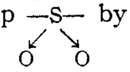
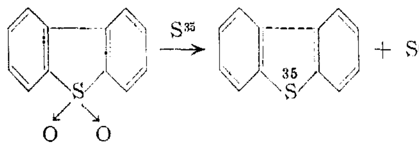
dioxide and diphenylene telluride.[3] Consequently it seemed to us that the second reaction, which is an exchange reaction, was the more likely. A rigorous method for establishing the mechanism was achieved by using radiosulfur. We now feel that it is highly probable that the replacement of the group  $-\mathrm{S}(\to\mathrm{O})_2-$ by sulfur is a direct one and is mainly



I II

This is in view of the fact that the sulfur dioxide and a small amount of hydrogen sulfide, which were both recovered as barium sulfate and counted as such, showed a radioactivity which was less than 4% of the activity of the original S^{35} containing barium sulfate. Moreover, the resulting dibenzothiophene was active and so this compound has become a useful starting material for the preparation of radiosulfur-containing carcinogenic compounds such as 3-acetaminodibenzothiophene (III).[4,5]

Acknowledgment.—The authors are very grateful to the Canadian Cancer Society for financial aid in support of this work. One of us (R.R.B.) is very grateful to the National Research Council of Canada for financial support during the summer of 1949. The authors also express their deep appreciation to Drs. J. A. Miller and E. C. Miller of the McArdle Memorial Laboratory, Madison, Wisconsin, for determining the biological properties of radioactive 3-acetaminodibenzothiophene. Their results will be published elsewhere.

Experimental

Radioactive barium sulfate[6] (0.2076 g.) with a specific activity of 47.6 × 10^5 counts per minute per gram of sulfur was converted to sodium sulfide according to the detailed procedure of Wood, Rachele, Stevens, Carpenter and du Vigneaud[7] who have prepared several mustard-type vesicants containing radiosulfur. Non-isotopic sodium sulfide (0.2645 g.) was added as carrier and the reduction to sulfur was carried out according to the directions of Wood, *et al.*[7] The sulfur (49.5 × 10^4 counts per minute per gram) was dissolved in *m*-xylene which was evaporated and replaced by carbon bisulfide. This solution was transferred to a 15-ml. exchange reaction flask which contained 2.57 g. of dibenzothiophene-5-dioxide. After the carbon bisulfide was evaporated the flask was heated in a potassium nitrate, sodium nitrite salt-bath. A dry inert atmosphere was supplied to the reaction flask by means of a nitrogen-filled gas holder. Nitrogen was also used to sweep the evolved sulfur dioxide and hydrogen sulfide through 3 ml. of a solution of 0.1 *M* zinc acetate and 0.2 *M* acetic acid contained in each of two bubbler tubes and through 3 ml. of 2 *N* NaOH contained in a third bubbler tube. The exchange reaction was carried out by heating for 2 hours at 320–330°, 30 minutes at 330–340°, 30 minutes at 360°, and finally for 15 minutes at 370–390°. The reaction mixture was steam distilled and the distillate was extracted with ether. After drying with anhydrous sodium sulfate and removal of ether, the residue was twice distilled under reduced pressure and crystallized once from ethanol. This afforded 0.2446 g. (31%) of dibenzothiophene, m.p. 98–99°; specific activity, 49.0 × 10^4 counts per minute per gram of sulfur. The dibenzothiophene was again twice distilled under reduced pressure and crystallized from ethanol. The activity of this material was 48.4 × 10^4 counts per minute per gram of sulfur. The sulfide precipitate from the first two bubbler tubes was centrifuged, oxidized to sulfate and counted as barium sulfate. The activity was less than 3% of the original barium sulfate. The centrifugate from the sulfide precipitate was combined with the material in the third bubbler tube, the sulfur oxidized to sulfate and counted as barium sulfate. The activity was less than 4% of the original barium sulfate.

Determination of Radioactivity.—All determinations were made with a windowless counter (Mark 9, Model 1, Nucleometer, purchased from the Radiation Counter Laboratories, Chicago, Illinois).

The gases collected from the exchange reaction were oxidized to sulfate and precipitated as barium sulfate. The precipitate was centrifuged, transferred in alcohol suspension to counting trays and counted as an infinitely thick layer. The activities of the dibenzothiophene and its derivatives were determined by counting infinitely thick layers of the pure crystalline substances. The same geometry was used in all measurements and a comparison was made with a reference standard. Corrections for self-absorption were applied.[8]

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[3] N. M. Cullinane, A. G. Rees and C. A. J. Plummer, *J. Chem. Soc.*, 151 (1939).

[4] J. A. Miller, E. C. Miller, R. B. Sandin and R. K. Brown, *Cancer Research*, **9**, 504 (1949).

[5] The conversion of active II into sulfur-labeled III was carried out by the 4-step process outlined by R. K. Brown, R. Christiansen and R. B. Sandin, THIS JOURNAL, **70**, 1748 (1948). The over-all yield of pure III was about 50%. The complete synthesis was carefully worked out with non-radioactive materials before the work with active materials was carried out.

[6] Barium sulfate containing radiosulfur was kindly supplied by the National Research Council of Canada, Division of the Atomic Energy Project, Chalk River, Ontario, Canada.

[7] J. L. Wood, J. R. Rachele, C. M. Stevens, F. H. Carpenter and V. du Vigneaud, THIS JOURNAL, **70**, 2547 (1948).

[8] W. F. Libby, *Ind. Eng. Chem., Anal. Ed.*, **19**, 2–6 (1947).

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Chain Electrolytes.[1] II

BY VICTOR F. H. CHU AND RAYMOND M. FUOSS

In a previous communication,[2] long chain polyelectrolytes were described in which nitrogen atoms of the chain were simultaneously the cationic sites; these were, however, also polyesters and hydrolyzed at an appreciable rate. In order to obtain stability in aqueous solution, compounds containing only carbon and nitrogen atoms in the chain seemed preferable. Searle[3] has described a number of such compounds obtained by the addition of α,ω-dibromides to α,ω-di-tertiary amines. Marvel and his co-workers[4] have shown that ω-halogenated amines undergo self-addition to give long chain quaternary salts when the nitrogen and the halogen atoms are separated by a sufficiently great distance to prevent cyclization. Both of these methods show promise of being very useful in the field of polyelectrolytes, because they permit the synthesis of compounds of known spacing between charges along the chain. The purpose of this note is to present some preliminary

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[1] Office of Naval Research, Project NR054-002; Paper No. 27.

[2] D. Edelson and R. M. Fuoss, THIS JOURNAL, **70**, 2832 (1948).

[3] N. E. Searle, U. S. 2,271,378, Jan. 27, 1942.

[4] M. R. Lehman, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **55**, 1977 (1935).

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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(5) L. Knorr and P. Roth, *Ber.*, **39**, 1428 (1906).

(6) H. T. Clarke, *J. Chem. Soc.*, **103**, 1699 (1913).

(7) V. F. H. Chu, Thesis, Yale University, June, 1950.

(8) R. M. Fuoss and D. Edelson, THIS JOURNAL, **73**, 269 (1951).

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.

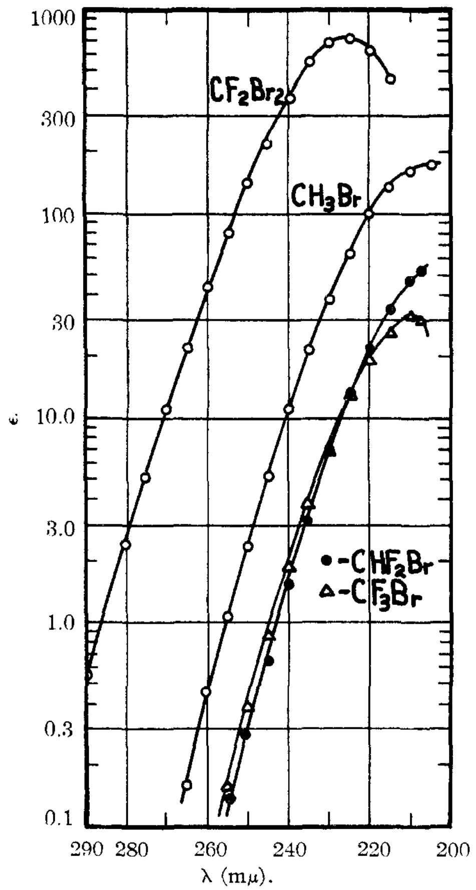

Fig. 1.—Absorption spectra of CF_2Br_2, CH_3Br, CHF_2Br and CF_3Br ($\epsilon = (1/lc)\log_{10}(I_0/I)$ liters/mole cm.).

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