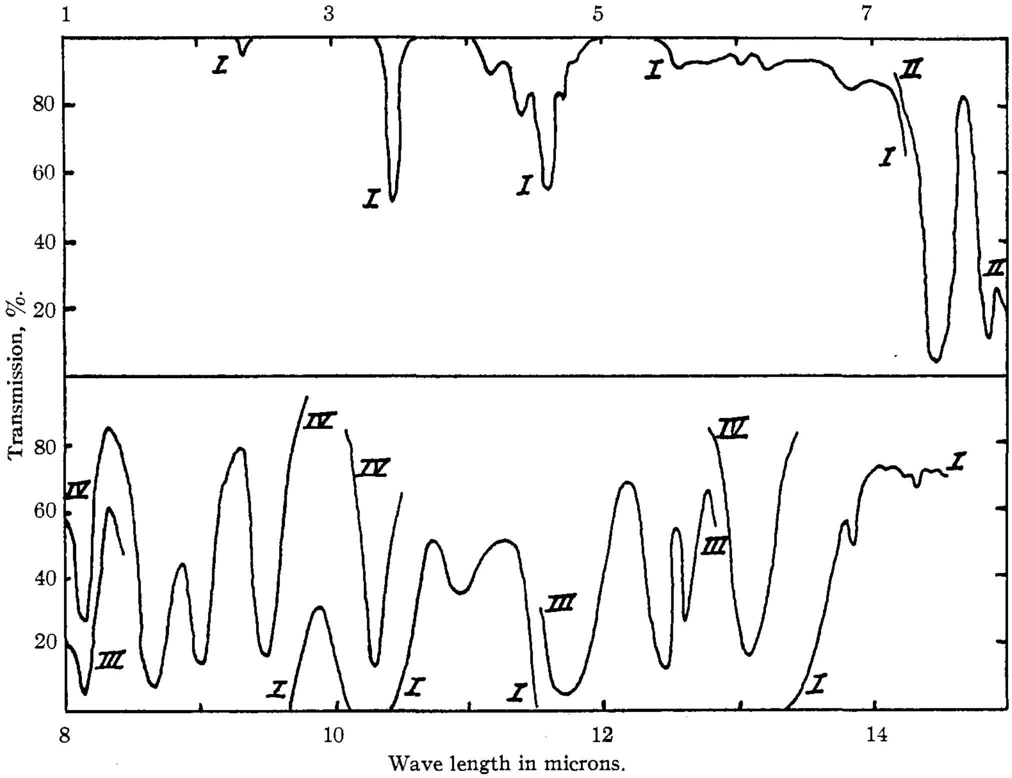

Fig. 2.—Infrared spectra of $CF_2Br-CFClH$ in 10-cm. cell: I, 237 mm.; II, 100 mm.; III, 30 mm.; IV, 10 mm.

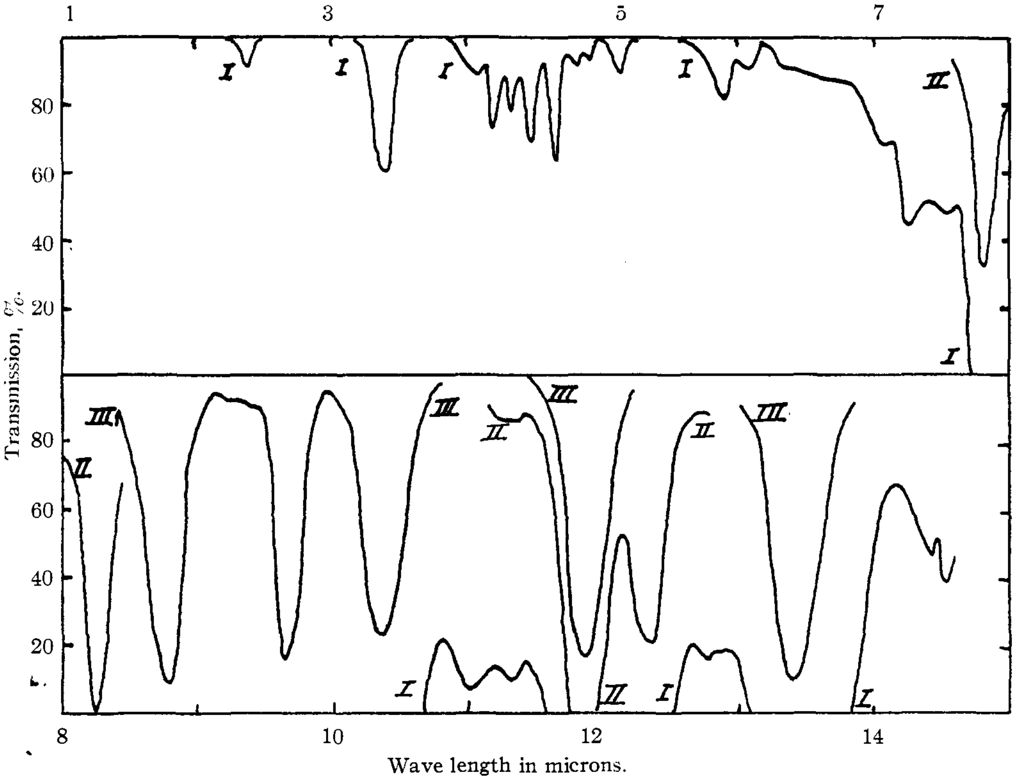

Fig. 3.—Infrared spectra of $CF_2Br-CCl_2H$ in 1-meter cell: I, 48 mm.; II, 6.5 mm.; III, 4 mm.

Experimental Results and Discussion.—The results on the individual calorimetric runs are given in Table I.

All runs are included except those which were obviously bad-equipment failures, analytical troubles, etc. The data are summarized in Table II.

TABLE II

THE HEATS OF HYDROBROMINATION

Compound	$-\Delta H_{367°K}$ cal./mole
$CF_2{=}CF_2$	32,992
$CF_2{=}CFCl$	26,074
$CF_2{=}CCl_2$	23,047
$CH_3{-}CH{=}CH_2$	20,050

Also included in the latter table is the heat of hydrobromination of propylene as determined in this Laboratory.[7] The hydrobromination reactions are considerably more exothermic than the values calculated from the tables of bond energies. Pauling's tables[8] give a value of −12.5 kcal. and Pitzer's revised table[9] gives even a lower value of −0.5 kcal./mole. The reactions must be quite exothermic or, as a simple statistical calculation will show, they will not proceed quantitatively.

The reaction heats also deviate considerably from a simple additivity rule. The reactions are all more exothermic with the fluorinated olefins than with propylene. The heat of hydrobromination of tetrafluoroethylene is 6.8 kcal. more exothermic than that of trifluorochloroethylene; whereas trifluorochloroethylene liberates 3.0 kcal. more heat than does 1,1-dichloro-2,2-difluoroethylene. Since the carbon–bromine bond which is formed is always present on a CF_2-group in case of the fluoroölefins, one might expect this bond strength to be nearly constant except for potentials across the carbon–carbon single bond in the ethane. The infrared absorption spectra of the hydrogen bromide adducts give qualitative information concerning the carbon–hydrogen bond. We have tentatively assigned the peaks at 3.42, 3.44 and 3.38 mμ for tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene, respectively, as those due to the carbon–hydrogen stretching frequency. This gives a force constant for the carbon–hydrogen stretching vibration of about 5.0×10^5 dynes/cm., which is the same as for normal hydrocarbons. This suggests that the carbon–hydrogen bond strength is nearly the same for all the hydrogen bromide adducts. This means that the main deviations from an additivity rule are due mainly to variations in carbon–carbon double and single bond strengths in the reactants and products. Steric repulsions of the large halo-

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(7) J. R. Lacher, C. H. Walden, K. R. Lea and J. D. Park, THIS JOURNAL, **72**, 331 (1950).

(8) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 52 and p. 131.

(9) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

gen atoms across the carbon–carbon single bond would be effective in lowering the heat of reaction.

Acknowledgment.—This work was made possible by a grant from the Research Corporation of New York.

Summary

The vapor phase heats of hydrobromination of tetrafluoroethylene, trifluorochloroethylene and 1,1-dichloro-2,2-difluoroethylene have been measured at 94°. The results are discussed.

BOULDER, COLO. RECEIVED NOVEMBER 10, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DELAWARE]

The Solubility of Hydrogen Bromide in Normal Paraffin Hydrocarbons[1]

BY EDWARD R. BOEDEKER[2] AND CECIL C. LYNCH

Introduction

The measurement of the solubility behavior of hydrogen bromide has been carried out in only a few organic solvents. The majority of the publications report solubility measurements in solvents where polar effects and unsaturation obscure the true solubility behavior of hydrogen bromide. Only recently, Fontana and Herold[3] reported measurements of the solubility of hydrogen bromide in *n*-butane and in *n*-hexane, in which solvents the solute would be expected to exhibit its true solubility behavior since polar effects and unsaturation are absent. These authors measured the solubility of hydrogen bromide at partial pressures of hydrogen bromide up to about 35 lb. absolute. They did not analyze the liquid phase but calculated the hydrogen bromide solubility from the amount of hydrogen bromide added to the system and from the total pressure of the system and assumed Raoult's law to be valid.

The primary purpose of the present work was to obtain solubility data for several hydrogen bromide–*n*-paraffin hydrocarbon systems at several temperatures. It was hoped that these data could then be used in predicting the solubility of hydrogen bromide in other hydrocarbons within the temperature range studied. As a secondary objective, the results of the present study, wherein liquid phase analyses were made, can be compared with the results obtained by Fontana and Herold on the basis of vapor pressure measurements.

Experimental

The apparatus which was used is shown schematically in Fig. 1 and is a modification of the apparatus used by Howland, Miller and Willard.[4] The method consists in saturating the solvent in an absorption flask with the solute vapor under known partial pressure and then analyzing a weighed sample of the solution to determine the amount of dissolved gas.

The apparatus consists of three parts, (1) an hydrogen bromide purification and storage system, (2) the portion of the system wherein the solubility measurements are made, and (3) a sampling tube for withdrawing samples from the liquid phase for analysis.

The solubility flask is a 250-ml. round-bottom flask to which is attached a glass coil of 10-mm. Pyrex tubing. The glass coils are approximately two inches in diameter with the coils about one inch apart. The length of the coiled section is about fifteen inches. The solubility flask is attached to the vacuum system by means of a ground glass joint. The solubility flask also has sealed to it a female ground joint through which the liquid phase sampling tube passes.

The hydrogen bromide reservoir is a three-liter flask which has an eight-inch piece of 20 mm. tubing sealed to the bottom. The reservoir connects to an open end manometer. By means of a three-way stopcock sealed to the top of the flask, the reservoir can be connected either with the vacuum manifold or with the solubility flask.

The entire system is connected to a mercury diffusion pump and a mechanical pump.

Agitation of the solubility flask during the measurements was obtained by attaching the glass coil, by means of an elastic band, to an eccentric on a slow speed motor.

The solubility flask was immersed in a constant temperature bath during the solubility measurements. Temperatures were maintained constant within 0.05° and were read on a thermometer which was checked against a calibrated Bureau of Standards thermometer.

Experimental Procedure

Prior to the solubility measurements, the solubility flask with stopcocks S-2 and S-3 closed and stopcock S-1 open to line L-2 was evacuated to a pressure of less than 10^{-3} mm. for at least one hour. Stopcock S-1 was closed, and a female ball joint with a tube bent at right angles and drawn down to a fine capillary was attached to the ball joint sealed onto stopcock S-3. This capillary was immersed in the solvent to be used, and by opening stockcock S-3 the solvent was drawn into the solubility flask. Since a small amount of air was always drawn into the system during the introduction of the solvent, the solubility measuring system was evacuated by opening stopcock S-1 for short intervals of time. To remove the air completely the solvent was allowed to boil under reduced pressure.

The following sequence of operations was followed in making the solubility measurements. Stopcock S-6 was turned so that the hydrogen bromide reservoir, containing the purified hydrogen bromide, was opened to line L-1. A small amount of hydrogen bromide was admitted to the solubility system by slightly opening stopcock S-1. After the required amount of solute gas had been admitted to the system, stopcock S-1 was closed. Stopcock S-3 was opened very carefully and the draw-off tube almost emptied of solvent. The flask was then shaken and the agitation continued until the pressure in the system became constant.

After the pressure in the system had become constant, a sample was withdrawn in the following manner. A

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[1] Abstracted from a thesis submitted by Edward R. Boedeker in partial fulfillment of the requirements for the degree of Master of Science, University of Delaware, June, 1949.

[2] Houdry Process Corporation, Linwood, Pennsylvania.

[3] Fontana and Herold, THIS JOURNAL, **70**, 2881 (1948).

[4] Howland, Miller and Willard, *ibid.*, **63**, 2807 (1941).