and on occasions the temperature was allowed to climb to 160° in order to remove all of this fraction at atmospheric pressure.

The pressure was subsequently reduced to 50 to 60 mm. and *n*-butanol (n^{20}D 1.390 to 1.398) was removed. After removing unreacted ethyl phosphate at pressures varying between 3 and 10 mm. of mercury (b. p. 66–69° at 3 to 4 mm.; n^{20}D 1.404–1.4055), diethyl *n*-butyl phosphate (b. p. 82–87° at 3 to 4 mm.) and ethyl di-*n*-butyl phosphate (b. p. 95–96° at 3 to 4 mm.) were fractionated out of the reaction mixture.

Anal. Calcd. for $C_8H_{19}PO_4$: P, 14.7; $M\text{R}$ 51.1.[8] Found: P, 14.9; $M\text{R}$ 51.5. Calcd. for $C_{10}H_{23}PO_4$; P, 13.0; $M\text{R}$ 60.5. Found: P, 13.2; $M\text{R}$ 59.8.[8]

The material balances in all runs including residues amounted to 97 to 99%.

Isolation of Ethyl *n*-Butyl Ether.—Fifty grams of the ethanol–ether fraction (b. p. 36–93°) was added to 180 ml. of water. The upper layer, amounting to 8.9 g., was separated, dried over activated silica gel and distilled. The main fraction boiled at 90–93° and was found to have the following constants: d^{20}_4, 0.752; n^{20}D 1.3818; $M\text{R}$ calcd., 31.6; found, 31.6.

Anal. Calcd. for $C_6H_{14}O$: C, 70.5; H, 13.8. Found: C, 70.6; H, 13.9.

Treatment of the ether with hydriodic acid yielded ethyl and *n*-butyl iodides.

Alkylation of Morpholine.—An equimolar mixture of morpholine and ethyl phosphate was charged to a round-bottomed flask equipped with a water-cooled reflux condenser. The mixture was heated by means of a Glas-Col mantle and brought to 150° in fifteen to twenty minutes. At this temperature, vigorous refluxing took place due to heat of reaction, and the mixture changed from a water white to a reddish brown color. If too well insulated, the reaction temperature may rise to 190°. It was found, however, that by maintaining the reaction temperature between 157 and 159° good results can be obtained. The product was poured into 500 ml. of water and heated with 10% excess (44 g.) of sodium hydroxide. The basic aqueous solution was charged to a still and the amine distilled with water as an azeotrope over the range 95–99.8°. The azeotropic distillate was saturated with potassium carbonate whereupon the amine was salted out. After separating from the aqueous layer, the amine was dried over sodium sulfate, filtered and distilled; b. p. 137–138°, d^{20}_4 0.919, n^{20}D 1.4418; yield 70%.

Anal. Calcd. for $C_6H_{13}NO$: C, 62.2; H, 11.4; N, 12.2. Found: C, 62.3; H, 11.5; N, 11.9.

All physical constants given for known compounds agree satisfactorily with those previously published.

Acknowledgment.—The authors are indebted to Messrs. N. Beitsch, S. Sass and B. Zeffert of this Laboratory for having performed the necessary analytical and physical determinations.

Summary

Sodium butylate behaves catalytically on a mixture of *n*-butanol and ethyl phosphate yielding diethyl *n*-butyl phosphate and ethyl di-*n*-butyl phosphate. This alcoholysis is accompanied by a side reaction which causes the alkylation of the butylate ion to ethyl *n*-butyl ether.

This behavior indicates that ethyl phosphate under the conditions employed behaves both as a true ester undergoing alcoholysis and as an alkylating agent. The degree to which each of the products of reaction is produced depends upon the concentration of sodium butylate as well as upon the mole ratio of *n*-butanol to ethyl phosphate.

The alkylation of morpholine to N-ethylmorpholine by means of ethyl phosphate is also described.

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[8] The molecular refractivities were calculated from that of ethyl phosphate by adding the proper value for the required number of methylene groups to that molecule.

[CONTRIBUTION FROM THE ESSO LABORATORIES, CHEMICAL DIVISION, STANDARD OIL DEVELOPMENT COMPANY]

Study of the Reaction of Buna Rubbers with Aliphatic Mercaptans[1]

BY G. E. SERNIUK, F. W. BANES AND M. W. SWANEY

Introduction

The relative proportion of 1,4- *versus* 1,2-addition of diene units and the elucidation of the partial structure of polymers and copolymers of butadiene have been investigated by various chemical and physical methods such as ozonolysis,[2–5] perbenzoic acid oxidation,[6,7] potassium permanganate oxidation,[6] and infrared absorption.[8] The work presented in this paper was undertaken in an attempt to obtain further information regarding the structure of butadiene polymers and copolymers by studying the reaction of these polymers with aliphatic mercaptans.

The reaction of mercaptans with unsaturated compounds including natural and synthetic rubbers is not new. Posner,[9] Gunnar, Axberg and Holmberg,[10] Hoag and Eichwald,[11] Kharasch, Read and Mayo,[12] Jones and Reid,[13] Cunneen,[14] and others have treated mercaptans with various types of unsaturated compounds. Holmberg[15] treated natural pale crepe rubber with thiogly-

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[1] This paper was presented before the Division of Rubber Chemistry at the American Chemical Society Meeting in Chicago, 1946.

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[10] Gunnar, Axberg and Holmberg, *ibid.*, **66B**, 1193 (1933).

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[12] Kharasch, Read and Mayo, *Chem. and Ind.*, **57**, 752 (1938).

[13] Jones and Reid, THIS JOURNAL, **60**, 2452 (1938).

[14] Cunneen, *J. Chem. Soc.*, 36, 134 (1947).

[15] Holmberg, *Ber.*, **65**, 1349 (1932).

colic acid, and more recently, Kolthoff and co-workers,[16] and Marvel and co-workers[17] studied the reaction of aliphatic mercaptans with butadiene polymers and copolymers in latex form.

From a preliminary study of the reaction of mercaptans with model compounds it was found that ethylenic bonds in conjugated, vinyl, terminal butenyl, and in closed ring structures added mercaptans readily, while internal, non-conjugated ethylenic bonds reacted at a relatively slower rate. Thioglycolic acid added to simple olefins more vigorously than *n*-aliphatic mercaptans. Since this paper was originally submitted, Cunneen[14] reported the reactions of unsaturated hydrocarbons and various thiols. An apparent order of reactivity was found to be cyclohexene > dihydromyrcene > squalene > rubber; and for the thiols, thioglycolic acid > thiophenol $\sim$ isopentanethiol. It is evident that the ease with which an ethylenic bond can add thiols is dependent, in part, upon the structural unit retaining the double bond.

It is quite probable that diene polymers contain several types of ethylenic bonds, but from ozonolysis data[2-5] it must be concluded that a major portion of these bonds results from either 1,2- or 1,4-addition of butadiene units to the polymer chains. These two types of ethylenic bonds should exhibit different rates of mercaptan addition and the determination of the proportion of mercaptan-reactive units in the polymer chains should represent a measure of the per cent. of ethylenic bonds present as side vinyl groups. Ethylenic bonds in structures formed by intramolecular cyclization reactions should likewise be mercaptan reactive. Obviously mercaptan addition reactions will not show complete selectivity for side vinyl groups but it is quite probable that mercaptan-reactive structures other than the side vinyl groups will represent only a very minor portion of the total unsaturation of the butadiene polymers.

This paper records the reaction of thioglycolic acid and *n*-aliphatic mercaptans of C_2 to C_{16} chain length with diene polymers, and the reaction of thioglycolic acid and a *n*-C_{12} mercaptan with model compounds. Polymer-mercaptan reactions were effected in solution, mass and in latex form at various temperatures, in the presence of air, or in the presence of additives which were evaluated as catalysts. The experimental data indicate a pronounced difference in the rate and extent of mercaptan addition by the various diene polymers, and the difference in rate and extent of addition has been utilized in estimating the relative proportion of external and internal ethylenic bonds in the polymer chains.

Experimental

Materials

Polymers.—The polymers used in studying the polymer–mercaptan reactions were natural rubber, polyisoprene, polybutadiene, and copolymers of butadiene and acrylonitrile, butadiene and styrene, and butadiene and alpha methyl para-methylstyrene. Both emulsion and sodium catalyzed polymers of butadiene were used, but in all other cases, emulsion polymers and copolymers were employed. The emulsion polymers were prepared by the standard technique. The polymerization reactions were discontinued when 75% of the monomers were converted to polymer. The latices were freed of unconverted monomers by steam stripping under a pressure of 50–60 mm. Polymers required for solution and mass reactions were obtained by coagulating the stripped latices with 99% isopropyl alcohol, followed by water washing and drying at 175° F. No attempt was made to fractionate the resulting polymers, or to free them of any developed peroxide materials.

Mercaptans.—Mercaptans of C_2 to C_4 chain length were obtained from Eastman Kodak and were used after distillation. Thioglycolic acid was first dried by removing the water as a benzene azeotrope before distilling under vacuum. Normal mercaptans of C_8 to C_{16} chain length were of research grade from the Connecticut Hard Rubber Company. These mercaptans were used directly without further purification. Sharples 3B mercaptan was used after distillation.

Procedure.—A modification of the procedure used by Holmberg[15] was used in effecting the reaction of various polymers with thioglycolic acid. A 5% solution of polymer in benzene was placed in a flask and agitated while a calculated amount of dry thioglycolic acid was added slowly to the solution at room temperature. The reactants were allowed free access to air throughout the course of the reaction. With butadiene polymers and copolymers the reaction was exothermic, and after a short time the solution became cloudy and an insoluble layer separated. The separated product was solubilized by the addition of *n*-hexanol and the reaction continued. Samples were withdrawn periodically for analysis. The polymer–thioglycolic acid reaction products were purified by water washing the benzene–*n*-hexanol solutions until no further test for free thioglycolic acid could be obtained by titration with 0.1 *N* iodine solution. The solvents were then removed by heating the solutions on a steam-bath under high vacuum. The reaction products were further dried in a vacuum oven at 70°. Sulfur analyses of the products were obtained by combustion in a Parr bomb.

Polymers in latex form were treated with mercaptans in 2 oz. and one quart glass reactors which were charged to varying levels and then agitated in a thermostated bath at 50° for varying periods of time. The amount of mercaptan employed corresponded to a 100% excess over the amount theoretically required for complete double bond saturation. Several conditions were employed wherein the free space of the reactors was flushed either with nitrogen, air, or pure oxygen; and the amount of persulfate in the systems was varied. The polymer–mercaptan reaction products were isolated from the emulsions by coagulating in an excess of 99% isopropyl alcohol. The products were thoroughly washed in fresh portions of alcohol and then dried in a vacuum oven at 70°.

Mass reactions of dry polymers and mercaptans were carried out under essentially the same conditions employed by Jones and Reid[18] in their study of the reaction of mercaptans with unsaturated compounds. The dry polymer was dissolved in the desired mercaptan, two mols of mercaptan being used per mol of diene in the polymer. The solutions were agitated in a glass reactor, sealed from the atmosphere without displacing the air in the reactor, at 180–200° for varying periods of time. Samples of the reaction mixture were removed at intervals for purification and analysis. The polymer–mercaptan reaction products were isolated by coagulating the reaction mixture with a large volume of 99% isopropyl alcohol followed by repeated dissolution of the mass in petroleum ether and coagulation until the mixed solvents showed no trace of free mercaptan as determined by titration with 0.1 *N* iodine solution. The purified reaction mass was stripped of solvents and moisture under vacuum at 80°.

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(16) Kolthoff and co-workers, private communication.

(17) Marvel and co-workers, private communication.

Calculations.—The calculation of the per cent. of double bonds saturated by a particular mercaptan is based on the sulfur content of the reaction product, molecular weight of the mercaptan, and the unsaturation value of the polymer expressed as Wijs number. It is assumed that the total sulfur of the reaction product minus the sulfur value of the original polymer represents the total sulfur introduced into the polymer by the additive fixation of the mercaptan. The percentage of double bonds saturated was calculated from the expression

$$\% \text{ D.B. saturated} = \frac{2.54 \times 10^6 (\% \text{ Sa} - \% \text{ Sp})}{[3200 - (\% \text{ Sa} - \% \text{ Sp})(\text{Mol. wt. RSH})]I_{2p}}$$

where

Sa = % Sulfur of the reaction product
Sp = % Sulfur of the original polymer
I_{2p} = Wijs number of original polymer

Results and Discussion

Reactions of Mercaptans and Unsaturated Compounds.—In determining the relative reactivities of various types of ethylenic bonds with aliphatic mercaptans, model compounds were employed which possessed either terminal or internal unsaturation. The results of these experiments are given below and indicate that compounds possessing terminal methylene groups or double bonds in closed ring structures add mercaptans vigorously while internally located double bonds react very slowly with mercaptans.

Oleic acid (0.1 mole), free of linoleic and linolenic acids, and thioglycolic acid (0.1 mole) when combined in benzene (50 cc.) at room temperature did not produce an exothermic reaction. The product isolated from the reaction mixture after standing at room temperature for ten days with access to air, contained 6.60% S (calcd. for $C_{20}H_{38}O_4S$: S, 8.53%). By treating linoleic acid (0.1 mole) and thioglycolic (0.2 mole) in the manner described above, a yield of 40.3 g. of adduct and unreacted linoleic acid was obtained after 29 days' reaction time at room temperature (calcd. amount of adduct 46.44 g.). On the other hand, when one-tenth molar proportions of 10-undecylenic acid and thioglycolic acid were combined as above, a highly exothermic reaction resulted. The solid, crude product, isolated from the water-washed benzene solution, contained 12.36% S (calcd. for $C_{13}H_{24}O_4S$: S, 11.58%).

Cyclohexene (0.1 mole), and thioglycolic acid (0.1 mole) also reacted exothermally in benzene in the presence of air. The product, after being water washed and dried under vacuum and undistilled, showed a sulfur content of 20% (calcd. for $C_8H_{14}O_2S$: S, 18.4%). This reaction was described by Cunneen.[14]

Molar proportions of 10-undecylenic acid and *n*-dodecyl mercaptan reacted exothermally in benzene solution in the presence of air. This reaction was less vigorous than when thioglycolic acid was used. The solid reaction product after a single crystallization from benzene showed a sulfur content of 8.20% (calcd. for $C_{23}H_{46}O_2S$: S, 8.30%).

Reaction of Polymers.—An emulsion copolymer of butadiene and styrene, prepared from an initial feed ratio of 78 parts of butadiene and 22 parts of styrene by weight, reacted exothermally with thioglycolic acid after a few minutes of contact. Reaction products isolated after 3, 25, 45, 70 and 144 hours, showed 47, 42, 38, 43 and 42% double bond saturation values, respectively. These data indicate that the reaction is exceedingly rapid and apparently reaches a saturation value corresponding to about 38–47% double bond saturation. Under the same conditions a copolymer prepared from an initial feed of 74 parts of butadiene and 26 parts of acrylonitrile, and a polybutadiene prepared by sodium catalysis, reacted exothermally with thioglycolic acid and after twenty-five hours the products were isolated and showed 42 and 39% double bond saturation values, respectively. Natural smoked sheet, purified by acetone extraction, solution, and precipitation showed no exothermic reaction with thioglycolic acid in benzene solution under the same conditions. After one month the isolated product showed a sulfur content of 7.04% which corresponds to 18.8% double bond saturation. Cunneen[14] found but a slight reaction between natural rubber and thioglycolic acid under peroxidic conditions and high vacuum. The above experiments emphasize a pronounced difference in the reaction rate between mercaptans and butadiene polymers and natural rubber. The difference in reaction rates is undoubtedly due to the presence of different double bond structures in the respective polymers.

The double bond saturation values obtained for butadiene polymers and natural rubber, treated in latex form with mercaptans, also indicate a pronounced difference in the reaction rate and the extent of reaction. Emulsion polymer latices, containing equivalent amounts of residual potassium persulfate catalyst, when sealed in reactor vessels with an excess of ethyl mercaptan in such a manner that the vessel was flushed with nitrogen and mercaptan vapor, reacted with a definite and reproducible amount of mercaptan. This addition proceeded rapidly during the first three to six hours of reaction time at 50°, and reached a limiting value which was unique for the type of polymer being treated. These observations are illustrated by the data of Table I. It will be noted that polymers and copolymers of butadiene showed a relatively greater proportion of double bonds reacted than emulsion polyisoprene or natural rubber in air-free systems containing equivalent amounts of persulfate catalyst.

The effect of oxygen and peroxides on the rate and extent of ethyl mercaptan addition to Buna N polymers was followed by effecting the reactions in vessels charged to varying levels. The charged reactors were flushed with air prior to sealing. It will be noted from the results presented in Table II that when the reactors were completely filled, the amount of ethyl mercaptan which added to the polymer double bonds was the same as when oxy-

TABLE I

REACTION OF ETHYL MERCAPTAN WITH EMULSION POLYMERS IN AIR-FREE SYSTEMS

Latex	Reaction time, hrs. at 50°	% double bond saturated
Buna-S	23	25
Sample A(1)	46	27
Sample B(2)	45	23
Buna-N (3)	2	9
	6	12
	48	12
Polybutadiene	3	10
	19	13
	65	14
Polyisoprene	3	3
	47	4
Natural rubber	20	2
	64	2

Weight per cent. monomers in polymerization charge:
(1) Butadiene, 78; styrene, 22
(2) Butadiene, 75; styrene, 25
(3) Butadiene, 72; acrylonitrile, 28.

gen had been flushed from the systems. However, when the amount of free air space of the reactors was increased, the amount of mercaptan reacting with the polymer also increased, apparently approaching a limiting value of 35–45% double bond saturation. This saturation value did not change appreciably as a result of a prolonged reaction time, increased or decreased potassium persulfate concentrations used in the original polymerization charge, or by substituting *n*-propyl or *n*-butyl for ethyl mercaptan. Further, it was observed that flushing the reactors with oxygen instead of air, or the addition to the reaction charge of 0.05 part of benzoyl peroxide, based on the polymer, did not affect the extent of mercaptan addition to the polymer. These data indicate that the reaction of mercaptans with Buna rubbers in latex form is catalyzed by oxygen, and the extent of double bond saturation is of the same order of magnitude as was found when this polymer reacted with thioglycolic acid.

TABLE II

REACTION OF BUNA LATICES WITH C_2–C_4 MERCAPTANS IN THE PRESENCE OF AIR

Latex	Charging volume[a]	RSH	Reaction time, hrs. at 50°	% double bonds saturated
Buna-N[b]	20	Ethyl	20	39
Sample A[c]	28	Ethyl	3	27
	28	Ethyl	17	40
	28	Ethyl	43	40
	35	Ethyl	20	36
	63	Ethyl	20	31
	87	Ethyl	20	17
	100	Ethyl	20	12
Sample B[d]	28	Ethyl	20	40
	100	Ethyl	20	13
Sample C[e]	28	Ethyl	20	40
	100	Ethyl	20	12
Buna-S[f]	30	Ethyl	48	45
	30	*n*-Propyl	48	35
	30	*n*-Butyl	48	41

[a] Per cent. of volume of 2-oz. reactor occupied by latex and mercaptan. [b] Monomer feed ratio, wt. %: butadiene, 74; acrylonitrile, 26. [c] Contained 0.30 parts $K_2S_2O_8$ on monomers in charge. [d] Contained 0.15 parts $K_2S_2O_8$ on monomers in charge. [e] Contained 0.60 parts $K_2S_2O_8$ on monomers in charge. [f] Monomer feed ratio, weight %: butadiene, 75; styrene, 25.

The data presented in Table III relate to the C_8 to C_{16} chain length mercaptan saturation values for polybutadiene, butadiene–styrene, and butadiene–α - methyl–*p* - methylstyrene copolymers. The reactions were effected in mass at high temperatures. The data do not include the reaction rates, but only summarize the values obtained during reaction times in which reaction apparently ceased. Although it was observed that the rate of mercaptan addition varied, the final polymer double bond saturation values were of about the same order of magnitude. Sharples 3B mercaptan gave rise to gel polymers of low sulfur content under the same reaction conditions.

TABLE III

MASS REACTIONS

RSH	% Double bonds saturated for polymer A	B	C
n-C_8	41	..	52
n-C_{10}	44	..	56
n-C_{12}	47	42	42
n-C_{14}	35	42	36
n-C_{16}	40	41	48
3B	Gelled	Gelled	..

A, Polybutadiene. B, Butadiene, 50; styrene, 50; wt. % composition. C, Butadiene, 43.5; α-methyl-*p*-methylstyrene, 63.5; wt. % composition. 3B, Sharples 3B (tertiary) mercaptan.

The selectivity of the mass reaction at elevated temperatures appears to be overcome when a continuous stream of air is passed through the reaction mixture. Under such conditions 75% of the double bonds in a butadiene–styrene copolymer were saturated by a normal mercaptan of C_{14} chain length. The presence of volatile reaction products possessing an odor suggestive of aldehydes would indicate that under such drastic conditions the polymer was degraded.

In further experiments polybutadiene reacted in mass with Lorol mercaptan in the presence of possible activating agents at various temperatures in order to determine whether the time of the reaction could be decreased, and whether activating agents have any effect upon the selectivity of the reaction. Piperidine, zinc dibutyldithiocarbamate, anthraquinone, benzoyl disulfide, sulfur, and benzoyl peroxide were evaluated in concentrations of 2 to 10%, based on the polymer, at temperatures of 75 to 180° for varying periods of time. Piperidine and anthraquinone exhibited an activating effect, but the extent of polymer double bond saturation was unaltered.

Based on the partially known structure of butadiene polymers and copolymers and upon the vast difference in the rate at which vinyl and internal ethylenic bonds add mercaptans, it would appear that the 38 to 47% of ethylenic bonds which added mercaptans readily are probably those derived from 1,2-addition of butadiene units to the polymer chains, or those arising from 1,2-addition and intramolecular cyclization reactions.

The saturation values obtained by the reactions between various types of mercaptans and butadiene polymers are in fair agreement in spite of a wide range of reaction conditions.

If it is assumed that the polymer double bonds which added mercaptans readily are those present in side vinyl groups, then the mercaptan saturation values found are in fair agreement with the value of 48% for a butadiene–styrene copolymer as determined by potassium permanganate oxidation,[6] and 34.5 and 42.8% as determined by ozonolysis[3] for a butadiene–styrene and a sodium catalyzed polybutadiene, respectively. The mercaptan saturation values are not, however, in full agreement with those found by perbenzoic acid oxidation whereby emulsion butadiene–styrene copolymers showed 1,2-values of 27[6] and 20–22[7] per cent. while sodium catalyzed polybutadiene showed 58[7] per cent. side vinyl groups.

Summary

Thioglycolic acid added exothermally to butadiene polymers and copolymers in benzene solution under mild conditions to give apparent double bond saturation values of 38 to 47%. When the same polymers reacted with aliphatic mercaptans of C_2 to C_{16} chain length, in mass or latex reactions, saturation values were obtained which were in accord with those found by thioglycolic acid addition.

It is suggested that the double bonds in butadiene polymers and copolymers which were readily saturated by the above mercaptans are predominately those present in the polymer chains as vinyl side groups.

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[CONTRIBUTION FROM THE CHARLES F. KETTERING FOUNDATION FOR THE STUDY OF CHLOROPHYLL AND PHOTOSYNTHESIS, ANTIOCH COLLEGE, AND FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Porphyrin Studies. V.[1] The Metal Complex Salts of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine

BY PAUL ROTHEMUND AND AMEL R. MENOTTI[2,3]

In the preceding paper of this series[1] we reported the synthesis of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (hereafter to be abbreviated T.P.P.) on a preparative scale. Thus sufficient quantities of this porphyrin became available for the preparation and study of a large number of its metal complex salts, fifteen of which have been obtained in the present investigation in crystalline form and five in solution only.

This is probably the largest number of metal complex salts ever prepared from any one porphyrin, and the work was undertaken with the aim of furnishing reliable material for physico-chemical studies on the structure of porphyrin metal complexes, especially in connection with the study of chlorophyll. Spectrophotometric measurements on the above-mentioned series of compounds are in progress at the Charles F. Kettering Foundation in order to determine possible correlations between absorption and fluorescence spectra; some of the findings have already been published.[4]

The metal complex salts described are the derivatives of T.P.P. which shows the "etio type"[5] spectrum and has its first absorption band in ether solution at 648 mμ. Derivatives of isomers and of other polynuclear pyrrole pigments, by-products in the synthesis of T.P.P., will be described in a separate publication.

In the preparation of these metal complexes three general methods were employed which are described in detail in the experimental part.

General Properties of the Metal Complex Salts.—All of the salts isolated were well-crystallized compounds of high surface luster. They showed selective absorption in the visible region of the spectrum and had melting points ranging from 400 to 520°. On heating from 400 to 450° all but the manganese chloride and the gold salts sublimed. During this sublimation partial decomposition of the complex occurred.

The complexes varied markedly in stability. Thus, the potassium and one thallium complex decomposed when dissolved in neutral solvents such as benzene and ether; the magnesium, mercury, and lead complexes split when shaken with 50% acetic acid. The zinc and silver complexes were stable to 50% acetic acid but decomposed slowly in hydrochloric acid solutions. In every case of these decomposition conditions the presence of free porphyrin in the solution was ascertained. The iron chloride, manganese chloride, cobalt, nickel, copper, stannous chloride, and gold complexes were heated in the steam-bath with

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[2] From the dissertation submitted by Amel R. Menotti to the Faculty of the Graduate School of the Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1940.

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