results on the conductance of the addition compound of 1,3-dibromopropane and N,N,N′,N′-tetramethyltrimethylenediamine.

N,N,N′,N′-Tetramethyltrimethylenediamine was prepared by decomposing its hydrobromide with sodium hydroxide. The hydrobromide was prepared by heating 15.5 g. (0.076 mole) 1,3-dibromopropane and 13.6 g. (0.30 mole) of dimethylamine in an equal weight of absolute methanol for 20 hr. at 140°. The methanol solution was then treated with two volumes of 40% sodium hydroxide solution. Three layers were obtained; the upper one (34% diamine in water) was dried with solid caustic and combined with the dried ether extracts of the other two layers. The main fraction distilled at 65–68° at 44 mm. The picrate melted at 207°, which agrees with literature values.[5,6]

Addition products of the diamine and 1,3-dibromopropane were made[7] in several ways. On heating an equimolar mixture of the reagents to 70°, a hygroscopic solid is obtained. Reaction in ethanol gives a soluble product which can be recovered by evaporation of the solvent or by precipitation with dioxane. Solutions of the reagents in nitrobenzene or in nitromethane precipitate a white solid on heating; this result was surprising, because nitrocompounds are usually good solvents for aliphatic quaternary salts. Depending on the terminal groups, three series of polysalts are possible; the $Br(CH_2)_3[Me_2N^+(CH_2)_3 \cdot Br']_{2p-1}NMe_2$ series, with 48.15% total bromine and ionic bromine less than 48.15%; the $Me_2N(CH_2)_3[Me_2N^+(CH_2)_3 \cdot Br']_{2q}NMe_2$ series with total bromine equal to ionic bromine, and both approaching 48.15% as q becomes large; and the $Br(CH_2)_3[Me_2N^+(CH_2)_3 \cdot Br']_{2r}$ Br series with total bromine greater than 48.15% and ionic bromine less than 48.15%. We determined total bromine by the Parr semimicro bomb method, and ionic bromine by potentiometric titration. The latter was subject to some error due to hydrolysis of terminal $(CH_2)_3Br$ groups. Our highest molecular weights were obtained by heating 20% solutions of the two reagents (equimolar amounts) in nitrobenzene at 100° for several hours; the analyses indicate 15–20 quaternary nitrogens per chain, depending on what terminal groups are assumed.

Data for a typical conductance curve are given in Table I; the salt, prepared in nitrobenzene, contained 45.3% ionic bromine. Concentrations are given as equivalents of bromide per liter and $\Lambda = 1000\ \kappa/c$, where κ is specific conductance. A plot of Λ against square root of concentration gives a sharply concave-up curve, which is much steeper than those exhibited by ordinary 1–1 salts; the latter change by about 5% in conductance over the above range of concentration, as contrasted with the 50% change of Table I. The shape of the curve indicates a fairly high degree of association of bromide ions with the positive nitrogens of the chain, despite the rather low molecular weight of the cation and the high dielectric constant of the solvent. We have, as a matter of fact, found appreciable association in water for electrolytes[8] in which only two quaternary nitrogens were attached to the ends of a chain of ten carbon atoms. The higher association of the present multivalent ion with correspondingly higher charge density is therefore to be expected.

TABLE I

CONDUCTANCE OF POLYELECTROLYTE IN WATER AT 25.00°

c	Λ
0.00291	92.02
.00699	78.23
.01259	70.44
.01747	66.84
.02089	64.99

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The Ultraviolet Absorption Spectra and the Refractive Indices of Some Fluorobromomethanes

BY NORMAN DAVIDSON

The ultraviolet absorption spectra and the refractive indices of the gases, CF_3Br, CF_2Br_2 and HCF_2Br, which were on hand for other work, have been measured.

Absorption spectra were taken with a Beckman model DU spectrophotometer using a 10 cm. cylindrical glass cell with cemented quartz windows and a stopcock lubricated with Apiezon grease. Samples were measured at pressures in the range of 760–0.3 mm. so as to give optical densities in the range 0.1–1.2. With the exception noted below, data obtained over a range of pressures checked Beer's law to ±5% or better. Because of the rapid increase in light absorption with decreasing wave length (Fig. 1) for the substances studied and because of a large component of scattered light for $\lambda \leq 220$ mμ, measured values of the optical density, D, in this wave length range were low when $D > 1.0$. However, for $D < 0.6$, data that satisfied Beer's law were obtained.

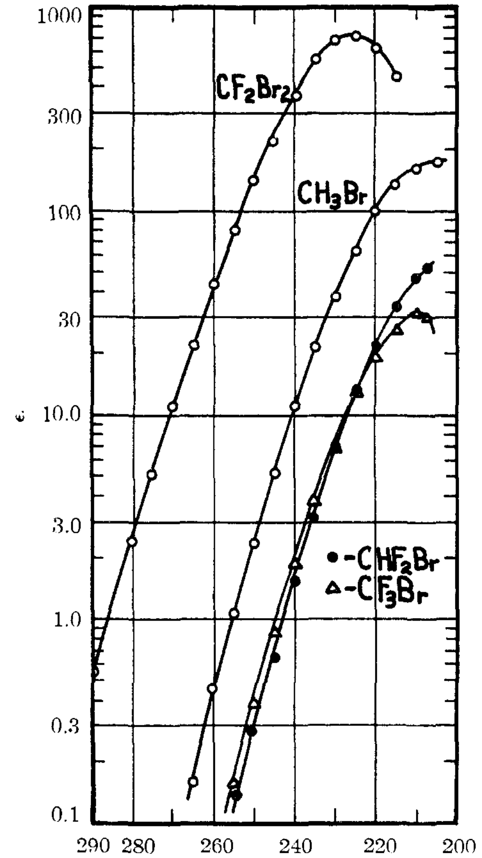

Fig. 1.—Absorption spectra of CF_2Br_2, CH_3Br, CHF_2Br and CF_3Br($\epsilon = (1/lc)\ \log_{10}(I_0/I)$ liters/mole cm.).

Refractive indices, relative to dry, carbon dioxide-free air, for the mercury line, $\lambda = 546$ mμ, were determined by Scott B. Kilner using a gas phase interferometer.

Pressures were measured to an accuracy of 0.5 mm. with a mercury manometer (i.d. = 8 mm.) and a meter stick. Known low pressures were obtained by expanding the gas from a small volume at a high pressure into a larger volume including the cell. Temperatures were measured to an accuracy of 0.2° with a calibrated copper–constantan thermocouple.

Trifluorobromomethane.—CF_3Br was prepared by the thermal vapor phase bromination of fluoroform.[1] Some measured vapor pressures were:

t, °C.	−108.3	−105.2	−80.8	−78.9
p (mm.)	30	38	201	245

The data fit the equation, $\log_{10} p(\text{mm.}) = -(984/T) + 7.46$ corresponding to a calculated boiling point of −58.6°, a heat of vaporization of 4.50 kcal. and a Trouton constant of 20.0 e.u. Brice, Pearlson and Simons[1] give −59.0 to −60.5° as the boiling point.

Difluorobromomethane.—HCF_2Br was prepared by the reaction of bromoform with antimony trifluoride.[2,3] A mixture of 0.14 mole of bromoform, 0.17 mole of antimony trifluoride, 0.018 mole of bromine and 0.018 mole of potassium fluoride was heated to 120–130° in an all-glass system in which volatile products were removed at a pressure of *ca.* 1 atm. After washing with aqueous sodium hydroxide, 0.054 mole of difluorobromomethane and 0.0025 mole of fluoroform were isolated by vacuum distillation. The low yield of difluorobromomethane is partly due to accidental losses during its isolation.

The observed vapor density of a sample of difluorobromomethane corresponded to a molecular weight of 131.1 (theor., 131.9). Some measured vapor pressures were

t, °C.	−78.5	−59.7	−49.6	−29.5	−18.5	−14.8
p (mm.)	19.5	75	140	407	678.5	786

The data lead to the equation, $\log_{10} p(\text{mm.}) = -(1255/T) + 7.745$. The calculated boiling point, heat of vaporization and Trouton constant are −15.1°, 5.75 kcal. and 22.3 e.u. The boiling point has been reported[2,3] as −14.5°.

Difluorodibromomethane.—CF_2Br_2 was obtained in a low yield (7.4%) by the thermal vapor phase bromination of trifluoroacetic acid. A mixture of 0.2 mole of bromine and 0.06 mole of trifluoroacetic acid was refluxed in a system in which there was a glass tube heated to 400° between the stillpot and the reflux condenser and in which volatile products were continuously removed. Small quantities of $CF_3H + C_2F_6$, CF_3Br and HCF_2Br were obtained also.

The vapor density of a sample corresponded to a molecular weight of 209 (theor., 209.8). Some of the observed vapor pressures were

t, °C.	−51.4	−42.5	−29.1	−6.8	0	11.2
p (mm.)	20	34.5	75.5	232	381	484

The vapor pressure equation is $\log_{10} p(\text{mm.}) = -(1387/T) + 7.567$. The calculated boiling point, heat of vaporization and Trouton constant are 23.8°, 6.35 kcal. and 21.3 e.u. Rathsburg[4] gives 24.5° for the boiling point.

The refractive index results are given in Table I. The quantity R is the ratio of pressure of air (500–760 mm.) to pressure of sample for equal optical paths in the interferometer at room temperature. The values of $n_{546} - 1$ are calculated, using the perfect gas law, for standard conditions, assuming that for air,[5] $n_{546} - 1 = 2.932 \times 10^{-4}$. The third column of the table gives the values of P, the molar refraction and the fourth column, P_F, the calculated values of the atomic polarizability of fluorine. For this calculation, the following atomic refractions at 546 mμ were used[6]: C, 2.426; H, 1.106; Br, 8.921. The value of 1.1 for the atomic refraction of fluorine obtained from Table I is in the expected range.[7]

TABLE I

REFRACTIVITY MEASUREMENTS

	R	$(n_{546}-1) \times 10^4$ (STP)	P (cc.)	P_F (cc.)
CF_3Br	3.335(±0.005)	9.78	14.61	1.09
HCF_2Br	3.365(±0.005)	9.87	14.75	1.15
CF_2Br_2	5.16(±0.01)	15.13	22.59	1.17

The absorption spectra of the fluorobromomethanes and, for comparison, of methyl bromide are give in Table II and illustrated in Fig. 1. For each of the substances, plots of log ϵ *vs.* λ are steep and almost linear on the long wave length side of the absorption maximum. Difluorodibromomethane has the largest maximum extinction coefficient (720 at 227 mμ) and its absorption extends the furthest toward long wave lengths. The data for methyl bromide are in good agreement with those reported by Fink and Goodeve[8]; these authors report a maximum ϵ of 182 at λ = 204 mμ. The absorption curves of trifluorobromomethane and difluorobromomethane are rather similar; they are displaced to shorter wave lengths as compared to that of methyl bromide. There is a maximum for ϵ of CF_3Br of 33 at *ca.* 208 mμ; the maximum for CHF_2Br occurs apparently for wave lengths slightly less than 207.5 mμ, and was not observed.

TABLE II

EXTINCTION COEFFICIENTS ($\epsilon = 1/lc)\log_{10}(I_0/I)$ LITERS/MOLE CM.) OF CH_3Br, CHF_2Br, CF_3Br AND CF_2Br_2

λ(mμ)	CF_2Br_2	CH_3Br	CHF_2Br	CF_3Br
290	0.54			
280	2.41			
275	5.16			
270	11.0	0.05		
265	22	.16		
260	44	.45		
255	80	1.065	0.134	0.158
250	140	2.35	.282	.374
245	233	5.2	.645	.86
240	370	11.0	1.52	1.85
235	550	21.7	3.36	3.80
230	680	38	7.0	7.0
225	710	63	13.2	13.1
220	620	98	22.0	19.4
215	460	136	34	26
210		162	47.5	32
207.5			53	31
205		175		

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