water held at 40°, 10 g. of the crude color base being obtained. This was dissolved in alcohol and thes mall amount of contaminating, inorganic salts filtered off. The pure compound recovered by the evaporation of the alcohol was used for analysis and also converted to the dye by solution in acids.

Anal. Calcd. for $C_{27}H_{30}N_2O_3$: N, 6.51. Found: 6.47, 6.45.

Summary

N-Phenyl-tetrahydro-*p*-oxazine has been prepared in considerable quantities through modifications of the Knorr, and the Kamm and Waldo methods. The advantages of each of these methods have been demonstrated. An improved method for the condensation of ethylene chlorohydrin and aniline has been described. It has been found advantageous to dehydrate di-β-hydroxyethyl-aniline by heating under reduced pressure rather than to do so by the use of sulfuric acid. The oxazine has been condensed with benzaldehyde to give a new triphenylmethane dye. Some of the properties of the new dye have been noted.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

SOME SUBSTITUTED AMMONIUM MOLYBDATES AND TUNGSTATES

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Introduction

Relatively few compounds of molybdic acid with organic bases have been made.

In 1856 Sonnenschein[2] prepared an ethylammonium molybdate from a solution of molybdic acid in ethylamine. Classen[3] in a like manner formed a tetramethylammonium molybdate. By the use of pyridine sulfate and sodium molybdate Pincussohn[4] prepared a pyridinium molybdate. Similarly, Ditte[5] made phenylammonium molybdate.

The compounds of organic nitrogen bases with tungstic acids are more numerous. Their method of preparation has been generally the same as that of the molybdic salts of the organic bases.

Kohn[6] precipitated a hydrated guanidinium tungstate from a solution of guanidinium carbonate. Knorre[7] prepared benzidinium tungstate from sodium paratungstate.

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[1] The material presented here is a portion of that used by A. C. Krause in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Sonnenschein, *J. prakt. Chem.*, **67**, 151 (1856).

[3] Classen, *ibid.*, **93**, 448 (1864).

[4] Pincussohn, *Z. anorg. Chem.*, **14**, 379 (1897).

[5] Ditte, *Compt. rend.*, **105**, 813 (1887).

[6] Kohn, *Ber.*, **38**, 783 (1905).

[7] Knorre, *Ber.*, **38**, 783 (1905).

Tschilikin[8] used α-naphthylamine to precipitate tungsten quantitatively. Ditte[5] obtained phenylammonium tungstate from aniline hydrochloride. From the aqueous solutions of some aliphatic amines Ekeley[9] crystallized a series of substituted ammonium tungstates.

It was believed to be worth while to study further the preparation of salts of molybdic acid and tungstic acid with organic bases.

A series of new compounds has been prepared from molybdic and tungstic acids by reaction with organic substituted ammonias. The formulas and behavior of the complex salts formed indicate that they are analogs of the ammonium salts of the same acids and they have been named accordingly.

Experimental Part

The ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, made by the J. T. Baker Chemical Company was used for the preparation of molybdic acid and was used as ammonium molybdate in the metathetical formation of basic organic nitrogen salts. The sodium tungstate, $Na_2WO_4.2H_2O$, was made by E. H. Sargent and Company and was used in the same manner as the ammonium molybdate. The molybdic acid was prepared from ammonium molybdate by precipitation with nitric acid.

Phenylammonium Molybdate, $C_6H_5NH_2.H_2MoO_4.MoO_3$.—The molybdic acid paste, freshly prepared from 50 g. of ammonium molybdate and 100 g. of aniline were added to 200 cc. of distilled water. The mixture was allowed to digest at 98° for about four hours. Upon cooling, the lower half of the mixture became solid with a brown gel of the molybdic acid and the aniline. The brown gel was filtered off, and the occluded aniline was extracted with xylene. The mass was dried and powdered. The powder was mixed with 200 cc. of hot water and allowed to digest for about 20 minutes on a hot-plate at a temperature of 95° to 98°. The residue after settling was separated by decanting the solution through a filter in a hot water funnel. Twenty hours after the solution had cooled microscopic crystals appeared. The residue on the filter and in the beaker was extracted exhaustively in a like manner until no further crops of crystals could be obtained. The remaining portion determined by analysis was chiefly molybdic acid. The total amount of crystals obtained by this method was very small. There was apparently a large amount of hydrolysis of the phenylammonium molybdate first formed.

Pressure apparently gave little if any increase in yield of crystalline compound. A paste of molybdic acid made from 50 g. of ammonium molybdate was mixed with 50 cc. of water and 50 g. of aniline in a pressure flask. The mixture was heated in an oil-bath at 140° for about four hours. After cooling, a brown gel formed from which a small amount of crystals was obtained.

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[8] Tschilikin, *Ber.*, **42**, 1302 (1909).

[9] Ekeley, THIS JOURNAL, **31**, 665 (1909).

Another method was tried to increase the yield of the salt. One-tenth mole or 29.6 g. of ammonium molybdate and 0.1 mole or 11.5 g. of aniline hydrochloride were separately dissolved in 100cc. portions of hot water, the solutions filtered, and then mixed during vigorous stirring. A white amorphous precipitate formed rapidly. It was filtered off and dried at room temperature. The dry powder was extracted with 200 cc. of hot water at 95° to

TABLE I

SALTS PREPARED

Salt	Method of preparation $M = MoO_3$ $N = (NH_4)_6Mo_7O_{24}$	Formula	Analysis in percentage N Calcd.	N Found	MoO_3 Calcd.	MoO_3 Found
		MOLYBDATES				
Phenyl ammonium	1. M + aniline 2. N + aniline hydrochloride 3. M + aniline (pressure)	$C_6H_5NH_2.H_2MoO_4.MoO_3$	3.51	3.50 3.44	72.18	71.96 71.92
Methyl (4) phenyl ammonium	1. M + *p*-toluidine 2. N + *p*-toluidine hydrochloride 3. M + *p*-toluidine (pressure)	$CH_3C_6H_4NH_2.H_2MoO_4.MoO_3$	3.38	3.66 3.76	69.73	69.06 69.08
Methyl (2) phenyl ammonium	1. M + *o*-toluidine 2. N + toluidine hydrochloride 3. M + *o*-toluidine (pressure)		3.38	3.51 3.56	69.73	69.28 69.44
Phenyl-dimethyl ammonium	1. M + dimethylaniline 2. N + dimethylaniline hydrochloride 3. M + dimethylaniline (pressure)	$(CH_3)_2NC_6H_5.H_2MoO_4.MoO_3$	3.26	3.52 3.64	67.40	67.22 67.38
Phenyl-diethyl ammonium	1. M + diethylaniline	$(C_2H_5)_2NC_6H_5.H_2MoO_4.MoO_3$	..	..	63.29	63.27 63.10
Methyl-pyridinium	1. M + pyridine	$CH_3C_5H_4N.H_2MoO_4.MoO_3$	3.51	3.48 3.36	72.18	72.41 73.02
Piperidinium	1. M + piperidine	$(C_5H_{11}N)_2.H_2MoO_4.MoO_3$	5.94	5.90 5.70	60.50	61.24 61.40
Ethylene diammonium	1. M + ethylenediamine	$C_2H_8N_2.2H_2MoO_4.2MoO_3.H_2O$	4.07	4.14 4.24	84.90	84.52 84.30
Dimethyl ammonium	1. M + dimethylamine	$(CH_3)_2NH.2H_2MoO_4$	..	..	78.05	77.86 77.80
		TUNGSTATES				
					WO_3 Calcd.	WO_3 Found
Methyl ammonium	1. WO_3 + methylamine	$(CH_3NH_3)_6W_7O_{24}.2H_2O$			83.36	83.35 83.38
Piperidinium	1. WO_3 + piperidine	$(C_5H_{11}N)_6W_7O_{24}.4H_2O$			71.90	72.06 72.18
Methyl (2)-phenyl ammonium	1. WO_3 + *o*-toluidine	$((CH_3)C_6H_4NH_2)_2.H_2W_6O_{16}$			80.33	80.30 80.22

Crystals were insoluble in ether, methyl alcohol, ethyl alcohol, amyl alcohol, benzene, toluene, xylene, acetone and ethyl acetate, chloroform, carbon tetrachloride, and quite soluble in aniline. Alkalies liberated the organic base from all compounds.

The formula of methylammonium tungstate differed from that of Ekeley by four molecules of water. The tungstates were analyzed for tungstic trioxide by ignition. The piperidinium molybdate and tungstate were recrystallized in 95% hot alcohol.

98°. Repeated extractions were necessary to remove completely all of the salt. Rapid crystallization in the dark gave small, white, rhombic crystals.

Upon recrystallization the product was analyzed for molybdenum by ignition. The nitrogen was determined by the Kjeldahl-Gunning-Arnold method.

Anal. Calcd. for $C_6H_5NH_2.H_2MoO_4.MoO_3$: MoO_3, 72.18; N, 3.51. Found: MoO_3, 71.96, 71.92; N, 3.44, 3.50.

The other salts of molybdic and tungstic acids prepared from organic nitrogen bases and the methods of preparation are given in Table I.

Discussion

The tungstic and molybdic acids have a great tendency to form complex acids and salts of variable composition. A well-known example of this is found in the precipitate of ammonium phosphomolybdate used in quantitative analysis. Arsenates give similar precipitates. The composition of the precipitate varies a little, especially as to its water content, with the conditions under which it is formed. Likewise, there was a difficulty in obtaining the basic organic nitrogen molybdates and tungstates, previously described in this paper, that appeared to be definite compounds as shown by analysis. In the present case, the difficulty may be referred to the tendency of molybdic and tungstic acids to condense and form complex salts of the type $R'_2O.nWO_3$, $R'_2O.nMoO_3$ where n represents the numerical ratio between the WO_3 and MoO_3 and R'_2O groups. The acids and salts may be hydrated also, more than $H_2MoO_4.H_2O$ or $H_2WO_4.H_2O$. Ordinary ammonium molybdate, for instance, is $(NH_4)_7Mo_6O_{24}.4H_2O$; ordinary sodium tungstate is $Na_{10}W_{12}O_{41}.28H_2O$ or $5Na_2O.12WO_3.28H_2O$.

All the basic organic nitrogen compounds used may be considered to be derived from ammonia by the replacement of hydrogen by organic radicals. Moreover, the nitrogen may become quinquivalent and so there may be a fourth hydrocarbon group attached, giving rise to the quaternary ammonium compounds.

The relative strength or activity of the basic organic nitrogen compounds can explain the difficulty of the formation and the ease of hydrolysis of their salts. The alkylamines are distinct bases; in fact at low temperatures they seem to be capable of forming acid salts with two or three molecules of haloid acid.[10] The successive introduction of alkyl groups in ammonia increases the basicity. As expected, the alkyl amines that are highly basic gave compounds with molybdic and tungstic acids of greater stability in water and of more constant composition than the alkyl amines of lower basicity. Ethylenediamine acted similarly to the alkylamines.

Phenylamines resemble alkylamines with regard to the formation of salts, but they are much weaker bases than the primary alkyl amines; they have

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[10] Korczynski, *Ber.*, **41**, 4379 (1908). Kaufler and Kunz, *Ber.*, **42**, 385 (1909).

no alkaline reaction and are but slightly soluble in water. The successive introduction of aromatic groups diminishes the basicity of the amine. The quaternary hydroxides, unlike the primary, secondary and tertiary aromatic bases, are strongly basic. Thus, in making organic nitrogen molybdates, it was noticed that apparently the *o*-toluidine salt was made more easily than the *p*-toluidine molybdate, which in turn was easier to prepare and to recrystallize than the phenylammonium molybdate. The salts of meta- and ortho-nitranilines were not prepared successfully. The *o*- and *p*-bromo-anilines gave compounds which could not be purified. These results can be explained by the work of other investigators. Farmer and Worth[11] determined the influence of nuclear substitutes on the basicity of aniline. They determined the degree of hydrolysis of the hydrochlorides by shaking the aqueous solutions with benzene and determining the concentration of the base in the benzene layer. Their general conclusions are that the *ortho* position gave the greatest effect, and the *meta* the least; and the order of the effect of the substituent groups is: (strongly negative) NO_2, COOH, $N:NC_6H_5$, Br, Cl, CH_3, CH_3O (weakly positive). In other words, in the order named, a negative group in the benzene ring decreased, and a positive group increased the basicity of the amino group in the substituted aniline. The great effect of the nitro group in weakening the basicity of the amino group and its dependence on position was shown by Lellmann.[12] He found that the *o*-nitro-aniline hydrochloride was decomposed 63.8% upon evaporation, the *meta* 3.4%, and the *para* 13.1%. Thus, the apparent ease of preparation or formation of molybdates and tungstates may be considered to vary with the basicity of the organic aromatic nitrogen base. The mixed tertiary aromatic amines, dimethylaniline and diethylaniline, which have very weak basic reactions since the influence of the phenyl group outweighs that of the two alkyl groups, gave salts the formation of which was similar chemically to that of phenylammonium molybdate. It is probable that quaternary bases of di-*ortho*-substituted anilines would give no salts because of steric hindrance.[13] Picoline which has a tendency to form double salts and which has a strength as a base similar to that of aniline,[14] formed a salt similar to that of methyl-4-phenylammonium molybdate in ease of crystallization. Piperidine acted like a secondary aliphatic amine toward molybdic and tungstic acids. The two naphthylamines, alpha and beta, gave precipitates through metathesis but not by direct union to form molybdates and tungstates, as they were too weak as bases. The various other organic nitrogen bases failed to give definite compounds.

The nature of the compound formed was dependent upon the strength

[11] Farmer and Worth, *J. Chem. Soc.*, **85**, 1713 (1904).

[12] Lellmann, *Ber.*, **17**, 2719 (1884).

[13] Fischer, *Ber.*, **33**, 345, 1967 (1900).

[14] Constam and White, *Am. Chem. J.*, **29**, 1 (1903).

of the base. Weak bases gave salts of the general formula $X.H_2MoO_4.MoO_3$, where X represents one molecule of a mono-acid base. In other words, a substituted mono-ammonium salt of a dimolybdic acid was formed. With strong bases, especially aliphatic bases, however, another molecule of water was added to the salt. The general formula, $X.H_2MoO_4.MoO_3.H_2O$, was indicated.

With tungstic acid a similar relationship developed. The salts tended to add more water of crystallization as the degree of strength of the base increased. Also, the ratio of the base to the tungstic oxide decreased with the increase of strength of the base.

Summary

The methods of preparation and some properties of some of the alkyl and aryl substituted ammonium molybdates and tungstates have been investigated. The aliphatic amines gave well-defined, crystalline, water-soluble molybdates and tungstates with little difficulty. On the contrary, the aromatic amines formed precipitates that were only slightly soluble in water. Large yields of pure crystals were not possible on account of the ease of hydrolysis of these aromatic compounds. The yield of the salts varied greatly with the temperature, pressure, solvents and the concentration of the reactants.

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[Contribution from Lafayette College]

THE INFLUENCE OF HYDROGEN-ION CONCENTRATION ON THE OPTICAL ROTATION OF GELATIN

By R. H. Bogue and M. T. O'Connell

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The optical rotation of gelatin has been studied by C. R. Smith, and reported by him in two important papers.[1] The purpose of Smith's work was (1) to observe the optical rotation of gelatin at various temperatures and (2) to determine the minimum gelatin concentration at which gelation takes place on cooling, this gelatin concentration being determined by an application of his findings on the relation of rotation to concentration.

Smith reported that the specific rotation, $[\alpha]_D$, of a 2% solution of the highest grade of commercial gelatin at 35°, and above was —141°, and that the specific rotation at 15° and below was —313°. Between these temperatures the rotation varied in a regular manner. On the basis of these and other findings, Smith concluded that the change in rotation is due to a reversible change between the gel and the sol, the gel having a specific rotation of —313° and being the only form stable at temperatures below 10°, while the sol has a specific rotation of —141° and is the only form

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[1] This Journal, **41**, 135 (1919); *J. Ind. Eng. Chem.*, **12**, 878 (1920).