NOTES

The Carrier-free Separation of the Radioactive Isotopes Co^{56}, Co^{57} and Co^{58} from a Manganese Target

By J. L. Dick[1] and M. H. Kurbatov

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Various organic reagents, by nature of their selectivity, are becoming more and more important in the field of nuclear chemistry. One of the more common complexing reagents, α-nitroso-β-naphthol, is best known for its application in the separation of cobalt from large quantities of nickel. The ability of the reagent to complex cobalt in the presence of manganese is the basis for applying it to the problem of preparing a carrier-free sample of radioactive cobalt from a manganese target. In as much as the sample was to be used for study[2] in the beta spectrometer, it was most important that it be prepared by a carrier-free method of separation. The presence of stable isotopes results in low specific activity and self absorption which hamper spectrometric studies.

Experimental

Reagents.—Manganese, Ajax 99.9%, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio. α-Nitroso-β-naphthol (practical) Eastman Kodak Co., Rochester, N. Y. Benzene (thiophene free) Analytical Reagent, Mallinckrodt Chemical Works, N. Y.

A sample of manganese was bombarded in the cyclotron at the University of California for 3.5 hours with 35 Mev. α-particles. Following a waiting period of several days in which the short lived activities disintegrated, the sample was dissolved in 25 ml. of 6 *N* hydrochloric acid and evaporated to dryness. The residue was then dissolved in 250 ml. of 3 *N* hydrochloric acid and stored in a 250-ml. volumetric flask. This solution became the parent material from which all experimental samples were taken.

The first phase of the study was to determine the length of time the complexing reagent should remain in the sample solution. Two ml. of the target solution was diluted to 12 ml. and the acidity adjusted to 0.5 *N*. To this was added 4 ml. of the complexing reagent (0.25 g. of α-nitroso-β-naphthol dissolved in 100 ml. of 50% acetic acid solution). After an interval of one-quarter hour the solution was extracted with three 25-ml. portions of benzene. The non-aqueous phase containing the complexed cobalt and excess organic reagent was evaporated to dryness in a platinum crucible and the resulting residue ignited in air. This residue was then transferred to a counting dish and the percentage of activity removed from the aqueous target solution was determined using a Potter Scaler and a mica end-window Geiger–Mueller Tube. Successive measurements were made on individual samples following intervals of $^1/_4$, $^1/_2$, 1, 2 and 4 hours. It was found that about 98% of the cobalt was extracted by benzene if the complexing reagent remained in solution one hour or more. Only 37% was extracted in a quarter hour and 69% in a half-hour.

Data were collected from a series of experiments in which the acidity was varied from *p*H 8.7 to 6 *N*. In each test, two ml. of target solution was diluted to 12 ml. with hydrochloric acid or ammonia solution of appropriate strength. The solution was heated to 80° and 4 ml. of the complexing reagent in acetic acid solution was added. After standing one hour the solution was transferred to a separatory funnel and extracted with three 25-ml. portions of benzene. The benzene solution was transferred to a platinum crucible, evaporated to dryness and the crucible ignited in air. There was no visible residue. Following this the material was treated with hot concentrated hydrochloric acid and the acid solution transferred to a counting dish. The percentage extraction was computed from the counting rate of the sample. The optimum acidity for extraction was in the range from *p*H 4 to 0.25 *N* in which range 100% of the cobalt was extracted. As shown in curve A of Fig. 1, 98% or more was extracted in the range from 0.5 *N* acid to *p*H 8.7.

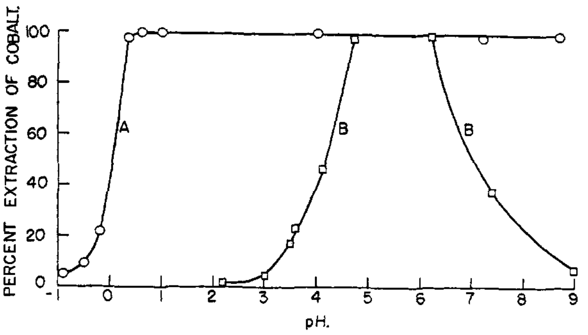

Fig. 1.—Complexing reagent used: A, 4 ml. of 50% acetic acid solution of α-nitroso-β-naphthol containing 250 mg./ml.; B, 0.5 ml. of aqueous solution of α-nitroso-β-naphthol containing 30 mg./100 ml.

A study was made of the effect of *p*H on the percentage of cobalt extracted when a saturated aqueous solution of α-nitroso-β-naphthol was used as complexing agent. The aqueous solution of the complexing reagent contained approximately 30 mg. of α-nitroso-β-naphthol per 100 ml. of water and 0.5 ml. of this solution was used in each sample. The maximum amount of activity was extracted when the acidity of the target solution was maintained between *p*H 4.7 and 6.2. The results of this experiment are shown in curve B of Fig. 1. It is evident that the *p*H of the solution must be maintained in a narrower range when using the lower concentration of complexing agent in aqueous solution than when using the acetic acid solution of complexing agent.

The purpose of using an extraction method rather than filtration for the removal of the cobalt complex of α-nitroso-β-naphthol from the aqueous solution was twofold. The amount of precipitate formed in the reaction of quantities of cobalt of the order of 10^{-9} *M* with α-nitroso-β-naphthol was so small that much of the activity could readily pass through the paper if filtered. Secondly, the ashing of the filter paper, although it is considered ashless by macro standards, contributed a sizeable residue in terms of the cobalt present.

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(1) Cambridge Research Center, Cambridge, Mass.

(2) L. Cheng, J. Dick and J. Kurbatov, *Phys. Rev.*, **88**, 887 (1952).

The Surface Area of Nickel Oxalate Precipitates

By J. A. Allen and C. J. Haigh

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In a recent paper[1] the rates of formation of precipitates of nickel oxalate dihydrate in solutions of nickel sulfate and oxalic acid were related to the concentrations of the reactants. A mechanism for the reaction based, in part, on the formation and

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(1) J. A. Allen, *J. Phys. Chem.*, **57**, 715 (1953).

rearrangement of a complex ion was proposed. This work suggested that the particle size and hence the surface area of precipitates prepared under different conditions should show significant variations. In this note the results of an investigation carried out with this object are reported.

Experimental

Two series of precipitates of $NiC_2O_4 \cdot 2H_2O$ were prepared at 20 and 40°, respectively, from solutions 0.1, 0.2 and 0.3 *N* with respect to nickel sulfate and 0.05–0.6 *N* with respect to oxalic acid. Precipitates which formed rapidly (oxalic acid in excess) were filtered off after 2–3 hours, while for more dilute solutions, especially those in which nickel sulfate was in excess, several days were required to complete the precipitation.

Surface areas were measured by two methods, (i) an air permeability method using an apparatus similar to that of Rigden,[2] and (ii) a standard optical method in which the amount of light cut off by a suspension of the solid material is measured by a photoelectric absorptiometer. The details of these methods and a comparison of them have been reported elsewhere.[3]

Results and Discussion

The results obtained by both methods for the series at 20 and 40° are shown in Figs. 1 and 2, respectively, in which the surface area is plotted against the concentration of oxalic acid for the three concentrations of nickel sulfate used. It is clear that the two methods yield concordant results. The differing ordinate scales for the two methods arise from the different sets of assumptions on which the methods are based and need not concern us here.

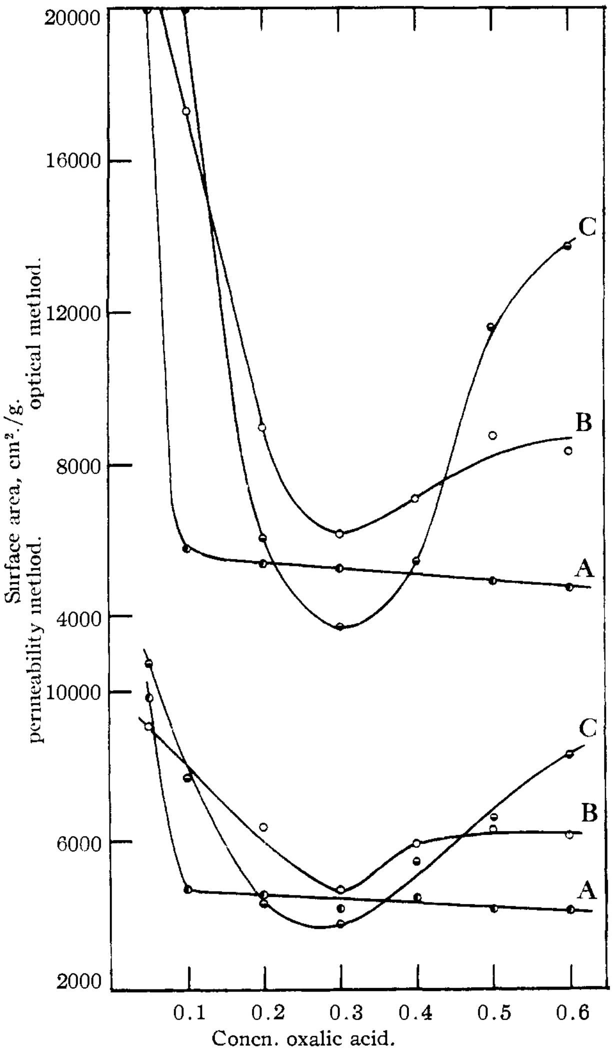

Fig. 1.—A, 0.1; B, 0.2; C, 0.4 *N* $NiSO_4$; temp. 20°.

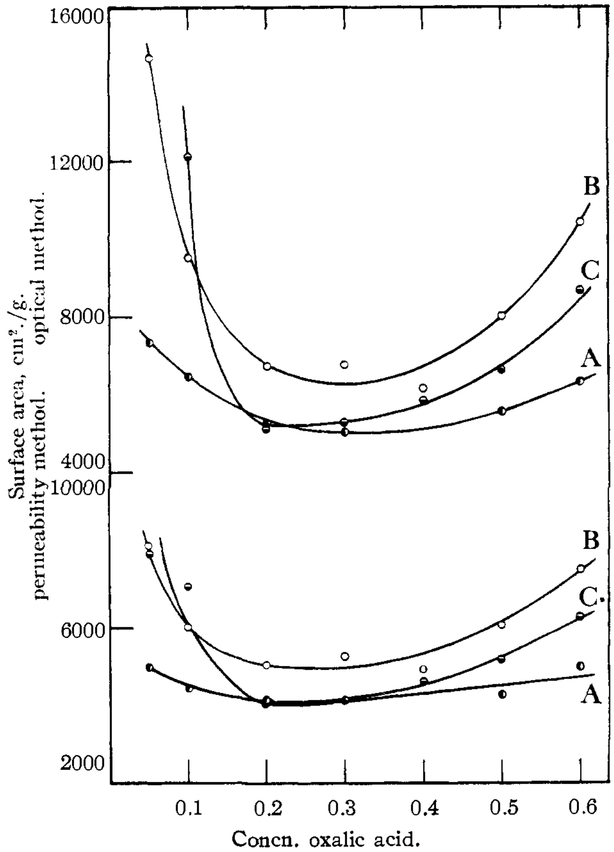

Fig. 2.—A, 0.1; B, 0.2; C, 0.4 *N* $NiSO_4$; temp. 40°.

Detailed examination of the curves at 20 and 40° show that they all have the same general character and are considered to result from a combination of two curves, such as AB and DE sketched in Fig. 3. The curve AB is to be associated with

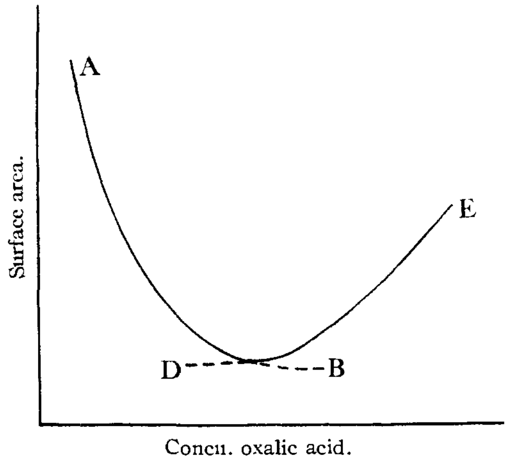

Fig. 3.

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(2) P. J. Rigden, *J. Soc. Chem. Ind.*, **62**, 1 (1943).

(3) J. A. Allen and C. J. Haigh, *J. Chem. Ed.*, in press.

nucleation and growth in which a complex ion, probably $Ni(C_2O_4)_2^{=}$, is the rate-determining species. DE is the curve for the equivalent processes determined by the simple ionic species in solution which become predominant under conditions in which the complex ion is unstable.

We represent, in general, the rates of nucleation and growth, respectively, by the equations

$$v_1 = \alpha_1 f_1(C)e^{-E_1/RT}$$
$$v_2 = \alpha_2 f_2(C)e^{-E_2/RT}$$

where α_1 and α_2 are steric factors, $f_1(C)$ and $f_2(C)$ are functions of the concentrations of the species in solution which determine the rates of nucleation and growth, respectively, and E_1 and E_2 are the activation energies. We make two reasonable assumptions

$$\left(\frac{\partial f_1(C)}{\partial C}\right)_T > \left(\frac{\partial f_2(C)}{\partial C}\right)_T \qquad (1)$$

and

$$E_1 > E_2 \qquad (2)$$

It is possible also that E_2 varies with the surface area of the particles, but the variation is probably small. We shall neglect this factor and also the steric factors.

For the curve AB the concentration of the complex C_c decreases as the concentration of the oxalic acid C_{ox} increases. At A, $v_1 > v_2$ results in a large number of small particles and hence a large surface area. As C_{ox} increases C_c decreases and because of assumption (1) above v_1 decreases more rapidly as C_{ox} increases than does v_2. The surface area will therefore decrease until at B $v_1 \sim v_2$. At higher temperatures, the complex will be less stable, that is, C_c will be smaller, v_1 and v_2 will both be smaller for given concentration conditions than at the lower temperature. Consequently, the curve will not extend to surface areas as large as those at the lower temperature. Further, since $E_1 > E_2$, v_2 will be increased more than v_1 with increasing temperature and the curve will be shallower. Both these facts have been found experimentally.

For the "ionic" curve DE, $v_1 \sim v_2$ at D, but as C_{ox} increases because of assumption (1) v_1 increases more rapidly than v_2. The surface area will therefore increase until at E, $v_1 > v_2$. At higher temperatures because of assumption (2) v_2 will be increased more than v_1 thus giving a shallower curve.

At 20° there is a noticeable tailing-off to a constant area when the concentration of oxalic acid is in marked excess over the nickel sulfate. In general, the ionic concentration function $f(C_i)$, will not depend in a simple way only on the total ionic concentration, but also on the ionic ratio,[4] and the dependence of $f_1(C_i)$ and $f_2(C_i)$ will be different. In consequence it is possible under suitable concentration conditions for v_1 and v_2 to become comparable in magnitude. The concentration conditions at which this state of affairs occurs will depend on the temperature since $E_1 > E_2$ and, in the present case, it appears that the onset of the tailing-off at the higher temperature is displaced to higher concentration values.

It is noticeable that the slopes of the "complex" curves, Figs. 1 and 2, are not in the order of concentration of nickel sulfate. This may be accounted for if, as is most probable, $f(C_c)$ is not a simple function of the concentration of the nickel sulfate and oxalic acid.

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(4) C. W. Davies and A. L. Jones, *Disc. Faraday Soc.*, **5**, 103 (1949).

The Association of Triethylamine and Chloroform

BY GORDON M. BARROW AND E. ANNE YERGER

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The use of chloroform as a solvent for the study of the reactions between acids and bases has an interesting advantage of providing a fairly specific type of solvent interaction. This interaction is mainly the stabilization by the formation of hydrogen bonds, of bases, or negatively charged ions, without the added complications encountered in hydroxylic solvents. For some recent work[1] on acetic acid–triethylamine reactions in chloroform it was necessary to establish the degree of interaction of the solvent with triethylamine itself. The results of this study are reported here.

Experimental

Triethylamine was purified by distillation and was stored over KOH.

Since chloroform has no absorption bands in the infrared spectrum suitable for following the reaction with triethylamine the deuterated compound was prepared. Three grams of deuterium oxide, 99.8%, from the Stuart Oxygen Company was added to a suspension of CaO in freshly distilled chloral according to the method of Truchet.[2] After refluxing for 5 hours a product was taken off at 60–65°. This material was placed over CaO and the liquid was separated by bulb-to-bulb vacuum distillation. Repetition of this step gave 5 cc. of a product whose infrared spectrum indicated a $CDCl_3$ purity of at least 95% and showed no evidence of any impurity other than $CHCl_3$.

The infrared spectrum of the $CDCl_3$ was obtained on a Baird Associates instrument; for the studies of $CDCl_3$ and triethylamine solutions a Beckman IR-2T instrument with a LiF monochromator was used.

The spectrum of $CDCl_3$, 4% by volume in CCl_4 in a 1-mm. cell, showed some difference compared to that reported by Earing and Cloke.[3] In addition to the $CDCl_3$ absorption bands at 740, 907, 1095 and 2254 cm.$^{-1}$ reported by them, bands also occur at 649(s), 1377(m), 1468(m) and 1805(vw) all of which are attributable to $CDCl_3$. The last three are overtones or combinations of the fundamentals at 365, 649, 740 and 907 cm.$^{-1}$ as assigned by Bernstein, Bordus and Cleveland.[4] The absorptions reported at 991 and 1171 cm.$^{-1}$ were not observed in the freshly prepared $CDCl_3$.

The hydrogen bonding interaction of $CDCl_3$, which is assumed to be no different than that of $CHCl_3$, with triethylamine is most conveniently studied with these reagents in CCl_4 solution. The spectrum of the $CDCl_3$ sample, about 1 molar in a 1.1-mm. cell, was used to determine the coefficient $1/\alpha l$ in the assumed Beer's law relation $C_{CDCl_3} = 1/\alpha l \log I_0/I_{2254\ cm.^{-1}}$. Using this coefficient the concentrations of free chloroform were calculated from

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(1) G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954).

(2) R. Truchet, *Compt. rend.*, **202**, 1997 (1936).

(3) M. H. Earing and J. B. Cloke, THIS JOURNAL, **73**, 769 (1951).

(4) R. B. Bernstein, A. A. Gordus and F. F. Cleveland, *J. Chem. Phys.*, **20**, 1979 (1952).