glycol with phosphorus tribromide. Since the glycol is a mixture of stereoisomers, the dibromide produced is composed of the racemic and *meso*-forms; *meso*-2,5-dibromohexane is readily obtained from the crude reaction mixture by cooling.

Experimental

meso-**2,5-Dibromohexane.**—In a typical run, 118 g. (1 mole) of 2,5-hexanediol (Carbide and Carbon Chemicals Corp.) was placed in a 1-liter, 3-necked flask, fitted with a mercury-sealed, Hershberg-type tantalum stirrer, a thermometer, and a dropping funnel. The glycol was cooled to −5° and, while stirring, 600 g. (2.2 moles) of phosphorus tribromide was added at such a rate that the temperature did not rise above +5°. The dropping funnel was replaced by a reflux condenser carrying a drying tube and the mixture was allowed to come to room temperature overnight. It was then heated for one hour on a steam-bath after which it was cooled and poured onto about 1 kg. of ice. The organic layer was washed successively with water, 96% sulfuric acid, water, aqueous sodium bicarbonate, water and then dried over Drierite. Removal of the Drierite by filtration gave 232 g. (96% yield) of a pale yellow liquid. This crude 2,5-dibromohexane, if distilled, boils at 98-100° (19-20 mm.) and has $n^{20}\text{D}$ 1.4997-1.4999.

However, when the *meso*-dibromide was desired, the crude, pale yellow product was not distilled. Instead, it was cooled to −5°; the *meso*-dibromide readily crystallized and was isolated by filtration. The filtrate was then cooled to −50° and seeded with crystalline *meso*-dibromide. On standing several hours at −50° a second crop of crystalline *meso*-2,5-dibromohexane was obtained. No attempt was made to learn whether further cooling would lead to the crystallization of more *meso*-dibromide. In one run this mother liquor was distilled; b.p. 87-89° (12-13 mm.).

The combined crops of *meso*-dibromide (120 g.) were melted and then dissolved in an equal volume of hot methanol. Upon cooling, first to room temperature and then in an ice-chest, there was obtained 105 g. of *meso*-2,5-dibromide, m.p. 39°. A second recrystallization from methanol raised the melting point only slightly; the yield was 90 g. (36% based on the glycol) of colorless *meso*-2,5-dibromohexane which sinters at 38° and melts at 39.1 to 39.4°. Further recrystallization from methanol, carbon tetrachloride or glacial acetic acid did not raise the m.p.; lit. m.p. 30°,[4] 36°,[3] 38.2°,[5] 38-39°.[6]

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(4) Fried and Kleene, THIS JOURNAL, **63**, 2691 (1941).

(5) Wislicenus, *Ber.*, **34**, 2565 (1901).

(6) Demjanoff, *Chem. Ztg.*, **14**, 145 (1890); *Chem. Centr.*, **61**, I, 521 (1890).

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Attempted Reduction of Neodymium to the Divalent State

BY H. A. LAITINEN AND EVA BLODGETT

Holleck and Noddack[1] reported that a partial reduction of several rare earths to the divalent state could be achieved by shaking a concentrated rare earth sulfate solution with dilute strontium amalgam. It was presumed that the divalent sulfate was stabilized by occlusion in the precipitated strontium sulfate which was formed. As was to be expected from previously known behavior, europium, ytterbium and samarium were reduced to a considerable extent. In addition, a smaller degree of reduction was reported for scandium, gadolinium, cerium, praseodymium and neodymium.

Glockler, *et al.*,[2,3] were unable to confirm for neodymium and gadolinium the polarographic evidence of Noddack and Brukl[4] which indicated that all of the rare earths are capable of existence in the divalent state as the reduction product of the trivalent ion at the dropping mercury cathode. We have likewise been unable to obtain polarographic waves which would correspond to one-electron reductions of the trivalent ions of neodymium or gadolinium, either in the absence or presence of indifferent electrolytes.

It appeared of interest, with a view toward possible applications in rare earth separations, to reinvestigate the reduction of rare earth sulfates with strontium amalgam. Neodymium and ytterbium were chosen for study.

Preliminary experiments with blank solutions of sulfuric acid shaken with strontium amalgam showed that it was extremely difficult to separate the last traces of amalgam and/or mercury from the precipitate and from the supernatant liquid. After removal of the spent amalgam in a separatory funnel, followed by centrifugation, the suspended precipitate was allowed to stand with a solution of ferric ammonium sulfate and titrated with permanganate. Both the blank experiments and experiments with saturated neodymium sulfate showed a consumption to permanganate which would correspond to the production of 0.9 to 10.8% of reduced neodymium. Since no mention of blank experiments was made by Holleck and Noddack, who reported 4.6% of the coprecipitated neodymium to be in the reduced state, some doubt was cast on the validity of their observations.

Repeating the blank experiments under essentially the same conditions as described by Holleck and Noddack, but removing only about one-third of the precipitated strontium sulfate from the top of the centrifuged precipitate, it was possible to decrease the blank to a consumption of 0.5 ml. of 0.01 *N* permanganate. Under the same conditions, starting with 30 ml. of 0.1 *M* neodymium sulfate, a strontium sulfate precipitate which consumed only 0.4 ml. of 0.01 *N* permanganate was obtained. A similar experiment with 0.1 *M* ytterbium sulfate showed by gravimetric determination of the residual ytterbium in solution that 62% of the ytterbium had been carried down with the precipitate. Of this, 78% was in the reduced form as shown by treatment with ferric iron and titration with permanganate. The remainder had been carried down in the trivalent state or had been reoxidized before titration. This observation was in agreement with that of Holleck and Noddack, who reported that 80% of the coprecipitated ytterbium was in the divalent state.

It was also of interest to attempt to prove the presence of divalent rare earth ions in the solution during the amalgam reduction. For this purpose, the dropping mercury electrode was used as a potentiometric indicator electrode.[5] Divalent rare earth ions would be expected to produce an anodic current at all potentials more positive than the reduction potentials of the trivalent ions. Consequently, the "cathodic" condenser current of the dropping mercury electrode which occurs at all potentials more negative than that corresponding to the electrocapillary maximum of mercury should be compensated by

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(1) L. Holleck and W. Noddack, *Angew. Chemie*, **50**, 819 (1937).

(2) S. W. Rabideau and George Glockler, THIS JOURNAL, **70**, 1342 (1948).

(3) C. R. Estee and George Glockler, *ibid.*, **70**, 1344 (1948).

(4) W. Noddack and A. Brukl, *Angew. Chemie*, **50**, 362 (1937).

(5) H. A. Laitinen, T. Higuchi and Michael Czuha, THIS JOURNAL, **70**, 561 (1948).

the anodic current of the reduced rare earth ions, with the effect that the null potential should be shifted in a negative direction from the electrocapillary maximum potential. A linear shift of potential, of the order of 0.1 volt per 10^{-6} mole/liter of divalent rare earth ion, would be expected.

Using strontium amalgam as the reducing agent, in a nitrogen atmosphere, potential readings of the order of -0.8 volt (*vs.* the saturated calomel electrode) were observed both with neodymium sulfate solutions and with sulfuric acid blanks. With ytterbium sulfate solutions, a reading of the order of -1.2 volts was observed. In view of the fact that the cathodic half-wave potential of trivalent ytterbium ions is -1.4 volts,[6] and considering the insolubility of ytterbous sulfate in the presence of strontium sulfate, this value is of the expected order of magnitude.

Similar experiments using 3% sodium amalgam as the reducing agent gave potential readings of 0.0 to -0.12 volt for the blanks and for neodymium sulfate solutions. In these experiments, the removal of the last traces of oxygen from the solid sodium amalgam was difficult, and the blank readings were probably shifted to abnormally positive values by traces of residual oxygen.[5] With ytterbium sulfate, potential readings of -1.30 to -1.37 volts were observed, again in the expected range.

Attempts were made to effect reductions in an alkaline medium in the presence of complexing agents, with the hope of decreasing the rate of reoxidation of divalent neodymium by hydrogen ions. Using Nulapon A (tris-[carboxymethyl]-amine) and Nulapon B (ethylenediamine tetraacetic acid), a *p*H value of 13 could be reached without precipitation of rare earth hydroxides. Using ytterbium chloride with sodium amalgam in a nitrogen atmosphere, a series of color changes from black to brown to orange was observed. The potential of the dropping mercury electrode was about -1.8 volts (*vs.* the saturated calomel electrode). Using neodymium chloride, no color changes occurred, and a potential reading of -0.6 volt was observed.

All attempts to prove the existence of divalent neodymium occluded in strontium sulfate, or in solution under conditions favorable to the reduction of ytterbium, have failed.

Acknowledgment.—The authors express their appreciation to the Office of Naval Research for financial support of this work.

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Degassing Low-Boiling Liquids by Liquid-Phase Condensation

BY MILTON MANES[1] AND HAROLD A. SCHERAGA[2]

Low-boiling liquids have often been degassed by trap-to-trap distillation to liquid air, in high vacuum, with or without discarding of first fractions. This method has failed to remove last traces of permanent gas,[3,4] presumably because of adsorption and entrapment of gas on the nonvolatile condensate. The discarding of first fractions on distillation is generally ineffective when dealing with traces of dissolved gases. In these cases the vapors escaping the boiling liquid tend to be closer in composition to the liquid phase than to the gas-rich composition calculated on the assumption of continual equilibrium. By contrast, if one approaches liquid–vapor equilibrium from the opposite direction, *i. e.*, by condensing liquid from vapor containing traces of permanent gas, then the gas content of the resulting liquid phase will be equal to, or less than, the equilibrium value. Failure to attain equilibrium is in this case favorable for separation of gases. This principle, which was in effect used by Keyes[5] for degassing water, has been successfully applied by the authors to the degassing of chlorine and carbon tetrachloride for kinetic studies.[6,7] The method of condensation to the liquid phase should be readily adaptable for degassing low-boiling substances which can be conveniently liquefied. There is no reason to believe that the fraction of gas removed at each step decreases with decreasing gas content.

Experimental

An outline is given here of the degassing of chlorine, which represents the unfavorable case of a low-boiling liquid whose corrosive properties require a grease-free system. The apparatus consisted essentially of several traps which led through a U-bend to a waste trap (in liquid air) and a McLeod gage, and thence through a stopcock to a mercury diffusion pump. The system was evacuated, liquid air placed on the U-bend, and liquid chlorine, after a preliminary purification, introduced and sealed into the system. Chlorine froze in the bend to form a gas-tight plug which then allowed the pressure in the closed system to rise during the next step without loss to the waste trap. The trap containing liquid chlorine was exposed to the atmosphere and the resulting distillate condensed in another trap with Dry Ice–alcohol. Neither condensation temperature nor distillation rate was critical, as long as the condensed phase was a liquid. At the end of the distillation the partial pressure of permanent gas in the uncondensed vapor was estimated in the McLeod gage by closing the stopcock and removing the plug in the U-bend. The gas-rich vapor phase was then pumped out. Liquid air could now be used to freeze the chlorine and keep liquid losses low. The system was again closed at the bend and the distillation repeated. In accordance with expectations the measured residual pressures decreased in rapid progression and became unmeasurable in a gage sensitive to 10^{-5} mm.

Chlorine thus degassed was then sublimed in a closed system to melting ethyl bromide[3] at $-119°$, which should have released any gases present. No pressure increase was found indicating the chlorine had been degassed prior to the sublimation step. Chlorine thus prepared and carbon tetrachloride similarly prepared (but without subsequent sublimation) were found by Manes and Hill[7] to show no induction period in the photochlorination of (similarly degassed) benzal chloride. Control experiments set the sensitivity of this test to oxygen at about 0.005% for chlorine and 0.00005% for carbon tetrachloride. In no case was any positive indication of oxygen observed.

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[1] Present address, U. S. Bureau of Mines, Pittsburgh, Pa.

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[3] P. M. Fye and J. J. Beaver, THIS JOURNAL, **63**, 1268 (1941).

[4] F. B. Young, *Phil. Mag.*, **20**, 797 (1910).

[5] F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, **68**, 550 (1933).

[6] H. A. Scheraga and M. E. Hobbs, THIS JOURNAL, **70**, 3015 (1948).

[7] M. Manes and D. G. Hill, in preparation.