for the gas observed with caproyl chloride but not with benzoyl or anisoyl chlorides.

Reaction of Trimethylacetyl Chloride with Diazomethane.—A solution of 24.1 g. (0.2 mole) of this acid chloride in 50 cc. of ether was added during eighty-five minutes to a cold solution of 20.4 g. (0.2 mole) of triethylamine and 8.5 g. of diazomethane in 275 cc. of ether. During the addition 0.022 mole (11%) of nitrogen was evolved, but on standing for twelve hours in the cold, no more nitrogen was liberated. The amine hydrochloride (96%) and crude diazoketone (98%) were isolated as described above. On treatment with acid, the crude diazoketone yielded 90% of nitrogen.

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Reduction of Anthracene and Phenanthrene with Lithium Aluminum Hydride

BY JOHN R. SAMPEY AND JESSIE M. COX

Nystrom and Brown[1] have found lithium aluminum hydride a useful reagent for a number of organic reductions. No work has been reported on the reduction of aromatic or condensed ring nuclei with this reagent. Preliminary attempts to reduce naphthalene and anthracene in ether and dioxane solutions were unsuccessful, but when the solid lithium aluminum hydride was shaken with molten anthracene and phenanthrene, reduction did take place, the former giving as high as 60% yields of tetrahydroanthracene, and the latter 22% of dihydrophenanthrene. These reductions take place even though the decomposition point of lithium aluminum hydride has been reported at 125–150°.[2] In all our reductions at high temperatures we mixed the powdered reagent thoroughly with the organic substances, and then employed vigorous shaking of the molten materials to ensure intimate mixing.

Method of Reduction.—A series of experiments is reported in which the temperature, the time and the ratio of reducing agent to anthracene and phenanthrene are varied. The experiments were run in a 200-ml. round-bottom flask, fitted with a calcium chloride tube, Bunsen valve and thermometer. The flask is heated with a Gyco heating jacket placed on a shaking machine. In each experiment 0.05 mole of the organic molecule was used. The molten material was shaken for the first two hours of each run, and then for fifteen minutes out of every thirty minutes; at the end of the time specified the hydride is decomposed by the slow addition of water. The reaction is vigorous and often flashes of fire were seen in the flask, but none of the reactions has gotten out of hand to date. After filtering and drying, the anthracene and its reduced form were extracted from the lithium and aluminum compounds with 200 ml. of hot chloroform and the phenanthrene with 200 ml. of ether or 95% alcohol. The unreduced hydrocarbons are less soluble than the hydrogenated products in the solvents used for the extractions, thus providing an effective method of separation. The tetrahydroanthracene was identified by a mixed melting point with a sample prepared by reduction of anthracene with Raney nickel (m. p. 103–104°). The dihydrophenanthrene and its picrate were identical with those prepared by Schmidt.[3]

Results of Reduction.—A 60% yield of tetrahydroanthracene was obtained by heating 0.05 mole of anthracene at 220–230° for six hours with 8 g. of lithium aluminum hydride; a 45% yield was obtained by cutting the hydride to one-half. Increasing the temperature to 240–270° or lengthening the time of heating also reduced the yield. A 22% yield of dihydrophenanthrene was obtained by heating 0.05 mole of phenanthrene at 220–230° for six hours with 8 g. of lithium aluminum hydroxide. Reducing the temperature to 180–200° and the quantity of hydride, reduced the yield to 10–17%.

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Electroseparation of Technetium from Rhenium and Molybdenum

BY L. B. ROGERS[1]

Heretofore, technetium has been plated from acidic solutions[2,3,4] under nearly the same conditions used for the deposition of rhenium. It seems quite likely, therefore, that the separation from rhenium would be poor. During the course of a polarographic study of technetium with G. E. Boyd[5] it was found that distinct reduction waves were found for pertechnitate in 2 *M* sodium hydroxide whereas perrhenate and molybdate did not reduce, at the platinum electrode, up to the potential at which hydrogen was evolved rapidly.

The brown-black precipitate which appeared on the electrode was soluble in a mixture of ammonia and hydrogen peroxide indicating that a lower oxide of technetium was formed since technetium metal is insoluble.[6] The height of the diffusion current confirmed the idea that the reduction step involved several electrons. Since the polarographic diffusion current reached a constant value at about -0.9 v. *vs.* the saturated calomel electrode (S.C.E.) and since the rapid evolution of hydrogen did not begin until about -1.2 v., the intermediate region of potential represented a promising one for the separation of technetium.

Experimental Results

A 100-μl. sample of 2 *M* sodium hydroxide containing 0.2 mg. of technetium (Tc^{99} – 9×10^5 years) as TcO_4^- plus a somewhat larger amount of molybdenum and a smaller amount of rhenium was placed upon a flat platinum foil used for the cathode. The anode was a large

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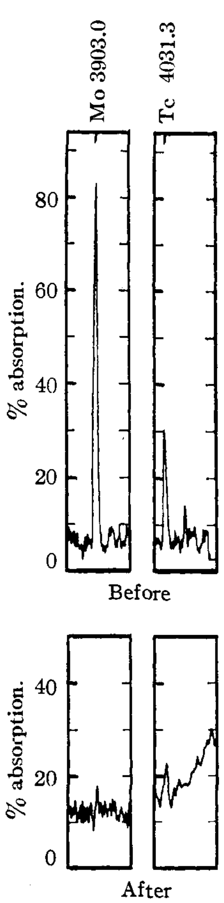

Fig. 1.

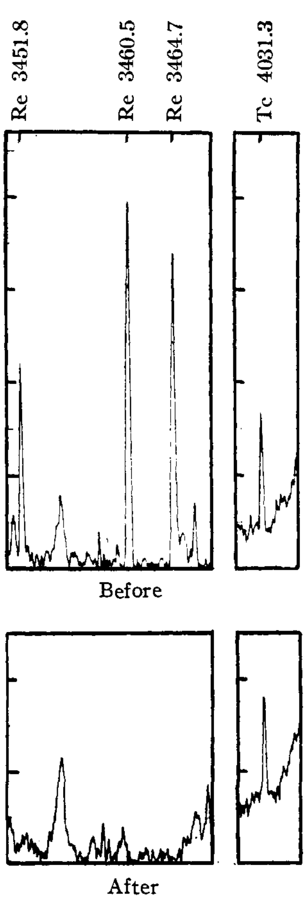

Fig. 2.

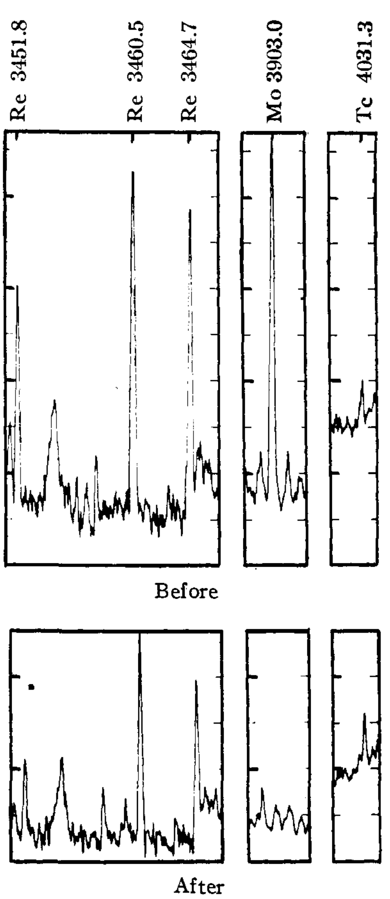

Fig. 3.

Purification of technetium by electrodeposition: selected portions of Leeds and Northrup densitometer traces of spectra obtained with a Dietert 1.5 Meter Grating Spectrograph.

saturated calomel electrode, and it was connected to the sample by means of a sodium perchlorate salt bridge. After two hours of electrolysis at −1.1 v. *vs.* the S. C. E., a count of the supernatant showed that more than 95% of the technetium had been precipitated. This yield was confirmed by counting the cathode after it had been washed with distilled water.

The precipitate was dissolved in a mixture of ammonia and hydrogen peroxide, the solution evaporated to dryness on a steam-bath, and the residue dissolved in 100 μl. of 2 *M* sodium hydroxide. A comparison of the spectrographic analyses of the solution before and after electrolysis is shown in Fig. 1. After electrolysis, the presence of the molybdenum line was questionable thereby showing that a good separation had been obtained. The technetium line was only slightly weaker after electrolysis.

The rhenium lines were so weak in the original solution (not shown in Fig. 1) that their absence from the second solution was not considered to be adequate proof of a satisfactory separation. Therefore, 0.1 mg. of rhenium, as perrhenate, was added to the solution and a second electrolysis carried out. Figure 2 shows that a good separation was obtained.

A third electrolysis was performed under somewhat different conditions: 0.2 mg. Tc, 0.1 mg. Mo, and 0.1 mg. Re—all in the same valence states as before but dissolved in 1.5 ml. of 2 *M* sodium hydroxide. The electrolysis was done in a small platinum dish at −1.2 v., and it lasted fifteen hours. Figure 3 shows that the separation from molybdenum was again excellent while that from rhenium was only fair. It seems likely the combination of a more negative cathode potential with a greater decrease in the concentration of hydroxide ion, as a result of picking up carbon dioxide from the air, favored the reduction of rhenium. The yield of technetium was only 85%, a decrease which may have been due to the lack of stirring or to the lower concentration of both technetium and hydroxyl ions.

The method appears to be limited to the purification of fairly concentrated solutions, *i. e.*, 10^{-4} *M* or greater, because in two experiments involving concentrations of the order of 10^{-6} *M*, essentially no technetium was found in the ammoniacal solution of peroxide after it had been in contact with the cathode. Raising the concentration of sodium hydroxide in the solution undergoing electrolysis to 4 *M* did not improve the recovery. One must conclude from these experiments with dilute solutions that the oxide has an appreciable solubility.

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