the base. The phosphate was purified by recrystallization from a mixture of acetone and methanol (1:4).

3-Substituted Thio-ethers.—To a mixture of 0.2 mole of butadiene sulfone, 0.2 mole of the desired mercaptan and 75 ml. of water was added slowly and with good agitation 0.4 mole of powdered sodium hydroxide. During this addition, the temperature rose to and was held at 70–80°. Stirring was continued and the temperature was maintained at 70–80° for four hours longer. Then the reaction was cooled and extracted with two 250-ml. portions of ether. The combined ether extracts were washed with 150 cc. of water and dried over anhydrous magnesium sulfate.

In the case of the benzylthio ether, the product crystallized directly from the cold ether solution. It was purified further by recrystallization from dry ether. With the diethylaminoethyl thio-ether, the base was converted to the hydrobromide by treatment of the dry ether solution with gaseous hydrogen bromide. Purification was accomplished by recrystallizing the salt from absolute alcohol.

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Thermal Exchange Experiments with Radioactive Zinc

BY LEON LEVENTHAL[1] AND C. S. GARNER

Duffield and Calvin[2] have reported an intensive study of thermal exchange reactions of copper chelate compounds in pyridine, most of which reactions proceeded at measurable rates. Other exchange experiments of the type considered here include those of Drehmann[3] on manganese(II) ions with manganese acetylacetone and manganese benzoylacetone in methanol (half-times of exchange less than one hour), Sue and Yuasa[4] on vanadyl and vanadate ions with solid vanadium 8-hydroxyquinoline and solid vanadium cupferronate (relatively slow exchange), and Johnson and Hall[5] on nickel(II) ions with various nickel chelate compounds in acetone, methyl or ethyl cellosolve (rapid to slow exchanges).

We have examined the thermal exchange reactions of zinc ions with some zinc complex compounds of the kind referred to above, partly to find conditions under which the kinetics of such reactions might be studied and partly to learn which of these zinc compounds, if any, might be suitable for use in the Szilard–Chalmers method of concentrating radioisotopes.

Complete exchange of radioactive zinc was found between dipyridine zinc acetate and the following zinc complex compounds in pyridine solution at 25° after exchange times as short as thirty seconds in each case: zinc acetylacetone, zinc acetylacetone ethylenediimine, zinc benzoylacetone ammoniate, zinc nicotinylacetone and dipyridine zinc thiocyanate. In the case of the nicotinylacetone, the exchange solution in pyridine was 0.0034 *f* in dipyridine zinc acetate and 0.0034 *f* in the zinc chelate. In all other cases, the pyridine exchange solutions were 0.01 *f* in the acetate and 0.01 *f* in the complex compound. The acetylacetone exchange was also run at 0° without any apparent difference. Thus, it appears either that rapid exchange was induced by the separation procedure utilized or, more probably, that the above zinc complex compounds are comparatively unstable with respect to ionization or displacement reactions (stability apparently comparable with that of copper salicylaldehyde, copper salicylaldehyde anil, and copper salicylaldehyde methylimine in pyridine solution[2]). If the rapid exchange was not induced, the above zinc complex compounds would not be suitable for Szilard–Chalmers separations, at least in pyridine solution.

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(2) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

(3) U. Drehmann, *Z. physik. Chem.*, **B53**, 227 (1943).

(4) P. Sue and T. Yuasa, *J. chim. phys.*, **41**, 160 (1944).

(5) J. E. Johnson and N. F. Hall, THIS JOURNAL, **70**, 2344 (1948).

Experimental

Radiozinc Tracer.—Several sections from a discarded copper cyclotron dee were obtained through the courtesy of Professor J. R. Richardson, to whom our thanks are hereby expressed. Since these copper parts had received lengthy deuteron and neutron bombardments and had been cooling for over a year, the principal activity in them was due to 250-day Zn^{65}, formed mainly by the reaction $Cu^{65}(d,2n)Zn^{65}$. Chemical separation and purification of the radiozinc was effected by a procedure similar to that outlined by Kamen,[6] giving a zinc fraction with the half-life and radiations characteristic of 250-day Zn^{65}.

Procedure.—Experiments were run in duplicate. All zinc compounds were synthesized and their identity established by chemical analyses. The pyridine was dried over potassium hydroxide and distilled through a column. Exchange mixtures were synthesized volumetrically from standardized stock solutions of the complex compounds and of radioactive zinc acetate in pyridine. After varying lengths of time the exchange mixtures were subjected to a separation procedure similar to that used by Duffield and Calvin[2] and consisting of the addition of water and chloroform followed by extraction of the complex compound into the chloroform–pyridine layer and of the acetate into the water–pyridine layer, re-extraction from each layer, then precipitation of zinc sulfide from the resulting extracts buffered with acetic acid–acetate mixtures. Since the zinc sulfide precipitates were found after drying to be of varying composition they were ignited to the oxide for weighing and subsequently mounted on filter paper discs. Both fractions from each experiment were counted in a reproducible geometry with a Geiger–Mueller counter and scale-of-64, the 0.45- to 1.14-Mev. gamma radiation associated with the decay of Zn^{65} being counted through a compound absorber. The total activity in each experiment was of the order of 1000 counts per minute, and corrections for decay and changes in counter efficiency (by use of a standard Zn^{65} aliquot) and for background were applied. The extent of exchange was calculated in the usual manner from the specific activities of the two fractions.

(6) M. D. Kamen, "Radioactive Tracers in Biology," Academic Press, Inc., New York, N. Y., 1947, p. 246.

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Thermal Exchange Experiments with Radioactive Chromium

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The only published work on exchange reactions of chromium compounds is the observation of