TABLE I

MATERIALS AND PHYSICAL CONSTANTS

Reactants			B.p., °C.		
Ketone	Amine	Product	°C.	Mm.	n^{25}D
Methyl *n*-propyl	Ethanol-	N-1-Methylbutylidenethanolamine	91–95	60	1.4491
Diisobutyl	Ethanol-	N-1-Isobutyl-3-methylbutylidenethanolamine	153–155	80	1.4564
Methyl *n*-amyl	Ethanol-	N-1-Methylhexylidenethanolamine	88–89	6.5	1.4480
Methyl *n*-amyl	N-Ethylethanol-	2-Methyl-2-amyl-3-ethyloxazolidine	129–130	65	1.4420
Cyclohexanone	Ethanol-	N-Cyclohexylidenethanolamine	108–110	50	1.4819
Cyclohexanone	N-Ethylethanol-	Spirocyclohexane-1,2′-(3′-ethyl)-oxazolidine	107–109	80	1.4722

Acknowledgment.—The interest of Dr. D. C. Smith in this work and the preparation of N-1-methylhexylidenethanolamine by Mr. Urho E. Hanninen are greatly appreciated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Spectrophotometric Study of Tetrabutylammonium Tribromide

BY ROBERT E. BUCKLES, ALEXANDER I. POPOV, WILLIAM F. ZELEZNY AND ROBERT J. SMITH

Crystalline tetrabutylammonium tribromide was prepared by two different methods. Its ultraviolet absorption spectrum was determined in ethylene chloride solutions. Such solutions were found to be relatively unstable because of the bromination of the solvent which was observed. The method of continuous variation and the slope-ratio method, applied to mixtures of the tetrabutylammonium bromide and bromine in various ratios of concentrations, both indicate that the tribromide was the only polyhalogen present in bromotrichloromethane solution. The equilibrium constant for the reaction: $(C_4H_9)_4NBr_3 \rightleftarrows (C_4H_9)_4NBr + Br_2$ at 25° in bromotrichloromethane was calculated to be 6.0×10^{-6}.

Polyhalides of organic molecules, especially those containing nitrogen, have been reported since the early days of organic chemistry. In many cases such compounds were prepared as solid derivatives of the parent compounds. Among the polyhalides which are often encountered are the quaternary ammonium polyhalides. Of these, the polyiodides and mixed polyhalides containing iodine are the most common. Less well known are the quaternary ammonium polybromides. Phenyltrimethylammonium tribromide[1] and pentabromide,[2] *p*-tolyltrimethylammonium tribromide[2] and pentabromide,[2] a number of other substituted phenyltrimethylammonium tribromides,[3] and tetramethylammonium tribromide[4] have been isolated as pure solids. Solid higher polybromides which exhibited fairly high bromine pressures have also been reported, but the compositions were variable. Solids whose analyses corresponded to the formulas: $(C_2H_5)_4NBr_9$,[5] $(CH_3)_4NBr_9$,[4b] $(CH_3)_4NBr_{11}$[5] and $(CH_3)_4NBr_{13}$,[4a] have been obtained. In the latter case the solid was reported to lose bromine easily on standing to yield the crystalline tribromide.

Although the stability of these solids has been observed no study of the stability of the polybromides in solution has been made. The ultraviolet absorption spectra of cesium tribromide and of *p*-bromophenyltrimethylammonium tribromide have been measured in water and in alcohol.[6] Although the spectra obtained were characteristic of species other than just the monobromides and bromine originally present, the actual compositions of the absorbing species in solution were not determined. In the present work a spectrophotometric study of the nature of the absorbing species has been made on the tetra-*n*-butylammonium bromide–bromine system in solution.

Experimental

Tetra-*n*-butylammonium Bromide.—This material was kindly supplied by Dr. Mervin Runner of this Laboratory. The solid had been recrystallized from anhydrous ethyl acetate and from benzene to give a product of m.p. 116–116.5°.[7] The m.p. reported is 103.1–103.3°.[8]

Preparation of Tetra-*n*-butylammonium Tribromide.—A solution of 0.40 g. (0.0012 mole) of tetrabutylammonium bromide in 25 ml. of carbon tetrachloride was mixed with 25 ml. of 0.05 *M* bromine in carbon tetrachloride. The immediate light orange precipitate was filtered to yield 0.54 g. (91%) of the tribromide, m.p. 70–72°.

An alternate method of synthesis involved allowing an excess of bromine vapor to come in contact with 0.50 g. (0.0016 mole) of solid tetrabutylammonium bromide for three hours. The excess bromine adsorbed was allowed to evaporate. The orange solid was washed repeatedly with carbon tetrachloride. A yield of 0.63 g. (84%) of the tribromide, m.p. 70–72°, was obtained. A mixture of the two preparations had the same m.p.

It was possible to crystallize the products of these preparations from glacial acetic acid–carbon tetrachloride. The m.p. of the resultant orange needles was 72.5–74.0°. Attempts to crystallize the product from aqueous alcohol were unsuccessful because the tribromide was reduced by the alcohol. The characteristic orange color of the solution gradually disappeared even in the cold.

Methods of Analysis of Tetrabutylammonium Tribromide.—Total bromine was determined gravimetrically after being converted to bromide ion. A weighed sample of the tribromide was dissolved in 85–90% ethanol saturated with sulfur dioxide. The solution was warmed on the steam-bath for several minutes, and then two or three drops of 6 *N* nitric acid was added. The gravimetric determina-

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(1) J. Tafel, *Ber.*, **31**, 1349 (1898).

(2) K. Fries, *Ann.*, **346**, 217 (1906).

(3) D. Vorlander and E. Siebert, *Ber.*, **52**, 283 (1919); H. McCombie and T. H. Reade, *J. Chem. Soc.*, **123**, 141 (1923).

(4) (a) F. D. Chattaway and G. Hoyle, *ibid.*, **123**, 654 (1923); (b) L. Farkas and O. Schächter, THIS JOURNAL, **71**, 2252 (1949).

(5) E. J. Bowen and A. W. Barnes, *Chemistry and Industry*, 254 (1945).

(6) F. L. Gilbert, R. R. Goldstein and T. M. Lowry, *J. Chem. Soc.*, 1092 (1931).

(7) All m.p.'s corrected.

(8) R. L. McIntosh, D. J. Mead and R. M. Fuoss, THIS JOURNAL, **62**, 506 (1940).

tion with aqueous silver nitrate was then carried out as usual.

The iodometric equivalent weight could not be determined by the reaction of the tribromide with iodide ion in water solution because insoluble polyiodides precipitated. The precipitate would not react appreciably with thiosulfate. The precipitation was avoided by the following method. About 0.2 g. of the tribromide was weighed into a glass-stoppered 125-ml. erlenmeyer flask, 20 ml. of glacial acetic acid was added, and the stoppered flask was heated on the steam-bath. When all of the solid had dissolved, 5 ml. of water containing 1 g. of potassium iodide and 0.5 g. of sodium bicarbonate was added. The resulting solution was titrated with 0.1 *N* thiosulfate while still warm. The addition of much more than 5 ml. of water before titration led to the polyiodide precipitate.

Anal. Calcd. for $C_{16}H_{36}NBr_3$: Br, 49.8; iodometric equiv. wt., 241. Found: Br, 49.3; iodometric equiv. wt., 240.

Purification of Solvents.—Commercial ethylene chloride was heated under reflux as it was stirred with barium oxide. Distillation from fresh barium oxide through a two-foot column packed with glass helices gave a product of b.p. 83.0–83.1° (745 mm.).

Commercial bromotrichloromethane (Dow) was washed with concentrated sulfuric acid, water and saturated sodium carbonate solution in that order. Drying and distillation were carried out as for ethylene chloride. The bromotrichloromethane obtained had b.p. 104.2–104.3° (745 mm.).

Stability of Solvents and Solutions.—Both ethylene chloride and bromotrichloromethane were stable when stored in brown bottles and kept in the dark most of the time. The bromotrichloromethane was especially susceptible to exposure to light, however. After a short period of such exposure the liquid assumed a bromine color and evolved phosgene. In tightly stoppered bottles with a minimum amount of air present this behavior was greatly diminished even with strong illumination. The metathetical reaction of two bromotrichloromethane molecules to form bromine and hexachloroethane is reported to take place in the vapor state only when the wave length of the illuminating light is less than 3360 Å.[9] Such wave lengths would not be transmitted to any appreciable extent by the Kimble glass vessels used in the experiments on the stability of the solvent to illumination. It would appear, then, that the main reaction of decomposition encountered was a photochemical oxidation.

Solutions of tetrabutylammonium tribromide in ethylene chloride decomposed, presumably because of bromination of the solvent even when a special effort was made to exclude light. The solutions were prepared under a red, photographic safelight. The only other light which the solutions encountered was that from the spectrophotometer. The absorption of light characteristic of the tribromide diminished steadily on standing in the dark. The decomposition was faster in a solution containing tetrabutylammonium bromide of a concentration 150 times that of the tribromide.

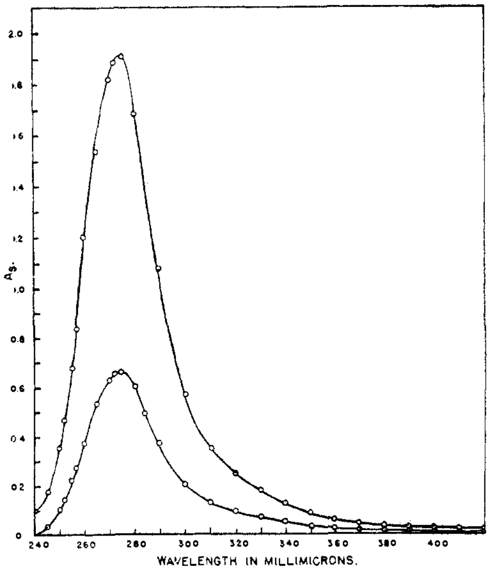

Fig. 1.—Absorption curves of the tetrabutylammonium tribromide in ethylene chloride: lower curve, 2.5 × 10^{-5} *M* soln.; upper curve, 5 × 10^{-5} *M* soln.

Solutions of the tribromide in bromotrichloromethane appeared to be relatively stable in the dark since bromination of the solvent was impossible and the oxidative decomposition of the solvent was photochemical.

Measurement of Absorption Spectra.—The stock solutions of the tetrabutylammonium bromide and tribromide were prepared from weighed amounts of the respective solids. The concentrations of the bromine solutions were determined by titration. Fresh stock solutions were prepared for each series of experiments. The absorbancies of the solutions were measured with a Beckman DU spectrophotometer. Calibrated silica cells of path length 1.000 ± 0.001 cm. were used. All measurements were made at 25 ± 2°.

Results and Discussion

In the determination of the absorption spectrum of tetrabutylammonium tribromide, the choice of the solvent proved to be of considerable importance. Solvents with no dipole moment would not dissolve appreciable amounts of the complex. The complex reacted readily with oxygenated solvents to brominate or oxidize them. Chlorinated solvents containing hydrogen were somewhat more stable to bromination, but even with them there was an appreciable reaction in a relatively short time. Bromotrichloromethane absorbed so strongly in the region of the maximum absorption of the complex that it was not a suitable solvent. Ethylene chloride seemed to be the best available solvent in spite of its tendency to brominate. Of course, freshly prepared solutions had to be used for each determination, and the measurements had to be made as rapidly as possible. The resulting absorption curves are given in Fig. 1. The molar absorbancy index at the maximum was 38,300 when measured immediately on a fresh solution. The curves obtained resemble the ones for the tribromide ion previously reported,[6] but the position of the maximum in Fig. 1 is at 275 mμ as opposed to 265 mμ. This difference cannot be due to appreciable dissociation since bromine does not absorb at this wave length and the absorbancy of the tetrabutylammonium bromide is very small. These previous determinations of the absorption spectrum of tribromide ion were made in alcohol or water–alcohol solutions. These are much more polar solvents than ethylene chloride, and the alcohol is also more susceptible than the ethylene chloride to bromination or oxidation by the tribromide.

In order to establish the nature of the complex in solution and to determine whether or not any other molecular or ionic species were formed when either component was present in excess of 1:1 ratio, both the method of continuous variation[10] and the slope-ratio[11] method were used.

For these determinations, ethylene chloride was unsuitable as a solvent because of the relatively rapid bromination it underwent. Bromotrichloromethane was used as a solvent, but the measure-

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(9) H. Grüss, *Z. Elektrochem.*, **29**, 144 (1923).

(10) P. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

(11) A. E. Harvey and D. L. Manning, This Journal, **72**, 4488 (1950).

TABLE I

ABSORBANCY OF BROMINE–TETRABUTYLAMMONIUM BROMIDE MIXTURES IN BROMOTRICHLOROMETHANE TOTAL CONCENTRATION 1.591 × 10^{-3} *M*

	Mole fraction bromine										
mμ	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
360	0.025	0.482	1.040	1.534	1.800	1.660	1.235	0.825	0.515	0.208	0.076
380	.016	.272	0.580	0.850	1.025	0.970	0.807	.618	.450	.289	.202
400	.014	.188	.400	.600	0.730	.721	.645	.550	.455	.370	.335
420	.010	.112	.236	.348	0.431	.450	.432	.412	.400	.380	.368

TABLE II

ABSORBANCIES OF BROMINE–TETRABUTYLAMMONIUM MONOBROMIDE MIXTURES IN BROMOTRICHLORMETHANE

mμ	5.35 × 10^{-3} Br_2 5.35 × 10^{-5} Bu_4NBr	5.35 × 10^{-3} Br_2 1.07 × 10^{-4} Bu_4NBr	5.35 × 10^{-3} Br_2 2.14 × 10^{-4} Bu_4NBr	5.35 × 10^{-3} Br_2 3.21 × 10^{-4} Bu_4NBr	5.35 × 10^{-3} Br_2 4.28 × 10^{-4} Bu_4NBr	5.35 × 10^{-5} Br_2 5.35 × 10^{-3} Bu_4NBr	1.07 × 10^{-4} Br_2 5.35 × 10^{-3} Bu_4NBr	2.14 × 10^{-4} Br_2 5.35 × 10^{-3} Bu_4NBr	3.21 × 10^{-4} Br_2 5.35 × 10^{-3} Bu_4NBr	4.28 × 10^{-4} Br_2 5.35 × 10^{-3} Bu_4NBr
360	0.332	0.510	0.850	1.188	1.530	0.183	0.330	0.648	0.885	1.170
380	0.690	0.798	0.965	1.135	1.310	.102	.182	.356	.490	0.638
400	1.143	1.205	1.295	1.400	1.500	.070	.127	.245	.332	.440
420	1.257	1.292	1.330	1.390	1.440	.043	.075	.143	.200	.257

ments were limited to the region of relatively low absorption by the complex because of the absorption of the solvent at wave lengths less than 350 mμ. Of course the accuracy of the methods suffered by this limitation.

Method of Continuous Variation.—Stock solutions, 1.59 × 10^{-3} *M*, of bromine and tetrabutylammonium bromide in bromotrichloromethane were used to make up mixtures varying in concentration ratio from 1:9 to 9:1. The absorbancies of the mixtures were immediately determined. The results are given in Table I.

The difference between the calculated absorbancy, *i.e.*, the sum of the absorbancies of bromine and the monobromide, and the experimentally determined value was plotted against mole fraction of bromine for each of several wave lengths (Fig. 2). The maxima all fall at about 0.45 mole fraction of bromine. This result indicates a 1:1 addition product of the formula $(C_4H_9)_4NBr_3$. From the shape of the curves, as well as from the fact the results are so nearly the same at the different wave lengths, the conclusion is that existence of higher bromides in solution is doubtful.

Slope-Ratio Method.—The absorbancy, A_s, of a solution in which a complex is formed according to equation (1) can be expressed by equation (2)[11] as long as the initial concentration of B, C_B, is large compared with that of A, C_A, and as long as B does not absorb at the wave length being considered.

$$mA + nB \rightleftarrows A_mB_n \qquad (1)$$

$$A_s = a_{comp.}\, b \frac{C_A}{m} \qquad (2)^{12}$$

If B does absorb appreciably, equation (1) must be changed to include this absorption, and equation (3) results. In this equation a_B is the molar absorbancy index of B and $\left(C_B - n\frac{C_A}{m}\right)$ is the equilibrium concentration of B.

$$A_s = a_{comp.}\, b \frac{C_A}{m} + a_B b\left(C_B - n\frac{C_A}{m}\right) \qquad (3)$$

If C_B is made relatively large the second term on the right of equation (3) will remain essentially constant as C_A is varied. A plot of A_s *vs.* C_A should give a straight line whose slope will be $a_{comp.}b/m$. A similar relationship holds when component A is in excess. In this case the slope of the line is $a_{comp.}$ b/n. The ratio of the two slopes is n/m.

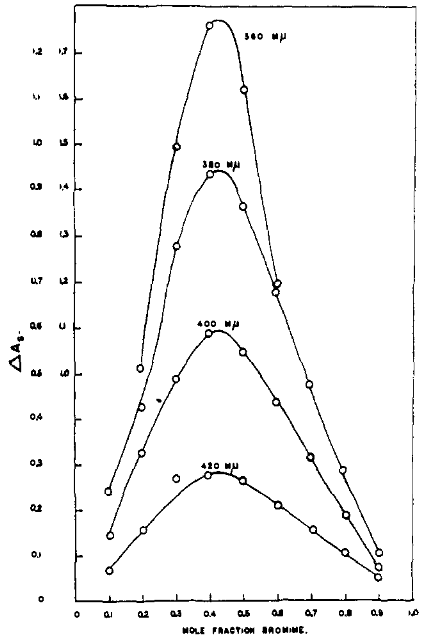

Fig. 2.—Method of continuous variation: first ordinate is for 420 mμ, 400 mμ and 380 mμ; second ordinate is for 360 mμ.

Two series of mixtures, one with bromine in excess and one with tetrabutylammonium bromide in excess, were used and the absorbancies at several wave lengths were measured. The results are given in Table II. Plots of absorbancy against concentration of the limiting component at the various wave lengths give straight lines as shown in Fig. 3.

The mean value of the ratios of the slopes for various wave lengths is 1.0; *i.e.*, the formula of the

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[12] The symbols and the nomenclature used throughout this article are changed to correspond to the practice recommended by the National Bureau of Standards Letter-Circular LC-857 (1947).

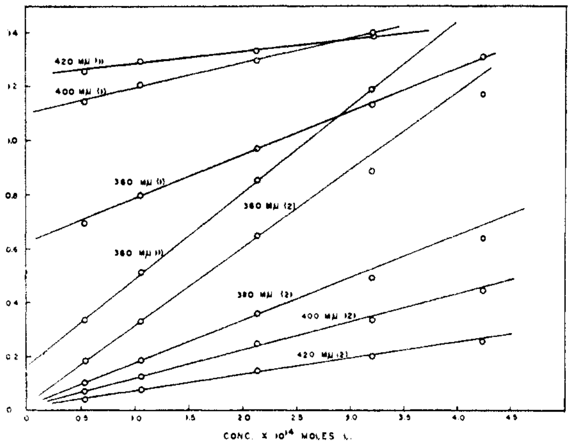

Fig. 3.—Slope-ratio method: 1, solutions with excess bromine; 2, solutions with excess tetrabutylammonium bromide.

complex is $(C_4H_9)_4NBr_3$. These results are in essential agreement with those of the method of continuous variation.

Equilibrium Constant.—The equilibrium constant for the reaction in bromotrichloromethane was calculated by the method

$$(C_4H_9)_4NBr_3 \rightleftharpoons (C_4H_9)_4NBr + Br_2$$

outlined in a previous article.[13] The mean value obtained was 6.0×10^{-5} at 25°. This result indicates that the tetra-*n*-butylammonium tribromide does not dissociate to any great extent in relatively non-polar solvents. It is a brominating agent, however, and reacts readily with solvents capable of being brominated. Consequently, measurements of properties made in such solvents must be regarded as semi-quantitative at best. The present measurements made in bromotrichloromethane are less likely to be subject to this deficiency since this solvent is not susceptible to bromination.

[13] A. I. Popov, K. Brinker, L. Campanaro and R. Rinehart, THIS JOURNAL, **73**, 514 (1951).

IOWA CITY, IOWA RECEIVED FEBRUARY 22, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Spectrophotometric Investigation of the Ionic Association of Thiocyanate Ion with Vanadium(III) and Vanadium(IV) in Aqueous Solution[1]

BY SYDNEY C. FURMAN[2] AND CLIFFORD S. GARNER

Application of Job's continuous variations method to a spectrophotometric study has shown that the complexes $VSCN^{++}$ and $VOSCN^{+}$ exist in aqueous solution. Their stability constants and heats of formation have been estimated in solutions having an ionic strength of 2.6. Evidence is presented that suggests that higher complexes of both vanadium(III) and vanadium(IV) are formed with thiocyanate ion. The spectra of the various complexes have been calculated and are presented. No evidence was found for an "interaction absorption spectrum" between vanadium(III) and vanadium(IV) in 3.9 *f* ammonium thiocyanate.

It has long been known that complex ions involving thiocyanate ions are formed with vanadium(III) and vanadium(IV). Meites[3] has found direct evidence for thiocyanate complexes of vanadium(II), vanadium(III) and vanadium(IV) in aqueous solution from polarographic studies. In some early exploratory work Locke and Edwards[4] observed that vanadium(III) is much more slowly oxidized by air in the presence of potassium thiocyanate than in solutions of other anions. Other indirect evidence for thiocyanate complexes includes the extractability of vanadium(III) thiocyanate compounds into organic solvents[5] and the preparation of solid salts of the types $M^{I}_{2}VO(SCN)_4$ and $M^{I}_{3}V(SCN)_6$.[4,6,7,8]

The absorption spectra of solutions containing these complexes have been determined[9] but no interpretation of the spectra was possible because of the lack of information regarding the species present in solution.

Investigations in progress in this Laboratory[10] have shown that the exchange of radiovanadium between vanadium(III) and vanadium(IV) perchlorates proceeds at a measurable rate in perchloric acid solutions and that this rate is enhanced in the presence of thiocyanate ion. These results suggest that thiocyanate complexes are formed under these conditions.

Accordingly, this research was undertaken to obtain information about the composition and stability constants of some of the thiocyanate complexes of vanadium(III) and vanadium(IV). The complexes of vanadium(III) were expected to be of particular interest because of the similarity of the (hydrated) tripositive ion V^{+++} to (hydrated) Fe^{+++} ion. It has been adequately shown that the $FeSCN^{++}$ ion is formed under certain conditions.[11,12,13] In addition higher complexes are known.[14,15]

[1] Presented at a symposium on "Equilibrium and Rate Behavior of Complex Ions," University of Chicago, February 21–23, 1951.

[2] General Electric Charles A. Coffin Predoctoral Fellow, 1950–1951. Present address: Knolls Atomic Power Laboratory, Schenectady, New York.

[3] L. Meites, Jr., Ph.D. Thesis, Harvard University, 1947.

[4] J. Locke and G. H. Edwards, *Am. Chem. J.*, **20**, 594 (1898).

[5] A. Rosenheim, E. Hilzheimer and J. Wolff, *Z. anorg. Chem.*, **201**, 162 (1931).

[6] J. Koppel and R. Goldman, *ibid.*, **36**, 281 (1903).

[7] A. Cioci, *ibid.*, **19**, 308 (1899).

[8] G. Scagliarini and G. Tartarini, *Gazz. chim. ital.*, **53**, 876 (1923), through *C. A.*, **18**, 1251[8] (1924).

[9] Y. Uzumasa, H. Okuno and K. Doi, *J. Chem. Soc., Japan*, **59**, 655 (1938), through *C. A.*, **32**, 6152[3] (1938).

[10] S. C. Furman and C. S. Garner, unpublished research.

[11] H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

[12] S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

[13] H. S. Frank and R. L. Oswalt, *ibid.*, **69**, 1321 (1947).

[14] M. Møller, Doctoral Thesis, Copenhagen, 1937, through ref. 28, p. 60.

[15] S. E. Polchlopek and J. H. Smith, THIS JOURNAL, **71**, 3280 (1949).