

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Anion-exchange Studies. XI. Lead(II) and Bismuth(III) in Chloride and Nitrate Solutions^{1,2}

BY FREDERICK NELSON AND KURT A. KRAUS

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The adsorbability of Pb(II) and Bi(III) from hydrochloric acid (0.25 to 12 *M* HCl), nitric acid (0.5 to 10 *M* HNO₃) and ammonium nitrate (1 to 10 *M*) solutions was studied with a strong base quaternary amine anion-exchange resin. Lead was weakly adsorbed at low HCl concentrations (distribution coefficient $D = 1$ in 0.05 *M* HCl), reached maximum adsorption ($D = ca. 25$) near 1 to 2 *M* HCl, and then showed decreasing adsorption at higher HCl concentrations. Bi(III) adsorbed strongly throughout the HCl concentration range studied; D decreased with increasing HCl concentration from 2×10^8 (0.25 *M* HCl) to 60 (12 *M* HCl). Both lead and bismuth showed some adsorption in HNO₃ solutions, although this adsorption was considerably smaller than in HCl solutions. In NH₄NO₃ solutions adsorption of lead remained low but for bismuth it increased to $D = ca. 200$ in 10 *M* NH₄NO₃. Typical separations involving Pb(II) and Bi(III) in these media are illustrated.

Previous studies of the anion-exchange behavior of metallic elements have shown that many elements have widely differing adsorbabilities which may form the basis of a large number of separations. In continuation of a systematic study of the metallic elements the present paper deals with the anion-exchange behavior of Pb(II) and Bi(III) in hydrochloric acid, nitric acid and ammonium nitrate solutions.

Experimental

Adsorbabilities were generally determined by the equilibrium method.³ To attain equilibrium, samples of resin and solution were agitated for one to two days. From the resulting decrease in metal concentration of the solution, the distribution coefficients D (amount per kg. dry resin/amount per liter solution) were calculated. Metal concentrations were determined radiometrically or polarographically. Concentrations were usually sufficiently low to yield loadings of the resin of less than 1% of capacity. When the adsorbability of the metal was low, distribution coefficients were evaluated by the column method.^{3,4}

The same batch of quaternary amine polystyrene divinylbenzene resin (Dowex-1) (200-230 mesh) used in the earlier studies was used throughout and resin weights refer to the weight of resin dried over Anhydron at 60°. All experiments were carried out in a thermostated room at 25 ± 2°. Further details of the experimental procedure will be given in connection with the discussion of the various systems.

Results and Discussion

1. Lead in Hydrochloric Acid Solutions.—The adsorption of Pb(II) was studied by the equilibrium method in the concentration range 0.05 to 12 *M* HCl with *ca.* 10⁻³ *M* Pb(II) solutions. The solutions were analyzed polarographically before and after equilibration and distribution coefficients D were computed. Adsorbability of Pb(II) (see Fig. 1) was low in dilute HCl ($D = 1$ in 0.05 *M* HCl) and increased at first with increasing HCl concentration. Adsorption reached maximum $D = 25$ near 1.5 *M* HCl and then decreased rapidly. Negligible adsorption ($D < 1$) occurred above 8 *M* HCl.

2. Bismuth in Hydrochloric Acid Solutions.—The adsorption of Bi(III) was studied by the equilibrium method in the concentration range 0.25 to 12 *M* HCl. Bismuth concentrations were determined radiometrically using Bi²⁰⁷ ($T_{1/2} = 50$ yr.)

tracer.⁵ This tracer was prepared by proton bombardment of lead in the ORNL cyclotron.⁶ The lead target was dissolved in nitric acid and hydrochloric acid added to precipitate the bulk of the lead. Bismuth was then adsorbed on an anion-exchange column in the chloride form from this medium which contained in addition to residual nitrate *ca.* 8 *M* HCl. Under these conditions lead is not adsorbed. To purify the bismuth the column was washed with 8 and 0.1 *M* HCl. Bismuth was then removed with nitric acid (see also Section 4). The tracer was converted to the chloride form by repeated fuming with hydrochloric acid.

The results of the distribution experiments are summarized in Fig. 1. Bismuth under all conditions studied was strongly adsorbed. Adsorption decreased with increasing hydrochloric acid concentration from $D = 2 \times 10^8$ in 0.25 *M* HCl to $D = 57$ in 12 *M* HCl.

3. Lead in Nitric Acid Solutions.—The adsorption of Pb(II) was studied in the concentration range 0.5 to 8.0 *M* HNO₃. Since the adsorbability of this element was very low throughout the whole concentration range studied, the column method was used rather than the equilibrium method. Approximately 0.1-ml. portions of nitric acid solutions containing Pb²¹⁰ (RaD)⁷ tracer were passed into 0.25 cm.² × 4 cm. columns of the resin in the nitrate form, which had been pretreated with nitric acid solutions of the same concentrations as were used in the tracer solutions. Elution was carried out in the same medium. The lead tracer had previously been purified, particularly from bismuth (Bi²¹⁰, RaE), by anion exchange. From the volume V , at which the tracer Pb appeared in maximum concentration in the effluent, the elution constant $E = dA/V$ was evaluated^{3,4} where d is the length of the resin bed and A its cross-sectional area. Distribution coefficients D were calculated with the equation $E = 1/(i + D\rho)$, where i is the apparent fractional interstitial space (assumed $i = 0.42^3$) and ρ the bed density (0.45 kg. dry resin/liter bed).⁴ The results are summarized in Fig. 2. The adsorption curve goes through a maximum near 2 *M* HNO₃ with $D = 4$. Since

(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper: K. A. Kraus and F. Nelson, *THIS JOURNAL*, **76**, 984 (1954).

(3) K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

(4) K. A. Kraus and G. E. Moore, *THIS JOURNAL*, **73**, 9 (1951).

(5) J. M. Hollander, I. Perlman and G. T. Seaborg, *Table of Isotopes*, *Rev. Mod. Phys.*, **25**, 469 (1953).

(6) We are indebted to Mr. J. A. Martin of the ORNL Cyclotron Group for the preparation of the tracer.

(7) We are indebted to Drs. P. S. Rudolph and B. H. Ketelle of the ORNL Chemistry Division for the RaD-RaE tracer.

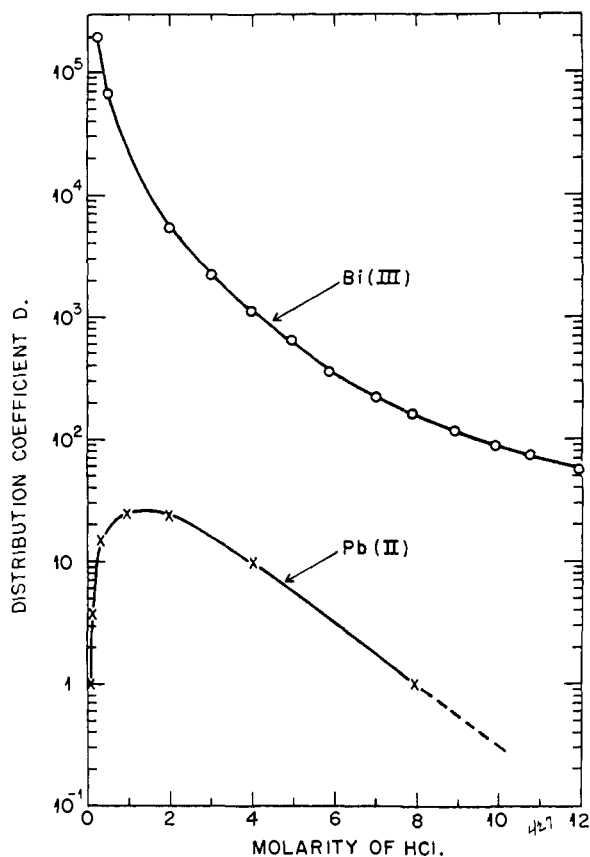


Fig. 1.—Adsorption of Pb(II) and Bi(III) from HCl solution.

at high nitric acid concentration some decomposition of the resin occurs (the resin becomes slowly discolored), the significance of this adsorption maximum is somewhat in doubt, and the distribution coefficients at high nitric acid concentration should only be considered approximate. Discoloration of the resin, which is very pronounced in 10 *M* HNO₃ after 20 hours is only slight in 6 *M* HNO₃ and essentially negligible in 4 *M* HNO₃.

4. Bismuth in Nitric Acid Solutions.—The adsorbability of Bi(III) was studied by the equilibrium method in the concentration range 0.5 to 10 *M* HNO₃, and bismuth concentrations determined radiometrically (Bi²⁰⁷). As shown in Fig. 2, adsorption of Bi(III) is small in 0.5 *M* HNO₃ ($D = 1.6$), it increases to a maximum near 4 *M* HNO₃ ($D = 26$) and then decreases to $D = 11$ in 10 *M* HNO₃. As in the case of lead, the distribution coefficients at high nitric acid concentrations should only be considered approximate because of possible attack of the resin by nitric acid.

5. Lead in Ammonium Nitrate Solutions.—The adsorbability of Pb(II) was studied in the concentration range 1 to 9 *M* NH₄NO₃ by both the column and equilibrium methods. In the evaluation of E, V was determined by comparing visually the amount of lead chromate precipitated in successive samples of the effluent. In the evaluation of D concentrations were determined polarographically. Adsorption of lead (see Fig. 2) was found

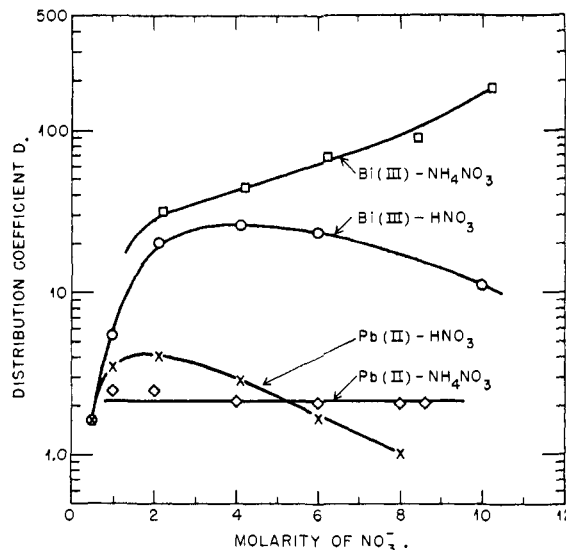


Fig. 2.—Adsorption of Pb(II) and Bi(III) from nitrate solutions.

to be small throughout the concentration range studied ($D = ca. 2$) and essentially independent of ammonium nitrate concentration.

6. Bismuth in Ammonium Nitrate Solutions.—The adsorbability of Bi(III) was studied in the concentration range 2 to 10 *M* NH₄NO₃ by the equilibrium method using radiometric analysis (Bi²⁰⁷). All solutions contained at least 0.25 *M* HNO₃ to avoid hydrolysis of Bi(III). Adsorption was found to increase continuously with increasing ammonium nitrate concentration (see Fig. 2) and reached $D = ca. 180$ in 10 *M* NH₄NO₃. The adsorption maximum which was found for Bi(III) in HNO₃ solutions did not occur in the NH₄NO₃ solutions. For good adsorption or processing of large volumes of bismuth solutions without breakthrough, relatively low acidity and high nitrate concentrations are thus preferable over high nitric acid concentrations.

7. Separation of Lead and Bismuth in Chloride Solutions.—The large differences in the adsorbability of Pb(II) and Bi(III) in HCl solutions permit excellent separation of these elements under a variety of conditions. As discussed in Section 2, advantage was taken of these adsorption differences in the isolation of Bi²⁰⁷ from the lead target after cyclotron bombardment.

A rather unique application of the anion-exchange technique for separating lead and bismuth was recently reported.⁸ The very short-lived lead daughter Pb^{207m} ($T_{1/2} = 0.8$ sec.) was separated from the long-lived bismuth parent Bi²⁰⁷ by adsorbing Bi²⁰⁷ on a small resin column from 0.5 *M* HCl. Under these conditions Bi(III) is strongly adsorbed while Pb(II) shows only little adsorption. Hence Pb(II) will diffuse to a considerable extent out of the resin particles in which it is formed into the surrounding interstitial solution while Bi(III) will only show negligible diffusion out of the resin. Separation of Pb(II) from Bi(III) is then achieved by rapidly removing the interstitial solution from the small resin bed. By removing the interstitial

(8) E. C. Campbell and F. Nelson, *Phys. Rev.*, **91**, 499A (1953).

solution under pressure (*e.g.*, as produced by applying a syringe) satisfactory separation was achieved in times short with respect to the half-life of the tracer (0.8 sec.).

Since Bi(III) is strongly adsorbed throughout the whole HCl concentration range studied, it can readily be separated from a large number of elements, including those elements which, like Fe(III),⁹ show good adsorption at high HCl concentrations and moderate or negligible adsorption at low HCl concentrations. The adsorption of Pb(II) which is relatively small even at its maximum is sufficient to permit its separation from most elements in the periodic table. Two illustrations of the various separations which are implied by the adsorption data are given in Figs. 3A and 3B. In the experiment, Fig. 3A, 0.02 ml. of a solution containing 0.05 M Fe(III), tracer Pb(II) (RaD (Pb²¹¹)) and tracer Bi(III) (RaE (Bi²¹⁰)) in 8 M HCl were passed into a small (0.3 cm.² × 4.7 cm.) resin column in the chloride form, pretreated with 8 M HCl and elution was begun with 8 M HCl. The effluent was analyzed for Pb and Bi radiometrically and for Fe(III) colorimetrically using the thiocyanate method.¹⁰ Pb(II) appeared practically immediately in the effluent separated from Bi(III) and Fe(III) which remained on the column. Fe(III) was removed with 0.5 M HCl leaving Bi(III) adsorbed on the column.

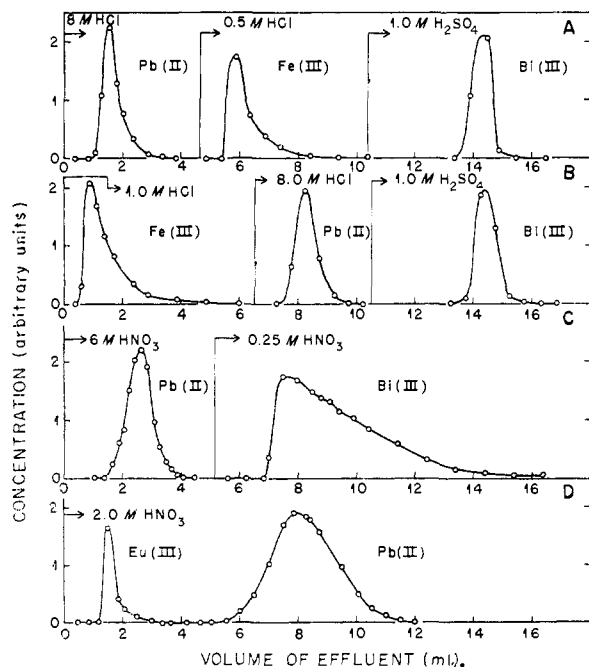


Fig. 3.—Separations involving Pb(II) and Bi(III) in HCl and HNO₃ solutions (0.30 sq. cm. columns, length A, 4.7 cm.; B, 4.7 cm.; C, 6.8 cm.; D, 12.2 cm., 200–230 mesh Dowex-1, flow rate *ca.* 0.5 cm./min.).

The removal of bismuth from the column with hydrochloric acid solutions appeared impractical with the relatively highly cross-linked resin used here because of the strong adsorbability of this

element from this medium. Removal in a satisfactorily narrow band was achieved by treatment of the columns with 1 M H₂SO₄. As shown in Fig. 3, appearance of the bismuth is somewhat delayed, probably because the column must first be converted essentially to the bisulfate form. In other experiments not illustrated in Fig. 3, removal of bismuth from chloride columns was attempted by elution with nitric acid. However, this procedure appears less satisfactory since at high nitric acid concentrations where conversion of the column to the nitrate form is reasonably rapid, bismuth shows some adsorption and because at low nitric acid concentrations some tailing of the bismuth band occurs (see also Section 8).

In the experiment illustrated by Fig. 3B, adsorption and elution conditions were chosen to reverse the order of elution of Pb(II) and Fe(III) to demonstrate further the flexibility of this separations technique. An aliquot (0.02 ml.) of a solution containing 0.05 M Fe(III), tracer Pb²¹⁰ and tracer Bi²¹⁰, in 1 M HCl was passed into a small (0.3 cm.² × 4.7 cm.) column of resin in the chloride form, pretreated with 1 M HCl. Elution was begun with 1 M HCl, which rapidly removed Fe(III) but retained Pb(II) and Bi(III) on the column. Pb(II) was then removed with 8 M HCl and Bi(III) again with 1.0 M H₂SO₄.

It might be mentioned that removal of Bi(III) with sulfuric acid presupposes very low chloride concentration of the solution, since presence of relatively small amounts of chloride in sulfuric acid causes reasonably good adsorption of Bi(III). Thus it was established with equilibrium experiments that values of $D = ca. 60$ were obtained when a Bi(III) solution containing 1 M H₂SO₄ and 0.05 M HCl was shaken with a sulfate form resin. In 1 M H₂SO₄ solutions containing less than 0.01 M HCl adsorption of Bi(III) was low ($D < 2$). Conversely one can conclude from these experiments that adsorption of Bi(III) from sulfate media can be achieved if a small amount of chloride is added to the solutions.

8. Separation of Lead and Bismuth in Nitrate Solutions.—The differences in adsorbability of Pb(II) and Bi(III) in nitrate solutions permit ready separation of these two elements. A typical example is illustrated in Fig. 3C. In this experiment 0.05 ml. of a solution of Pb²¹⁰–Bi²¹⁰ tracer in 6 M HNO₃ was passed into a 0.30 cm.² × 6.8 cm. column pretreated with 6 M HNO₃. On elution with 6 M HNO₃, Pb(II) rapidly appeared in the effluent and Bi(III) was retained by the column. Although continued elution with 6 M HNO₃ could have removed Bi(III) slowly, elution was actually carried out with 0.25 M HNO₃, since under these conditions the bismuth band moves considerably more rapidly. However, it may be noticed from Fig. 3C that the bismuth band shows considerable tailing in this medium.

A similar separation of Pb(II) and Bi(III) was carried out from nitrate solutions in a low acid medium where, as mentioned in Section 6, excellent adsorption of Bi(III) can be achieved at high nitrate concentrations. An 0.25-ml. aliquot of a solution containing Pb²¹⁰–Bi²¹⁰ tracers and 5×10^{-3} M

(9) G. E. Moore and K. A. Kraus, *THIS JOURNAL*, **72**, 5792 (1950).

(10) "Scott's Standard Methods of Analysis," Vol. 1, p. 486, D. Van Nostrand Co., Inc., New York, N. Y., 5th Edition, 1939.

Pb(II) in an 0.7 *M* HNO₃-8 *M* NH₄NO₃ solution was passed into a 0.25 cm.² × 4.3 cm. column pretreated with the same nitrate mixture. Elution with the same nitrate solution rapidly removed the Pb(II) from the column while Bi(III) was retained. Bi(III) was then removed with some tailing with 0.5 *M* HNO₃. More satisfactory removal could probably have been achieved with sulfuric acid as discussed in Section 7, although at the expense of changing the composition of the resin.

Adsorption of Pb(II), though small in 2 *M* HNO₃, is sufficient to permit its separation from non-adsorbable elements. Such a separation is demonstrated in Fig. 3D, with lead and europium, using Pb²¹⁰ and Eu¹⁵⁵ tracers to permit radiometric analysis of the effluent. Europium was chosen for the separation since it is a non-adsorbable element for which a tracer was conveniently available. An aliquot (0.1 ml.) of a mixture of the tracers in 2 *M* HNO₃ was passed into a 0.28 cm.² × 12.2 cm. column of the nitrate form of the resin pretreated with 2 *M* HNO₃ and elution was carried out with 2 *M* HNO₃. As shown in Fig. 3D the non-adsorbable element appeared immediately in the effluent and was essentially completely separated from the lead.

9. Some Considerations Regarding Species in Solution.—As mentioned earlier^{2,3} it appears reasonable to correlate the shape of the adsorption curves as a function of HCl concentration with the existence and possible dominance of negatively charged species in the aqueous phase. Thus it appears that in those regions of HCl concentrations where *D* increases with *m*_{HCl}, positively charged species are dominant, while when *D* decreases with increasing *m*_{HCl} the fraction of the metal in the form of negatively charged complexes in the aqueous phase is close to unity. Adsorption maxima would then be expected approximately at those hydrochloric acid concentrations where the negatively charged species become dominant. On the basis of such semi-quantitative considerations one would conclude that Pb(II) becomes predominantly negatively charged near 2 *M* HCl and that Bi(III) is predominantly negatively charged even in 0.25 *M* HCl.

The existence of negatively charged complexes of lead (*e.g.*, PbCl₃⁻ or PbCl₄⁼) has repeatedly been suggested^{11,12} but the stability constants of such complexes have not been evaluated. The solubility of lead chloride in NaCl or LiCl solutions was found¹³ to reach a minimum near 1 *M* Cl⁻ and to increase with increasing chloride concentration (*m*_{Cl⁻}) up to the practically saturated solutions. Since the solid phase remained PbCl₂, these solubility data suggest, as do the anion-exchange results, that negatively charged complexes become dominant for *m*_{Cl⁻} somewhat greater than 1 *M*. In view of the difficulties connected with estimation of activity coefficients at very high ionic strength these data cannot readily be used to identify the complexes formed.

Negatively charged chloride complexes of Bi(III)

(11) See *e.g.* H. Fromherz and K. H. Lih, *Z. physik. Chem.*, **153A**, 321 (1931).

(12) A. B. Garrett, M. V. Noble and S. Miller, *J. Chem. Ed.*, **19**, 485 (1942).

(13) G. E. R. Deacon, *J. Chem. Soc.*, 2063 (1927).

have been suggested by Noyes, Hall and Beattie.¹⁴ These authors concluded from conductivity and solubility measurements that BiCl₅⁼ is the principal species at low bismuth concentrations in the presence of considerable excess of HCl, and that BiCl₄⁻ is probably formed at high bismuth concentrations where the amount of HCl in their solutions was insufficient to permit formation of BiCl₅⁼. On the other hand, McAlpine¹⁵ favors the complex BiCl₄⁻ over BiCl₅⁼, although he does not give additional data to support this view. It is interesting to note that Noyes and co-workers suggested that a negatively charged complex is already formed in 0.3 *M* HCl, which is in general agreement with the anion exchange results.

Comparison of the anion-exchange behavior of Pb(II) and Bi(III) in HCl solutions with that of other elements in the same medium suggests that both elements form complex ions of charge more negative than minus one, particularly at high *m*_{HCl}. This conclusion is mainly based on the observation that those elements (Au(III),² Ga(III)³ and Fe(III)⁹) which almost certainly form complexes of charge minus one (MCl₄⁻), adsorb very much better at high *m*_{HCl} than either Bi(III) or Pb(II). Since, furthermore, the adsorbabilities of Pb(II) and Bi(III) differ greatly from each other, it is unlikely that they carry the same negative charge at high *m*_{HCl}. At the present time one might favor the assignment BiCl₅⁼ (*i.e.*, an ion of charge minus two) for Bi(III) and PbCl₅⁼, or an ion of greater negative charge for Pb(II). These particular assignments are based on the observation that the adsorption of Bi(III) is rather similar to that of Hg(II)¹⁶ and a number of other ions for which a complex of charge minus two appears probable at high *m*_{HCl}. Good evidence for the existence of a negatively charged Hg(II) complex of charge minus two (HgCl₄⁼) has recently been reported by Sillén and co-workers.¹⁷ The assignment of a highly negatively charged complex for lead has to be considered tenuous. It is essentially based on the fact that adsorption of lead is very low even at its maximum, which is reminiscent of similarly low or even lower adsorption found for In(III) and Ir(III)³ for which the complex MCl₆⁼ appears probable. However, it is realized that this assignment is at variance with the usual assignment of a maximum coordination number of 4 for lead with respect to chloride ions.¹⁸

Nitrate complexing of Pb(II) has been demonstrated.¹⁹ Although negatively charged nitrate complexes have also been suggested,¹⁹ it is questionable if such complexes are formed to any appreciable extent, since Pb(NO₃)₂ does not show the expected increase in solubility with increasing nitrate concentration.²⁰ Rather the observed decrease in

(14) A. A. Noyes, F. W. Hall and J. A. Beattie, *THIS JOURNAL*, **39**, 2526 (1917).

(15) R. K. McAlpine, *J. Chem. Ed.*, **24**, 395 (1947).

(16) F. Nelson and K. A. Kraus, unpublished results.

(17) See *e.g.*, L. G. Sillén, *Acta Chem. Scand.*, **3**, 539 (1949).

(18) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(19) See *e.g.*, H. M. Hershenson, M. E. Smith and D. N. Hume, *THIS JOURNAL*, **75**, 507 (1953).

(20) See *e.g.* (a) A. C. Cummings, *Trans. Faraday Soc.*, **2**, 199 (1906); (b) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940.

solubilities combined with the fact that the solid phase is almost certainly $\text{Pb}(\text{NO}_3)_2$ ²¹ suggests that even an undissociated soluble lead nitrate complex is improbable and that only the positively charged complex $\text{Pb}(\text{NO}_3)^+$ is formed. The extremely low adsorption of lead in both nitric acid and ammonium nitrate solutions thus almost surely is not due to the existence of appreciable concentrations of negatively charged complexes in the aqueous phase.

There appears to be little evidence for the formation of either neutral or negatively charged bismuth nitrate complexes. The solubility data on bismuth oxynitrate appear inconclusive since on the basis of these data formation of nitrate complexes has been postulated by Smith²² and challenged by Swinehart and Garrett.²³ However, the anion-exchange results appear to be conclusive that negatively charged nitrate complexes of Bi(III) are formed to some extent ($\text{Bi}(\text{NO}_3)_4^-$?). However, the fraction of bismuth in the form of a negatively charged complex cannot be determined since an adsorption maximum does not exist in the ammonium nitrate solutions and since the meaning of

(21) H. G. Denham and J. O. Kidson, *J. Chem. Soc.*, 1757 (1931).

(22) D. F. Smith, *THIS JOURNAL*, **45**, 360 (1923).

(23) D. F. Swinehart and A. B. Garrett, *ibid.*, **73**, 507 (1951).

the maximum in nitric acid solutions is in doubt.

In an earlier paper,³ a striking parallel between solvent extraction by ethers and anion-exchange adsorbability was discussed and it was pointed out that solvent extraction from chloride solutions might occur most readily if the extracted species has the formula MCl_4^- . The postulated complexes for HCl solutions of Pb(II) and Bi(III) (with charge more negative than minus one) are in agreement with these earlier conclusions since negligible solvent extraction is found for these elements.²⁴ Moderate extraction of Bi(III) from nitric acid solutions has been found,²⁵ which would indicate that these considerations relating anion-exchange and solvent extraction are also applicable for nitrate solutions. However, in this extension caution appears indicated since slight extraction from nitric acid solutions has also been reported for Pb(II)²⁵ where solvent extraction apparently could not proceed by the same mechanism.

Acknowledgment.—The authors are greatly indebted to Mrs. L. W. Magnusson, Jr., for valuable technical assistance.

(24) H. M. Irving, *Quart. Rev.*, **5**, 200 (1951).

(25) R. Bock and E. Bock, *Z. anorg. Chem.*, **263**, 146 (1950).

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. VI. Formation of Nitrito- and Nitrocobalt(III) Complexes. O-Nitrosation^{1, 2, 3}

BY RALPH G. PEARSON, PATRICK M. HENRY, JOHN G. BERGMANN AND FRED BASOLO

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The mechanism of formation of nitro derivatives in the case of aquopentamminecobalt(III) and *cis*-nitroaquobis-(ethylenediamine)-cobalt(III) ions in weakly acid solutions of nitrite ion is shown to involve first a nitrosation to the nitrito complex which then rearranges to the nitro complex in an intramolecular process. The nitrosation is generally rapid but may become rate determining at low nitrous acid concentrations. Nitrosation follows the rate law, rate = $k[\text{hydroxo complex}][\text{nitrous acid}]^2$ similar to that found for amines. It is suggested that N_2O_3 is the active agent which forms the nitrito complex without breaking the cobalt-oxygen bond.

In an earlier paper⁴ we reported the rates of formation of dinitro complexes from *cis*- and *trans*-nitroaquobis-(ethylenediamine)-cobalt(III) ions at 35° in aqueous solution with a ratio of nitrite ion to nitrous acid of 100 to 1 and with varying nitrite ion concentration. It was initially assumed that formation of the unknown nitrito (Co-ONO) complexes either did not occur or that they rearranged very rapidly to the nitro form (Co-NO₂). An interesting result was that the rate of the reaction increased with nitrite ion concentration for low concentrations but became independent of nitrite ion at high concentrations. This result was at one time thought to indicate an S_N1 mechanism in which the limiting rate was equal to the rate of dissociation of water from the aquo complex.⁵

(1) Previous paper in this series, R. G. Pearson, C. Boston and F. Basolo, *J. Phys. Chem.*, in press.

(2) Investigation supported by U. S. Atomic Energy Commission under Contract AT (11-1)-89, Project No. 2.

(3) Presented in part at the 125th Meeting of the American Chemical Society at Kansas City, Mo., March, 1954.

(4) F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, *THIS JOURNAL*, **76**, 3079 (1954).

(5) F. Basolo, *Chem. Revs.*, **51**, 459 (1953).

A similar study was then undertaken with the aquopentamminecobalt(III) ion and nitrite ion. Very similar results were obtained except that the rate of formation of the nitro complex never quite leveled off at high nitrite ion concentrations (Fig. 1). The region of nearly constant rate, however, corresponded to a reaction some 5–10 times faster than the rate of isotopically labelled water exchange at the same temperature, pH and ionic strength.⁶

Furthermore the nitritopentammine ($[(\text{NH}_3)_5\text{Co-ONO}]^{+2}$) complex is known^{7a} and its rate of rearrangement to the nitro form^{7b} was approximately the same (within a factor of 2) as the rate of formation of nitro complex from the aquo complex as determined by us. Accordingly a study was made of the rate of formation of the nitrito complexes from the aquo complexes in the case of *cis*-[Coen₂NO₂-H₂O]⁺² and [Co(NH₃)₅H₂O]⁺³. This involved preparing *cis*-[Coen₂NO₂ONO]NO₃, the first time

(6) H. Taube and R. K. Murmann, personal communication.

(7) (a) S. M. Jorgensen, *Z. anorg. Chem.*, **5**, 169, 172 (1894); *ibid.*, **19**, 149 (1899); (b) B. Adell, *ibid.*, **252**, 232 (1944); *Svensk. Kem. Tids.*, **56**, 318 (1944); *ibid.*, **57**, 260 (1945); *Acta Chem. Scand.*, **5**, 941 (1951).