BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1237—1238(1972)

The ^{60}Co Recoil Reactions in the Benzene Solutions of Tris(nitrosonaphtholato)cobalt(III)

Takeshi TOMINAGA and Takuhiko SAKAI

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received July 30, 1971)

While several works had been reported on the hot-atom chemistry of organic solutions of organometallic compounds[1,2] the hot-atom reactions of irradiated organic solutions of metal complexes had not been studied before our preliminary work on the tris(acetylacetonato)cobalt(III) benzene solutions.[3] We have thus far investigated the ^{60}Co and ^{51}Cr recoil reactions in neutron-irradiated benzene solutions of tris(acetylacetonato)cobalt(III)[3,4] and tris(acetylacetonato)chromium(III)[5] and found that metallic salts can well be used as scavengers to suppress the thermal reactions.

In the present article we will report that a similar scavenger effect of metallic salts can be observed in the irradiated benzene solutions of other chelate complexes, such as tris(nitrosonaphtholato)cobalt(III), and that the apparently high retentions in solid tris(nitrosonaphtholato)cobalt(III)[6] may be ascribed to the thermal reactions taking place in the solutions of the irradiated solid complexes.

1) I. C. Yang and D. R. Wiles, *Can. J. Chem.*, **45**, 1357 (1967).
2) U. Zahn, *Radiochim. Acta*, **7**, 170 (1967).
3) T. Tominaga and K. Fujiwara, This Bulletin, **43**, 2279 (1970).
4) T. Tominaga, T. Sakai, and K. Fujiwara, *ibid.*, **44**, 3036 (1971).
5) T. Tominaga and Y. Nishi, *Radiochem. Radioanal. Lett.*, **8**, 151 (1971).
6) N. Saito, T. Tominaga, and H. Sano, This Bulletin, **35**, 1739 (1962).

Experimental

The procedures used in preparing the solutions with various scavengers and the conditions of irradiation are similar to those described previously.[3,4]

The 0.01M solutions of tris(α-nitroso-β-naphtholato)cobalt(III) and tris(β-nitroso-α-naphtholato)cobalt(III) in benzene containing 10% (by volume) of ethanol and various amounts of metallic salts as scavengers were prepared and irradiated with thermal neutrons (flux: 5×10^{11} n/cm²·sec) for 5 min at room temperature in a TRIGA Mark II reactor. Solid samples of the above complexes were irradiated with thermal neutrons for 5 min in dry ice and then dissolved in benzene containing 10% (by volume) of ethanol and metallic salts. The irradiated benzene solution or the solution of the irradiated solid was diluted to 5 m*l* with benzene and extracted with three 5-m*l* portions of (1: 1) nitric acid.[6] The radioactivity of each fraction was measured with a well-type NaI scintillation counter at least one week after the neutron irradiation. The ^{60}Co retention, or the radiochemical yield of the parent chemical form, was obtained as a percentage of the total ^{60}Co activity found in the organic phase. No significant decomposition of the target complexes was observed during irradiation.

Results and Discussion

The effects of the scavenger salts on the ^{60}Co retention are summarized in Figs. 1 and 2.

The ^{60}Co Retention in the Irradiated Solutions. While the apparent ^{60}Co retentions in the irradiated 0.01M solutions of both complexes were as high as 80—90% in the absence of scavengers, they decreased sharply with an increase in the concentration of the salts of such metals as cobalt and copper.[7] The nickel salt appeared to be less effective as a scavenger, and the magnesium salt had practically no effect on the retention. As in the case of the acetylacetone complexes,[4,5] it seems that salts of the metals which can form more stable complexes with free nitrosonaphthols work as more effective scavengers. Carbon tetrachloride showed a slight scavenger effect.

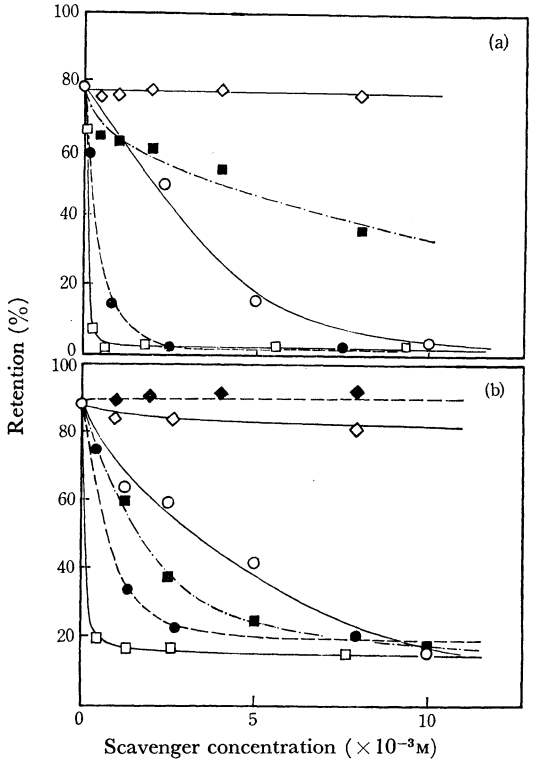

Fig. 1. Scavenger effect of various metallic salts on ^{60}Co retention (a) in the irradiated 0.01M solutions of tris(α-nitroso-β-naphtholato)cobalt(III) and (b) in the 0.01M solutions of irradiated solid tris(α-nitroso-β-naphtholato)cobalt(III).
—□— $CoCl_2$; —○— $CuCl_2\cdot2H_2O$;
--●-- $Cu(CH_3CO_2)_2\cdot H_2O$; -·-■-·- $NiCl_2\cdot6H_2O$;
—◇— $MgCl_2\cdot6H_2O$; --◆-- $ZnCl_2$;
--▨-- $MnCl_2\cdot4H_2O$. (Symbols common to Figs. 1 and 2).

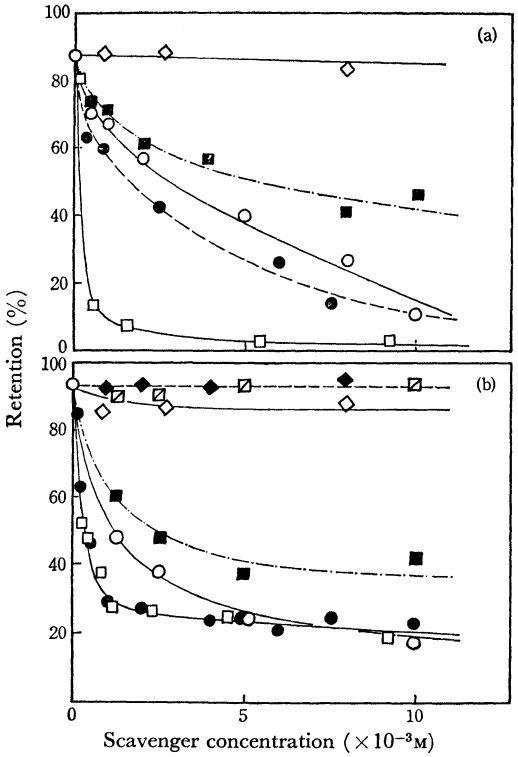

Fig. 2. Scavenger effect of various metallic salts on ^{60}Co retention (a) in the irradiated 0.01M solutions of tris(β-nitroso-α-naphtholato)cobalt(III) and (b) in the 0.01M solutions of irradiated solid tris(β-nitroso-α-naphtholato)-cobalt(III).

The ^{60}Co Retention in the Irradiated Solid. The apparent retentions in the irradiated solids were nearly 90% when dissolved in scavenger-free benzene, whereas they decreased to 15—20% when dissolved in benzene containing cobalt or copper salts. This indicates that the thermal reactions after the dissolution of the irradiated solid contribute greatly to the apparently high retentions in solids. The nickel salt was a less effective scavenger, and the magnesium, zinc, and manganese salts had no scavenger effects. The effects of the scavenger salts on the retention in solids seem essentially similar to those observed in the irradiated solutions.

In conclusion, it has been confirmed that the use of adequate scavengers (such as metallic salts) which can suppress the thermal reactions will be useful in determining the primary retention in irradiated solutions or the true retention in irradiated solids.

The authors wish to thank Professor Nobufusa Saito of the University of Tokyo for his encouragement and support during this work.

7) The lowest retention observed in the well-scavenged solutions was 1.1—1.6%.