Isotopic Exchange of Zinc Chelate Compounds in an Anhydrous Organic Solvent

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Isotopic exchange of zinc in its complexes has been studied by a few workers with various chelate compounds1-3). It is generally agreed that the exchange is rapid, except that of zinc phthalocyanine complex, which has a "fused ring" struc-All these experiments, however, involve the use of water, either as solvent or as separating agent for the two compounds between which the isotopic exchange is to be examined. The present authors are of the opinion that the exchange might be accelerated by water, as is in the case of other metal complexes, and that, when the experiment is carried out in the absence of water, a measurably slow exchange might be expected even for those ions having filled inner d-orbitals.

Attempts have been extensively made to separate two chelate compounds of zinc in an anhydrous organic solvent. It was eventually found that pure zinc oxinate is precipitated, when dioxane solution of zinc oxinate and acetylacetonate is treated with a large excess of isopropylether, trichloroethylene or chloroform. The yellow precipitate was spectrophotometrically examined in methanol and found to be free from acetylacetonate. The isotopic exchange was examined with inactive oxinate and acetylacetonate labelled with radioactive zinc-65. A linear relationship was observed, when the counting rate of the photo-multiplier pulse due to photo-electric peak of the γ -ray spectrum (1.114 MeV.) of zinc-65 is plotted against the amount of the labelled compound. In order to avoid the influence of water, all procedures were carried out in a dry box (relative humidity, less than 10%; dew point, below -14° C).

It was elucidated that the exchange proceeds instantaneously, even under an anhydrous condition. Since the exchange between zinc acetylacetonate in solution and solid zinc oxinate proceeds slowly, it appears evident that the rapid exchange took place in the homogeneous solution rather than between the solute and the precipitate in the nascent state.

Further work with other chelate compounds is in progress. Details of the study will be published later.

Experimental.—The chelate compounds were prepared by the usual methods and dried at 110°C immediately before use. The organic solvents were refluxed with sodium and distilled with dry apparatus. The presence of water was tested with various reagents, including anhydrous copper sulfate and cobalt chloride, but the results were all negative. It appears as if the water content is less than 0.01%.

Dioxane solution of zinc oxinate (0.000125

TABLE. EXCHANGE OF ZINC BETWEEN OXINATE AND ACETYLACETONATE acetylacetonate oxinate

No.	acetylacetonate		oxinate				exchange
	used mg.	c.p.m.	used mg.	recovered mg.	obsvd. c.p.m.	calcd.*	%
1)	32.7	3277	44.2	29.0	1137	1075	106
2)	33.6	2208	44.3	41.7	1062	1039	102
3)	29.3	1966	44.2	40.4	77	1236	7
4)	32.9	2161	44.2	42.0	772	1026	7 5

1) 2): Both chelates in dioxane; time of exchange, 30 sec.

Acetylacetonate, in the mixed solvent; oxinate, solid; time of exchange, 3) 1 hr.,
12 hr.

* Calculated on the assumption that a complete exchange has taken place.

¹⁾ Don C. Atkins, Jr. and C. S. Garner, J. Am. Chem. Soc., 74, 3527 (1952).

²⁾ L. Leventhal and C. S. Garner, ibid., 71, 371 (1949).

A. Turco, G. Sordillo and M. Scatena, Ricerca Sci., 25, 2361 (1955).

mol. in $15\,\mathrm{ml.}$) and that of zinc acetylacetonate (0.000125 mol. in $25\,\mathrm{ml.}$) were mixed (at room temperature, $18^{\circ}\mathrm{C}$) and, after 30 sec., iso-propylether (ca. 300 ml.) was added. The precipitate was filtered off with a detachable sintered glass filter plate, thoroughly washed with iso-propylether, weighed and submitted to γ -ray counting. Precipitation of the oxinate was completed within one hour. (No. 1 and 2 in the table).

Exchange between solid oxinate and acetylacetonate in solution was examined in a mixture (100 ml.) of dioxane and isopropylether (1+3, by volume). About 7 and 75 per cent exchange were observed after one hour and 12 hours, respectively. Since the mixed solvent assumed yellow, the exchange appears to proceed through partial dissolution of the oxinate.

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