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.

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.

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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).

(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

BY H. E. MENKER AND C. S. GARNER

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

TABLE I

THERMAL EXCHANGE OF LABELLED CHROMIUM (Cr*) BETWEEN CHROMIUM COMPOUNDS

Ions	Composition, f.	$HClO_4$ f.	Temp. °C	Activity of Separated Fractions, net c./m.:[a] Orig. act.	Orig. inact.	Std. aliq.	Exchange Time Hr.	%
$Cr(H_2O)_6^{+++}$, $Cr_2O_7^{--}$	0.010 $Cr^*(ClO_4)_3$, 0.0050 $K_2Cr_2O_7$	0.05	Rm.	4290	41	4333	72	<2
				1913	27	1952	456	<3
			45.1	2645	108	2838	72	8
				1840	129	1981	264	13
				435[b]	119[b]	530	1200	43
		2.0	Rm.	2509	23	2470	72	<2
			45.1	2534	70'	2838	72	5
Cr(III), $Cr_2O_7^{--}$	.0020 $Cr^*_2(SO_4)_3$,[c] .0020 $K_2Cr_2O_7$	[d]	25.1	310	1	354	72	<1
$Cr(OH)_4^-$, CrO_4^{--}	.010 $Cr^*(ClO_4)_3$, .010 K_2CrO_4	[e]	25.1	2713	18	2838	72	<3
$Cr(H_2O)_6^{+++}$, $Cr(SCN)_6^{---}$	.010 $Cr^*(ClO_4)_3$, .010 $K_3Cr(SCN)_6$	0.05	Rm.	1297	1	1300	72	<1
		2.0	Rm.	1363	1	1300	72	<1
$CrCl_2(H_2O)_4^+$, $Cr(SCN)_6^{---}$	.0067 Cr^*Cl_3,[c] .0067 $K_3Cr(SCN)_6$	[f]	25.2	617	3	626	24	<2
$Cr(H_2O)_6^{+++}$, $Cr(CN)_6^{---}$	.010 $Cr^*(ClO_4)_3$, .010 $K_3Cr(CN)_6$	pH 3–4	Rm.	498	275	773	72	71
$CrCl_2(H_2O)_4^+$, $Cr(CN)_6^{---}$	.0049 Cr^*Cl_3,[c] .0049 $K_3Cr(CN)_6$	[g]	25.1	501	2	...	72	<2
Cr(III), $Cr(CN)_6^{---}$	.0080 $Cr^*(OOCCH_3)_3$,[c] .0080 $K_3Cr(CN)_6$	[h]	25.1	608	38	668	96	12
$Cr(H_2O)_6^{+++}$, $Cr(C_2O_4)_3^{---}$	.010 $Cr^*(ClO_4)_3$, .010 $K_3Cr(C_2O_4)_3$	0.025	Rm.	700	0	734	72	<1
$CrCl_2(H_2O)_4^+$, $Cr(C_2O_4)_3^{---}$	.0050 Cr^*Cl_3,[c] .0050 $K_3Cr(C_2O_4)_3$	[g]	25.1	350	5	477	1	<5

[a] Statistical counting error, taken as the square root of the sum of the squares of the standard deviations of sample and of background, was 1%. [b] Analyses gave same amount of chromium in each fraction, thus showing that oxidation of chromium(III) by perchloric acid is negligible under the experimental conditions. [c] Green form. [d] H_2SO_4 (pH 2–3). [e] 3.1 f. NaOH. [f] 0.067 f. HCl. [g] 0.050 f. HCl. [h] CH_3COOH (pH 3–4).

Muxart, Daudel, Daudel and Haissinsky[1] that no appreciable exchange of radiochromium occurs between chromium(III) and dichromate ions in sulfuric acid solutions.

We have confirmed this observation and have extended the studies to exchange measurements in 2 *f* and 0.05 *f* perchloric acid and in 3.1 *f* sodium hydroxide. In addition, some exchange reactions of chromium(III) ions with hexathiocyanatochromate(III), hexacyanochromate(III), and trioxalatochromate(III) ions, respectively, have been investigated with radiochromium.

Table I summarizes the results. Appreciable exchange was observed only for Cr(III)—$Cr(CN)_6^{---}$ in low concentration of perchloric acid or acetic acid and for the pair hexaaquochromium(III) and dichromate ions in 0.05 *f* perchloric acid at 25° and 45°. In the latter case the exchange results obey approximately the exponential exchange law,[2,3] as is shown by Fig. 1. The half-time for the exchange under the stated conditions is 60 ± 6 days at 45° and greater than 430 days at 25°.

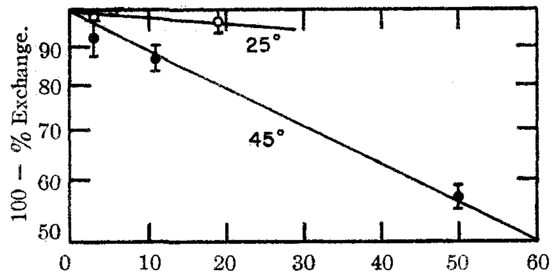

Fig. 1.—Hexaaquochromium(III)—dichromate exchange, 0.010 *f* $Cr^*(ClO_4)_3$, 0.0050 *f* $K_2Cr_2O_7$, 0.05 *f* $HClO_4$.

Experimental

Radiochromium Tracer.—Radiochromium was prepared by the Cr(*n*, γ) reaction in the Oak Ridge pile and allocated by the U. S. Atomic Energy Commission. Chemical purification gave a chromium fraction with the half-life and radiation characteristics of 27-day Cr^{51}.

Procedure.—Experiments were run in duplicate. The exchange mixtures were synthesized volumetrically from the standardized stock reagent solutions, placed inside glass-stoppered flasks immersed in a thermostated bath, and subjected to chemical separation at the end of the exchange times. In the hexathiocyanatochromate (III) and hexacyanochromate (III) exchanges separation was effected by the addition of silver nitrate to precipitate $Ag_3Cr(SCN)_6$ and $Ag_3Cr(CN)_6$, respectively. Separation in the case of the trioxalatochromate (III) exchanges was achieved by the addition of barium chloride and ethanol to precipitate $Ba_3[Cr(C_2O_4)_3]_2$. In all other cases separation was brought about by precipitation of hydrous chromium(III) oxide. Both fractions in each exchange experiment were mounted and counted, in a few cases in the form precipitated (except for drying), but in most cases as $BaCrO_4$. Samples were suction-filtered onto Whatman No. 50 paper discs held in a cylindrical glass "chimney" device, then mounted on cardboard plates for counting. The 0.33-Mev gamma radiation associated with the decay of Cr^{51} was generally used in the detection, the samples usually being counted through 108 mg./sq. cm. aluminum (to eliminate variable X-radiation) in a reproducible geometry with a Geiger–Mueller counter and scale-of-128. Corrections for decay and changes in counting efficiency (by use of a standard Cr^{51} aliquot) and for background (~19 c./m.) were made.

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[1] R. Muxart, P. Daudel, R. Daudel and M. Haissinsky, *Nature*, **159**, 538 (1947).

[2] H. A. C. McKay, *ibid.*, **142**, 997 (1938).

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