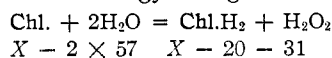
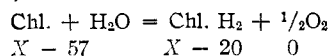


serve to decompose water. It is interesting to note that the free energy change of the reaction



is +63 kcal., while that of the reaction



would be only +37 kcal.

Acknowledgments.—We are indebted to the General Research Council of the Oregon State System of Higher Education for the grant of a research assistantship to one of us (A. H. G.) and for continued support in the purchase of equipment and materials. We are also indebted to Dr. Leroy E. Detling of the Department of Biology, University of Oregon, for the location and identification of the *Vaucheria* sp. used in our work.

Summary

1. Polarograms obtained with solutions of the

chlorophylls in ether and in dioxane added to aqueous solutions of tetramethylammonium bromide are described.

2. A characteristic reduction wave near 1.9 volts *vs.* the saturated calomel electrode is exhibited by the chlorophylls and by the phytol separated from the chlorophylls by saponification. This wave is ascribed to the hydrogenation of the double bond in the phytol chain. Similar waves are exhibited by allyl alcohol and by geraniol.

3. Some chlorophyll preparations exhibit reduction current peaks at low cathodic potentials. These peaks are tentatively ascribed to the hydrogenation of the vinyl group.

4. The addition of carbon dioxide results in a merging of the phytol wave with that of carbon dioxide, while the vinyl peak is suppressed.

5. The effect of acids and bases on the phytol reduction is described.

EUGENE, OREGON

RECEIVED JUNE 29, 1946

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXVI. The Conductance of Some Onium Type Salts in Ethylene Chloride at 25°¹

BY ERNEST R. KLINE² AND CHARLES A. KRAUS

I. Introduction

Conductance measurements have been* made with a series of onium type picrates and perchlorates in ethylene chloride in order to determine the effect produced on the dissociation constant by certain attainable structural variations in the cations. The structural variations accomplished in this investigation were: (a) in the number of the alkyl (or aryl) groups attached to the central atom; and (b) in the nature of the central atom to which they were attached. The effect of variation in the size of the substituent alkyl groups has already been studied in ethylene chloride.³

The salts prepared for this investigation were tetrabutylphosphonium picrate, tetrabutylarsonium picrate, tributylsulfonium picrate, tributylsulfonium perchlorate, diphenyliodonium picrate and diphenyliodonium perchlorate. The results obtained with these compounds, when combined with those of Mead⁴ for tetrabutylammonium picrate, permit of evaluation of the two above mentioned constitutional factors on ionic equilibria.

(1) This paper comprises part of the subject matter of a thesis submitted by Ernest R. Kline in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1938.

(2) University Fellow at Brown University, 1926-1927; 1927-1928. Present address: Connecticut State College, Storrs, Conn.

(3) Tucker and Kraus, *THIS JOURNAL*, **69**, 554 (1947).

(4) Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936); compare, also, Tucker and Kraus, *ref.* 3.

II. Experimental

Solvent. Apparatus and Procedure.—The details appertaining to these have been fully described in earlier papers.⁴

Salts.—Tetra-*n*-butylphosphonium iodide was obtained by the interaction of *n*-butyl iodide and tri-*n*-butylphosphine. The salt was purified by precipitation from benzene solution by addition of petroleum ether; m. p., 98°.

Tetra-*n*-butylphosphonium picrate was prepared by the metathesis of an alcoholic solution of the iodide with the calculated amount of silver picrate in hot aqueous solution. After filtering, cooling in ice gave a crystalline product. The salt was recrystallized from a water-alcohol mixture; m. p., 55°.

Tri-*n*-butylarsine was prepared according to the method described by Davies and Jones⁵ by the careful interaction of butylmagnesium bromide with arsenic tribromide in ethereal solution in the cold. Vigorous stirring was necessary during the addition. After treatment with ice and hydrochloric acid, the ether layer was separated, washed repeatedly with water and dried with calcium chloride. At this stage, some decolorizing carbon was added, the solution filtered and the ether removed by distillation. The residue was fractionated at low pressure and the tri-*n*-butylarsine which came over at 117-120° (at 8 mm.) was collected separately.

Tetra-*n*-butylarsonium iodide was obtained by the interaction of a slight excess of *n*-butyl iodide with the tri-*n*-butylarsine. The mixture was heated gently under reflux for several minutes. Amyl ether was then added and the mixture boiled to remove the excess butyl iodide. On cooling, the salt crystallized out. One portion was recrystallized by precipitation from ethanol with dry ether and another by precipitating from benzene with petroleum ether; m. p., 86°. Mannheim⁶ reports that the

(5) Davies and Jones, *J. Chem. Soc.*, **33** (1929).

(6) Mannheim, *Ann.*, **341**, 204, 222 (1905).

salt decomposes without melting at 140–145°. Analyses of our product for iodine and arsenic gave 29.3 and 17.5%, respectively, while the theoretical values are 29.5 and 17.44%, respectively. The lower melting point is in accord with those of the corresponding nitrogen, phosphorus and arsenic derivatives, giving decreasing temperatures of 144, 98 and 86° for the nitrogen, phosphorus and arsenic compounds.

Tetra-*n*-butylarsonium picrate was obtained by metathesis of the iodide with silver picrate in alcoholic solution. The filtrate from the silver iodide separation was concentrated in a slow stream of dry air. Crystallization occurred on cooling in a refrigerator and the crystals were freed from mother liquor on a porous plate in the refrigerator. The product was dissolved in a minimum amount of absolute alcohol, excess anhydrous ether was added and the solution placed in the refrigerator to crystallize (at room temperature, the product forms two liquid layers with ether). The ether layer was decanted and the crystals were treated with more dry ether in the cold. After a final decantation, the residual solvent was pumped off under low pressure. The product was then dissolved in alcohol and water was added until a slight turbidity appeared. It was then alternately chilled in liquid ammonia and allowed to warm up to encourage the formation of filterable crystals. After each chilling, a few drops of water were added to induce further precipitation. Finally, when the solvent contained about 50% water, the precipitate was filtered off and pumped dry; m. p., 43°.

Tri-*n*-butylsulfonium iodide was obtained by the interaction of *n*-butylsulfide and *n*-butyliodide in nitromethane. The mixture was sealed in an ampule at low pressure after which the tube and contents were heated for about four weeks at 35–40°. After standing for another four weeks period at room temperature, the tube was opened and the nitromethane removed at 40° under reduced pressure. The crystalline mass which resulted on cooling was washed with cold ethyl acetate; m. p., 97–98°. This salt was used without further purification in the preparation of the picrate and perchlorate.

Tri-*n*-butylsulfonium picrate was prepared by metathesis; the iodide, in alcohol solution, was reacted with silver picrate in aqueous solution. After filtration from the silver iodide, the solution was diluted with water and the picrate extracted with ethylene chloride. The latter was then removed under low pressure and the residue was recrystallized from alcohol; m. p., 70°. Analysis for sulfur (Parr bomb method) gave 7.36%; calculated, 7.42%.

Tri-*n*-butylsulfonium perchlorate was obtained by metathesis of the iodide with silver perchlorate in alcoholic solution. The mixture was heated to boiling and filtered; the filtrate was pumped to dryness at room temperature. The residue was dissolved in ethyl acetate and precipitated by addition of heptane; m. p., 94°. Initially, the product was pure white in color, but after a few days, it was noticeably brown.

Diphenyliodonium picrate was obtained by metathesis of diphenyliodonium iodide (prepared in the usual way) with silver picrate. The product was freed from traces of silver picrate by extraction with ethylene chloride. The ethylene chloride solution was evaporated to dryness and the residue recrystallized from alcohol; m. p., 145°.

Diphenyliodonium perchlorate was prepared by reaction of the iodide with silver perchlorate in alcoholic solution. The mixture was kept just below the boiling point for an hour and then filtered while hot. After evaporation to dryness, the residue was dissolved in ethylene chloride and precipitated by addition of petroleum ether; m. p., 165°.

III. Results

Two independent series of measurements (agreeing within 0.1%) were made with each salt, although the results are here recorded for only one. In Table I, concentrations are expressed in moles per liter of pure solvent of density 1.2455. In the

computation of constants, the dielectric constant was taken as 10.23 and the viscosity as 0.00785. All measurements were carried out at 25 ± 0.01°.

TABLE I
CONDUCTANCE OF VARIOUS ELECTROLYTES IN ETHYLENE CHLORIDE AT 25°

$C \times 10^4$	Λ	$C \times 10^5$	Λ
Tetra- <i>n</i> -butyl-phosphonium picrate		Tetra- <i>n</i> -butyl- arsonium picrate	
62.90	26.26	40.19	28.37
31.14	31.65	21.07	33.54
16.26	36.91	9.586	39.87
8.485	41.93	4.608	45.10
5.565	44.95	2.376	48.50
3.257	48.11	1.146	52.34
1.923	50.77	0.5529	55.75
Tri- <i>n</i> -butyl-sulfonium picrate		Tri- <i>n</i> -butylsulfonium perchlorate	
138.24	12.84	124.32	14.17
74.13	16.08	61.49	18.27
41.65	19.75	30.84	23.35
25.49	23.42	17.01	28.17
16.17	27.23	9.397	33.93
11.19	30.52	4.113	42.44
7.005	35.01	1.583	51.81
3.423	41.78		
2.564	44.38		
1.494	48.86		
Diphenyliodonium picrate		Diphenyliodonium perchlorate	
60.94	4.197	110.52	8.214
29.37	5.816	46.23	11.71
18.44	7.172	30.77	13.85
11.186	8.972	17.62	17.37
5.851	11.915	11.304	20.66
3.090	15.64	5.786	26.57
1.710	19.87	2.913	33.63

IV. Discussion

The experimental values of Table I were analyzed graphically by the method of Fuoss.⁷ On plotting values of F/Λ against those of $Cl\Lambda^2/F$ on an adequate scale, the experimental points were found to lie on a straight line within the limit of experimental error. These plots are not reproduced here but examples may be found in earlier papers of this series.⁸ From the intercept (on the F/Λ axis) and the slope of the plots, values of the limiting conductance, Λ_0 , and the dissociation constant, K , of the ion-pair equilibrium have been computed. Values are given in columns 2 and 4, respectively, of Table II.

From the previously determined limiting conductance of the picrate and perchlorate ions,⁸ ion conductances have been calculated for the cations of the salts used in this investigation. The values are given in column 3 of Table II. The discrepancy in the values for the tri-*n*-butylsulfonium ion

(7) Fuoss, *THIS JOURNAL*, **57**, 488 (1935).

(8) Gleysteen and Kraus, *ibid.*, **69**, 451 (1947); see also ref. 4.

TABLE II
CONSTANTS OF ELECTROLYTES IN ETHYLENE CHLORIDE

Salt	Λ_0	Λ_0^+	$K \times 10^4$
(<i>n</i> -C ₄ H ₉) ₄ NPi ⁺	57.40	26.2	2.28
(<i>n</i> -C ₄ H ₉) ₄ PPi	57.27	26.1	1.60
(<i>n</i> -C ₄ H ₉) ₄ AsPi	57.14	25.9	1.42
(<i>n</i> -C ₄ H ₉) ₃ SPi	62.31	31.1	0.449
(<i>n</i> -C ₄ H ₉) ₃ SClO ₄	68.72	29.5	.394
(C ₆ H ₅) ₂ IPi	62.50	31.3	.0233
(C ₆ H ₅) ₂ IClO ₄	70.42	31.2	.115

may well be due to the fact that the perchlorate is somewhat unstable as has been mentioned above.

The conductance of the tetra-*n*-butylammonium, phosphonium and arsonium ions shows a very slight decrease with increasing size of the central element. The dissociation constant of the picrates of these ions shows a marked decrease on going from the nitrogen to the arsenic derivative. The larger diameter of the heavier elements may provide a more open structure for the substituted groups and thus permit a closer approach of the picrate ion.

The sulfonium and iodonium ions, each possessing 12 carbon atoms, have almost the same conductance, 31.1 and 31.3, respectively. This indicates that, in ions of this type, the arrangement of the carbon atoms of the substituent groups has but little influence on conductance. It may be noted in this connection that the conductance of the tetra-*n*-propylammonium ion, also having 12 carbon atoms, is 31.4,³ while that of the phenylpyridonium ion with two closely joined six-membered rings, is 36.7.³

A comparison of the dissociation constants of picrates of tetra-*n*-propylammonium,³ tributylsulfonium, diphenyliodonium and phenylpyridonium ions, containing nearly the same number of carbon atoms, brings to light the influence of steric factors on short-range ion-interactions. The dissociation constants for these picrates are, respectively, 1.94×10^{-4} , 0.44×10^{-4} , 0.023×10^{-4} and 0.86×10^{-4} .

The dissociation constant of the picrate of the sulfonium ion, with its planar structure, is only one-fourth that of the ammonium ion with tetrahedral structure. The constant of the picrate of the iodonium ion, with linear structure, is one-twentieth that of the corresponding salt of the sulfonium ion. The more open the structure of the cation, the nearer can the charge on the picrate ions approach the center of positive charge. In this connection, it is of interest to note that for phenylpyridonium picrate, the constant is nearly half that of tetrapropylammonium picrate and twice that of tributylsulfonium picrate. The phenylpyridonium ion is a small one, considering the number of atoms that it contains as evidenced by its high conductance. Although it bears some structural resemblance to the iodonium ion, its atoms are very closely packed as a result of which the negative ion is kept at a distance and the constant is relatively large.

V. Summary

1. Conductance measurements have been made with solutions of tetra-*n*-butylphosphonium picrate, tetra-*n*-butylarsonium picrate, tri-*n*-butylsulfonium picrate and perchlorate and diphenyliodonium picrate and perchlorate in ethylene chloride at 25°.

2. The limiting conductances and dissociation constants for these salts have been evaluated.

3. It has been found that the size of the central atom of these large quaternary onium ions has little influence on the ion conductances. The dissociation constant of their picrates decreases somewhat with increasing size of the central atom.

4. While the arrangement of a given number of carbon atoms around the central atom has but a small effect on ion conductance, it plays a major role in determining the value of the dissociation constant of the ion-pair equilibrium.

PROVIDENCE, R. I.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Reactivity of Hydrrous Alumina toward Acids¹

BY RONALD P. GRAHAM² AND ARTHUR W. THOMAS

Introduction

Although the reactivity of hydrrous alumina toward aqueous solutions of acids has been the subject of a number of studies, the phenomena exhibited are not yet clearly understood. The literature of the last hundred years contains an appreciable amount of factual information, but it

(1) Part of a Dissertation submitted in 1942 by Ronald Powell Graham in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

(2) Present address: Department of Chemistry, McMaster University, Hamilton, Ontario.

is only recently that attempts have been made to explain the results of study in an integrated manner.

An early observation was that freshly precipitated gelatinous hydrrous oxide is readily peptized to the colloidal condition by the action of certain acids. It has been found, for example, that hydrochloric and acetic acids are effective in this respect whereas sulfuric and phosphoric acids are not good peptizing agents. Thomas and Vartanian³ made an extensive study of the relative

(3) Thomas and Vartanian, *THIS JOURNAL*, **57**, 4 (1935).