Hot-atom Chemistry of Tris-(acetylacetonato)-cobalt(III) in Benzene Solutions and Frozen Benzene Solutions

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We have initiated a systematic work to irradiate the organic solutions and frozen organic solutions of metal complexes with slow neutrons in order to elucidate the mechanism of hot-atom reactions in the systems. In the present paper we report our preliminary data on the ^{60}Co recoil reactions in benzene solutions and frozen benzene solutions of tris-(acetylacetonato)-cobalt(III) and the scavenger effect of ferric chloride added to the systems for the purpose of removing free acetylacetone.

Solid $Co(acac)_3$, 0.2 M $Co(acac)_3$ benzene solutions and frozen 0.2 M $Co(acac)_3$ benzene solutions were irradiated with slow neutrons for 5 min in a TRIGA Mark II reactor (thermal neutron flux: 5×10^{11} n/cm^2·sec.). The solutions were irradiated at room temperature, the solid samples and the frozen solutions at dry-ice temperature. Various amounts of $FeCl_3\cdot6H_2O$ dissolved in small amounts of ethanol, or various amounts of anhydrous $FeCl_3$, were added to the benzene solutions and frozen benzene solutions (before freezing) before irradiation. An aliquot of the irradiated benzene solution (or frozen solution) was diluted to 5 ml with benzene and extracted with three 5-ml portions of 3% EDTA aqueous solution containing 0.8% sodium potassium tartrate and 10 mg of $CoSO_4\cdot7H_2O$ as carrier. Another aliquot of the irradiated benzene solution was stored overnight at room temperature and extracted the following day. All the ^{60}Co-labeled species exchangeable with Co^{2+} are extracted into the aqueous phase whereas $^{60}Co(acac)_3$ remains in the organic phase (as retention). The broken curves in Fig. 1 correspond to retentions obtained with the stored aliquots while the solid curves represent retentions in the aliquots extracted immediately. The irradiated solid samples (30—50 mg) were dissolved in 5 ml of benzene, ethanol, chloroform, or acetic acid, all with or without ferric chloride additive, and analyzed by means of solvent extraction or ion exchange.

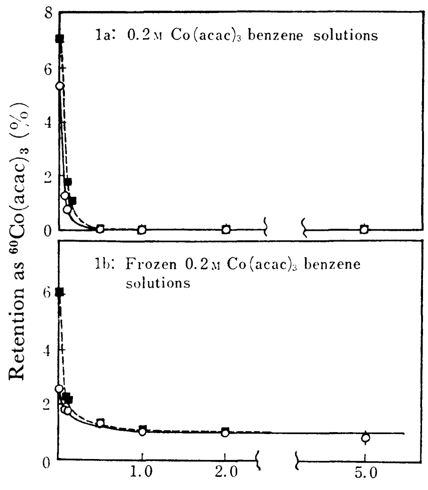

Fig. 1a-1b. Retention *vs.* ferric chloride concentration in irradiated $Co(acac)_3$ benzene solutions.

From the results we may draw the following conclusions:

1) As shown in Fig. 1a, the retention in $Co(acac)_3$ benzene solutions sharply decreases to 0% with the increase in the $FeCl_3\cdot6H_2O$ concentration. Although thermal reactions (recombination reactions) in the solutions during and after irradiation contribute appreciably to the apparent retention, their contribution can be eliminated effectively by the addition of $FeCl_3\cdot6H_2O$,*[1] and the initial retention due to hot reactions alone can be estimated.

2) As seen in Fig. 1b, the retention in frozen 0.2 M $Co(acac)_3$ benzene solutions decreases rapidly to a constant value (~1%) with increasing $FeCl_3\cdot6H_2O$*[1] concentration. Since the most solute molecules (complex) should be precipitated as microcrystals in the frozen solutions at this concentration, it seems reasonable that the above retention value is fairly close to that observed with solid samples.

3) Retentions in solid samples fall within the range 1.3—1.5%, irrespective of solvents used, if they contain ferric chloride. Higher retentions 2.0—2.2% are obtained in the absence of ferric salts. The retention remains unchanged even after standing the solutions of the irradiated solid samples for several days if they contain ferric salts, whereas the retention increases appreciably after standing in solutions without ferric salts.

4) The effect of the ferric salt addition on the retention may be explained by assuming that ferric salts which can be easily complexed with acetylacetone work as good scavengers for free acetylacetone in solutions, and thus minimize the recombination of recoil species with acetylacetone through thermal reactions.

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*[1] Addition of anhydrous $FeCl_3$ is nearly as effective as $FeCl_3\cdot6H_2O$.