White's value 8×10^{-13} at 0.06 M ionic strength (and based on $[H^+]$ instead of a_{H^+}).

The partition and spectrophotometric methods agree in indicating a value a little greater than 1×10^{-15} for K_2 of perosmic acid at 1.0 M ionic strength. Greater weight should be given the spectrophotometric value (3×10^{-15}) than the partition value (1.4×10^{-15}), so that instead of averaging the two figures, we shall accept 3×10^{-15} as the value of K_2.

If one assumes the applicability of the general rule that successive ionization constants of an oxygen acid differ by the factor $\sim 10^{-5}$, the primary ionization constant of perosmic acid should be about 10^{-10}. Since the apparent constant based on total osmium in solution is 10^{-12}, some support is thus obtained for the belief that a large fraction of the osmium tetroxide exists as such in solution. It may also be noted that the value 10^{-10} for K_1, the true ionization constant, agrees with K_1 for acids of the type $X(OH)_n$, most of which have primary ionization constants of 10^{-9} to 10^{-11}.

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Lead Citrates, Complexes and Salts, their Composition, Structure and Behavior

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RECEIVED DECEMBER 1, 1952

The composition and structure of the complexes and salts of lead citrate were studied at low and high *p*H's. The phenomena observed may be accounted for as follows. A soluble complex of the composition $[PbCi_2]^{4-}$ is obtained quantitatively from the components at *p*H $\sim$7.0. The latter gives on addition of lead an insoluble salt of the composition Pb_3Ci_2 or $Pb_2[PbCi_2]$, which redissolves at *p*H $\leqslant$ 3.0. At high *p*H's (*p*H $\geqslant$ 9.5) the anion complex $[PbCi']^{2-}$ is formed quantitatively. Between *p*H 7–9.5 the complexes $[PbCi_2]^{4-}$ and $[PbCi']^{2-}$ are obtained side by side in solution. At *p*H $\sim$8.0 $[PbCi']^{2-}$ forms, on the addition of lead, the insoluble salt $Pb[PbCi']\cdot[PbCi']^{2-}$ may be presented as an anion of an acid $[PbCi]^{1-}$ for which $pk = 7.5$. Under different experimental conditions two insoluble salts of different structures but of the same empirical composition Pb_3Ci_2, may exist.

The investigation of lead citrate is a continuation of the studies of metal complexes with citrate or tartrate.[1] The study of lead citrate may be of special interest because of its role in physiology and the therapy of lead poisoning, where lead is removed by complex formation with citrate.[2]

Experimental Details

Reagents and Solutions.—Stock solutions of lead nitrate and sodium citrate were prepared by weighing the salts $Pb(NO_3)_2$ and $Na_3C_6H_5O_7\cdot 2H_2O$ (both C.P. Baker Analyzed), and solutions of the required concentration were then prepared by dilution with distilled water.

Apparatus and Procedure. Heterometer.—A "Heterometer" designed and constructed by the first author specially for electrophotometric titrations involving suspensions was used. The light passed vertically during the titration through the cylindrical absorption cell (diameter = 5.2 cm.) and fell on the photoelectric cell. The readings on the galvanometer were made with an accuracy of ±0.001 microamp., and the optical density ($D = \log I_0/I$) was calculated to three decimal places. The readings were recorded at 0.1–0.2 cc. intervals only after a constant value was obtained, usually after a few seconds to a minute. The usual rate of stirring of the solution was 600 r.p.m. and was generally the maximum consistent with stable measurements. Experiments were repeated after several months to check the reproducibility of the density curves, which, in general, was very good. The maximum optical density values varied somewhat, but the critical points on the horizontal axis remained the same in all cases.

Heterometry[3] deals with the photometric study of chemical reactions in suspensions on a quantitative basis. It is concerned with reactions which occur in the *solution* as well as in the *solid* state. *Heterometric titration curves* (optical density curves) are obtained and the *critical points* determined. From each heterometric curve at least two or three critical points may be derived. They are: the point of the "initial precipitation," the "maximum density" point and the point of "complete dissolution." In most cases additional critical points are obtained.

Since heterometry deals primarily with end-points it does not matter whether the particles are of unit or varying size.

Many thousands of heterometric curves were obtained by the author with co-workers in the past four years. We were convinced by the results that heterometry is especially suitable for the study of soluble and insoluble complex compounds and for the heterometric microdetermination of metals or other compounds.

***p*H Measurements.**—A Beckman Model H2 *p*H meter in conjunction with a "Beckman Glass electrode" and a "Beckman saturated calomel electrode" was used for all *p*H titrations. Readings were taken at 0.1–0.2 cc. intervals after each addition of titrating solution and with continuous stirring. The time required for the reading to become constant varied with the reactions studied, especially when redissolving occurred, but in no case was a *p*H value recorded until the reading became constant.

Conductivity Measurements.—A "Serfass Conductivity Bridge Model R.C.M. 15," manufactured by Industrial Instruments, Inc., U.S.A., was used for the conductometric experiments. The conductance cell has been described in a previous paper.[4] The heterometric and *p*H titrations were carried out at room temperature (18–27°).

Results and Discussion

This study of lead citrate was made by physical methods only. No claim is made that the problem presented is in any way exhausted. The reactions occurring at different *p*H's are much too complicated for a detailed analysis. Nevertheless, an attempt was made by us to present formulas for the compounds obtained which conform with the experimental results. Here, as in many other reactions studied by us, we assume that the hydrogen of the hydroxy group of citrate is quantitatively released at high *p*H and replaced by the cation.

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(1) M. Bobtelsky and A. E. Simchen, THIS JOURNAL, **64**, 2592 (1942); *Compt. rend.*, **208**, 1646 (1939); *Bull. soc. chim.*, **17**, 870 (1950); M. Bobtelsky and J. Jordan, THIS JOURNAL, **67**, 1824 (1945); **69**, 2286 (1947); M. Bobtelsky and C. Heitner, *Bull. soc. chim.*, **18**, 494 (1951); **19**, 358 (1952).

(2) S. S. Kety and T. V. Letonoff, *C. A.*, **35**, 37149 (1941); **36**, 2028^3 (1942); **37**, 2460^5 (1943); F. Auerbach and H. Weber, *Z. anorg. Chem.*, **147**, 68 (1925).

(3) M. Bobtelsky and Bar-Gadda, (a) *Bull. soc. chim. France*, 278 (1953); (b) *Ann. Chim. Acta*, 1953; M. Bobtelsky and B. Graus, (a) *Bull. Research Council of Israel*, 1953; (b) *Ann. Chim. Acta*, 1953.

(4) M. Bobtelsky and A. E. Simchen, THIS JOURNAL, **64**, 445 (1942).

TABLE I

Composition[a]: *a* cc. 0.1 *M* Na_3Ci + *b* cc. NaOH + (20 − *a* − *b*) cc. H_2O + *X* cc. $Pb(NO_3)_2$.

		Lead, cc., found			Calcd. lead, cc., soluble as			Calcd. lead, cc., for precip. of	
Na_3Ci, cc. (1)	NaOH, cc. (2)	At begin of precip. (3)	At end of precip. (4)	$PbCi_2$ (5)	$PbCi_2'$ (6)	$PbCi'$ (7)	$\left\{+\begin{matrix}PbCi_2\\PbCi'\end{matrix}\right.$ (8)	$\left\{+\begin{matrix}Pb_2[PbCi_2]\\Pb[PbCi']\end{matrix}\right.$ (9)	Pb_3Ci_2 (10)
3	..	1.8	4.5	1.5	...	...	*1.5*	*4.5*	4.5
3	3	3.1	6	1.5	1.5	1.5	*3.0*	*6*	4.5
4	3	3.7	7.5	2.0	1.5	1.5	*3.5*	*7.5*	6.0
3	2	2.7	5.6	1.5	1.0	1.0	*2.5*	*5.5*	4.5
10	8	8.8	...	5	4	4	*9.0*		
10	4	6.3	...	5	2	2	*7.0*		
5	6	5	...	2.5	2.5	2.5	*5.0*		

[a] *X*, in exper. 1–4, concn. = 0.05 *M*; exper. 5–7, concn. = 0.1 *M*.

This conforms to the view now generally accepted by workers in this field.

1. **Heterometric Measurements.**—The results are presented in the form of curves in which the optical density is plotted against the amount of titrant (expressed in cc.). Figure 1 presents two titrations carried out in neutral solution. As curve 1 shows, the solution remains clear until the molar ratio of $1[Pb^{2+}]:2[Ci^{3-}]$ is reached (= $[PbCi_2]^{4-}$). The first maximum point lies at the molar ratio of $3[Pb^{2+}]:2[Ci^{3-}]$. Pb_3Ci_2 is quantitatively formed, but its real structure may be presented as $Pb_2[PbCi_2]\downarrow$. Figure 2 shows the results of reverse titrations. A sharp maximum point is obtained in all cases at the molar ratio of $3[Pb^{2+}]:2[Ci^{3-}]$. Excess citrate redissolves the precipitate approximately at the molar ratio of $1[Pb^{2+}]:2[Ci^{3-}]$ (= $[PbCi_2]^{4-}$).

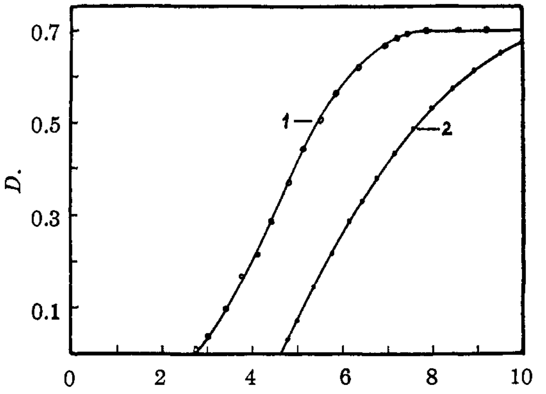


Fig. 1.—(1) 5 cc. 0.05 *M* Na_3Ci + 15 cc. H_2O + *x* cc. 0.05 *M* $Pb(NO_3)_2$; (2) 5 cc. 0.1 *M* Na_3Ci + 15 cc. H_2O + *x* cc. 0.05 *M* $Pb(NO_3)_2$.

A number of experiments were carried out in basic solutions. On addition of sodium hydroxide to solutions containing $[PbCi_2]^{4-}$, no *visible* change occurs even when a large excess of sodium hydroxide is added. Moreover, a suspension of lead citrate (obtained by mixing lead nitrate solution with a solution of sodium citrate in the molar ratio of 3:2) is dissolved completely on addition of approximately *one* equivalent of sodium hydroxide per *one* citrate.

A series of heterometric titrations were carried out by adding lead nitrate to solutions containing different quantities of sodium citrate and sodium hydroxide. The points of *initial* precipitation and of *complete* precipitation (= maximum density) were determined in each case. The evaluation of these results is made in Table I. Columns (1) through (4) contain the composition of each experiment and the results obtained. Columns (5) through (10) contain calculated values which were obtained on the basis of the values of columns (1) and (2). If we compare the values of columns (3) and (5) we find that the amount of lead which can be retained in solution is considerably higher than the amount which conforms to the quantitative formation of $[PbCi_2]^{4-}$ *alone*. All calculations in Table I are based on the assumption that reaction (I) occurs quantitatively at high *p*H.

$$Pb^{2+} + Ci^{3-} + OH^- \rightleftharpoons [PbCi']^{2-} + H_2O \qquad (I)$$

In addition, if these solutions contain an *excess* of sodium citrate relative to sodium hydroxide reaction (II)

$$Pb^{2+} + 2Ci^{3-} \rightleftharpoons [PbCi_2]^{4-} \qquad (II)$$

takes place quantitatively, with the free citrate in solution. Columns (3) and (8) in Table I are in good agreement. The reactions which may take place during the precipitations are

$$Pb^{2+} + [PbCi']^{2-} \rightleftharpoons Pb[PbCi']\downarrow \qquad (III)$$

$$2Pb^{2+} + [PbCi_2]^{4-} \rightleftharpoons Pb_2[PbCi_2]\downarrow \qquad (IV)$$

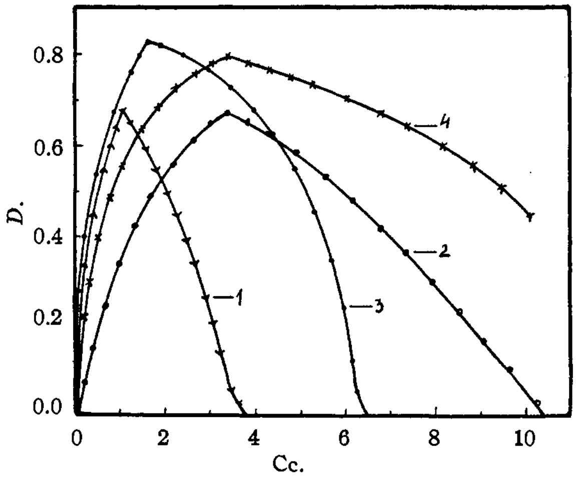


Fig. 2.—(1) 3 cc. 0.1 *M* $Pb(NO_3)_2$ + 17 cc. H_2O + *x* cc. 0.2 *M* Na_3Ci; (2) 5 cc. 0.05 *M* $Pb(NO_3)_2$ + 15 cc. H_2O + *x* cc. 0.05 *M* Na_3Ci; (3) 5 cc. 0.1 *M* $Pb(NO_3)_2$ + 15 cc. H_2O + *x* cc. 0.2 *M* Na_3Ci; (4) 5 cc. 0.1 *M* $Pb(NO_3)_2$ + 15 cc. H_2O + *x* cc. 0.1 *M* Na_3Ci.

If we compare the values of columns (4) and (10), we find that the possibility that the precipitate is composed of the insoluble Pb_3Ci_2 *solely*, is excluded in all cases in which sodium hydroxide is present. On the other hand the values of column (4) agree well with those of column (9). The assumption that an anion complex $[PbCi_2]^{6-}$ may be obtained in solution instead of $[PbCi']^{4-}$ is not in accordance with the values of column (3).

2. ***p*H Measurements.**—The *p*H of a solution of sodium citrate decreases somewhat on the addition of lead nitrate, but the formation of $[PbCi_2]^{4-}$ is not especially marked on the curve. On the addition of Na_3-citrate to lead nitrate, a minimum *p*H of >3.0 is obtained during the precipitation. When the precipitation is complete an inflexion point is obtained at *p*H ~4.5. As soon as the precipitate begins to dissolve through the formation of a complex, the *p*H rises to >6.0 and then remains almost constant during the redissolving (*p*H ~6.5). On the addition of lead nitrate to a solution of Na_3Ci which also contains sodium hydroxide an inflexion point is obtained at *p*H ~9.5 at the approximate molar ratio of $1[OH^-]:1[Pb^{2+}]$. On the addition of sodium hydroxide to a solution which contains the soluble complex $[PbCi_2]^{4-}$ an inflexion point is obtained at *p*H ~9.5. The reaction taking place in solution may be presented as

$$[PbCi_2]^{4-} + OH^- \underset{pH\ \sim 7.0}{\overset{pH\ \sim 9.5}{\rightleftarrows}} [PbCi']^{2-} + Ci^{3-} + H_2O \quad (V)$$

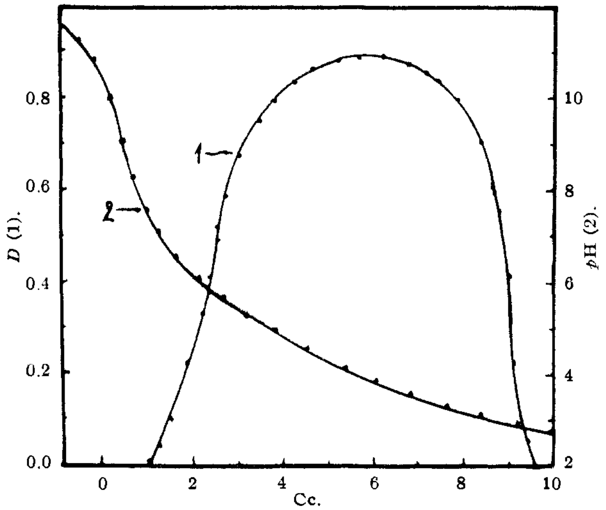


Fig. 3.—3 cc. 0.1 *M* $Pb(NO_3)_2$ + 6.5 cc. 0.1 *M* Na_3Ci + 6 cc. 0.1 *M* NaOH + 4.5 cc. H_2O + *x* cc. 0.2 *M* HNO_3.

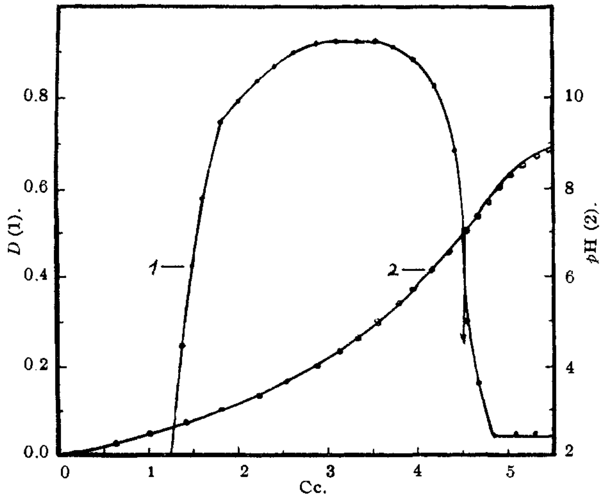


Fig. 4.—3 cc. 0.1 *M* $Pb(NO_3)_2$ + 6.1 cc. 0.1 *M* Na_3Ci + 2 cc. 1 *M* HNO_3 + 2 cc. 1 *M* NH_4NO_3 + 6.9 cc. H_2O + *x* cc. 0.5 *M* NaOH.

Reaction (V) may be presented by the following two partial reactions which are in equilibrium

$$[PbCi_2]^{4-} \leftrightarrows [PbCi]^{1-} + Ci^{3-} \quad (VI)$$

$$[PbCi]^{1-} + OH^- \rightleftarrows [PbCi']^{2-} + H_2O \quad (VII)$$

$[PbCi]^{1-}$ would act as a monobasic acid which has a $pk = 7.5$.

Parallel heterometric and *p*H titrations were carried out in buffered solutions covering the *p*H range 2–11. The titrated solutions were all clear at the beginning but, during the titration, insoluble salts appeared which on continued addition of the titrant were redissolved. Figures 3–4 present the composition of the experiments and the results obtained.

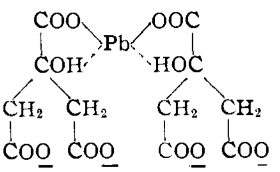
Figure 3 shows a *p*H inflexion point at ~9.5. Reaction (I) may now be completed. At *p*H ~7.0 the solution may contain $[PbCi_2]^{4-}$ only (reaction V). At *p*H ~4.5 lead citrate is precipitated and then redissolved between *p*H ~4 and ~3. Figure 4 shows the following: the precipitation of lead citrate begins at *p*H <3.0 and is completed at *p*H >4. Between *p*H ~5.5 and *p*H ~7.5 the precipitate redissolves (= $[PbCi_2]^{4-}$).

If we compare Figs. 3 and 4 we see the following: on decreasing the *p*H of the titrated solution (Fig. 3), the precipitation of Pb_3Ci_2 begins at *p*H ~7.0 and is completed at *p*H $\geqslant$ 4.5. On the other hand, on increasing the *p*H (Fig. 4) of the titrated solution, the precipitation of Pb_3Ci_2 begins at *p*H $\leqslant$ 3.0 and is completed at *p*H ~4.0. To explain this difference in behavior, we may assume that in the titration of Fig. 3, the precipitate has the structure represented by the formula $Pb_2[PbCi_2]$, whilst in the titration of Fig. 4, the precipitate may be formulated as a non-complex salt Pb_3Ci_2. A transformation of the more soluble salt into the less soluble salt during the titration does not seem probable, as this would require much more time than is afforded by a titration which lasts only a few minutes.

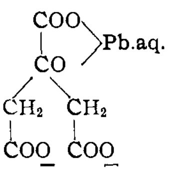
Parallel heterometric and *p*H titrations were carried out in a solution in which the molar ratio was $[Pb^{2+}]:[Ci^{3-}] = 3:2$, (composition: 4.5 cc. 0.1 *M* $Pb(NO_3)_2$ + 3 cc. 0.1 *M* Na_3-citrate + 5 cc. 0.2 *M* HNO_3 + 7.5 cc. H_2O + *X* cc. 0.2 *M* NaOH). The precipitation of lead citrate begins at *p*H < 3 and is completed at *p*H ~4 just as in Fig. 4. The *p*H curve shows an inflexion point at *p*H ~7. A redissolving occurs probably through the formation of $[PbCi']^{2-}$. The end of the redissolving is marked by a second *p*H inflexion point.

The structure of the anion complexes may be presented as

$[PbCi_2]^{4-}$:



$[PbCi']^{2-}$:



The coördination number of lead in the anion complex $[PbCi_2]^{4-}$ is four. Nothing certain can be said about the coördination number in the case of $[PbCi']^{2-}$. The latter may be hydrated.

3. **Conductometric Measurements.**—Figure 5 presents the composition and the results of three titrations. No change in conductivity (curve 1) occurs during the precipitation of $Pb_3Ci_2 \downarrow$. A break is obtained on the quantitative formation of the insoluble salt. A linear increase in conductivity occurs during the redissolving of the precipitate. In the reverse titration (curve 2) a break occurs at the point of complete precipitation of Pb_3Ci_2. Curve 3 is entirely different. It is composed of four branches with breaks between them. *The breaks lie at the calculated end-points of the formation of the various predicted compounds* (compare Table I). At the first break all the sodium hydroxide present in solution is used up for the quantitative formation of the soluble anion complex $[PbCi']^{1-}$. The free citrate remaining in solution reacts now with the lead, forming quantitatively the anion complex $[PbCi_2]^{4-}$ at the second break. On further addition of lead, the insoluble salts $Pb[PbCi']$ and $Pb_2[PbCi_2]$ are formed quantitatively at the third break.

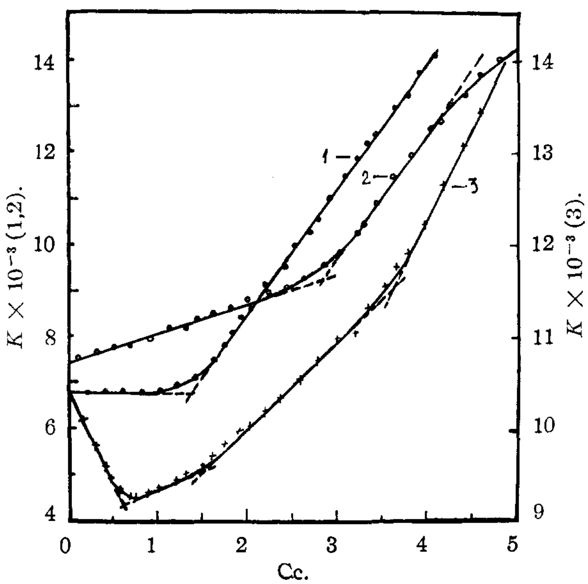


Fig. 5.—(1) 5 cc. 0.2 *M* $Pb(NO_3)_2$ + 45 cc. H_2O + *x* cc. 0.5 *M* Na_3Ci; (2) 5 cc. 0.2 *M* Na_3Ci + 45 cc. H_2O + *x* cc. 0.5 *M* $Pb(NO_3)_2$; (3) 4.5 cc. 0.25 *M* Na_3Ci + 3.75 cc. 0.1 *M* NaOH + 41.75 cc. H_2O + *x* cc. 0.5 *M* $Pb(NO_3)_2$.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Dinitrogen Tetroxide. II. Reactions with Tertiary Amines[1]

BY DEREK A. DAVENPORT, HAROLD J. BURKHARDT AND HARRY H. SISLER

RECEIVED APRIL 2, 1953

In ethereal solution at low temperatures, dinitrogen tetroxide reacts with tertiary amines to form yellow precipitates of the general formula $N_2O_4 \cdot 2B$, where B is pyridine, quinoline, isoquinoline, acridine, β-picoline, α-picoline or triethylamine. Addition compounds in which the mole per cent. of dinitrogen tetroxide is greater than that required by the formula $N_2O_4 \cdot 2B$ are also found with certain of these amines. All are unstable at room temperature. 2,6-Lutidine and 2-methylquinoline do not give addition compounds with dinitrogen tetroxide under the experimental conditions studied. The significance of these results is briefly discussed.

A recent communication[2] from this Laboratory reported the discovery of a new series of molecular addition compounds of dinitrogen tetroxide with a number of ethers. The results discussed in that communication indicated further that the compounds are true adducts of N_2O_4 molecules and do not contain NO_2 radicals or NO_2^+, NO_2^-, NO^+, NO_3^- ions. It was, therefore, of interest to us to see if similar compounds are formed with other Lewis bases, such as the tertiary amines, and, if so, to examine their properties.

Preliminary experiments showed that it would be necessary to carry out the reactions of dinitrogen tetroxide with tertiary amines in a solvent and at low temperatures in order to avoid oxidation–reduction or nitration reactions. Diethyl ether was used as a solvent and the reactions were run at about −75°. The addition compounds formed as insoluble, usually yellow, precipitates. The amines studied include pyridine, quinoline, isoquinoline, acridine, α-picoline, β-picoline, γ-picoline, 2,6-lutidine, 2-methylquinoline and triethylamine.

Reaction with Pyridine.—Pyridine combines with dinitrogen tetroxide, in ethereal solution at low temperatures, to yield a yellow precipitate. The results of a series of these reactions using various mole ratios of reactants are summarized in Table I, section a. Since, as discussed in the experimental section, the total weight of product could not be determined with a high degree of accuracy, the percentage figures listed in the last column of this table do not have a high degree of precision. This accounts for the total per cent. rising in a few cases

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(1) Presented at the March, 1953, Meeting of the Am. Chem. Soc. in Los Angeles.

(2) The first paper in this series: B. Rubin, H. Shechter and H. H. Sisler, THIS JOURNAL, **74**, 877 (1952).