

## CHEMISTRY

## Valency State of Chromium in Seawater

THE valency state in which chromium occurs in seawater not only provides important information concerning the geochemical behaviour of this element in marine environment but has also in recent years become significant in connexion with the problem of disposal of radioactive waste. For example, Osterberg *et al.*<sup>1</sup> investigated the variation of the spread of the Columbia River water along the Oregon coast of the Pacific by using chromium-51 which was originally released from the Hanford reactor as a radioactive tracer. In this case, it was reported by Cutshall *et al.*<sup>2</sup> that the major part of chromium-51 stayed in the original hexavalent state in seawater even at several hundred kilometres from the river mouth. In order to understand the cycle of radioactive chromium in the seawater, therefore, it seems indispensable to know the valency state in which chromium in seawater is stable. Unfortunately, the present day knowledge of this is very limited. In his recent compilation Riley<sup>3</sup> gave six references for the chromium content of seawater but these data are not sufficient to indicate general trends in the behaviour of chromium in seawater. In these investigations, except for the two investigations by emission spectrography, chromium was separated with hydroxides of aluminium, iron or chromium itself. These separations are only effective when chromium in seawater is present in a trivalent form.

Goldschmidt<sup>4</sup> suggested that chromium was present in seawater in the hexavalent state (chromate), and this was accepted by Krauskopf<sup>5</sup>. Arrhenius and Bonatti<sup>6</sup> supported the idea of a hexavalent state and pointed out the possibility of coprecipitation of chromate with strontium or barium sulphate *in situ*. Fukai and Huynh-Ngoc<sup>7</sup> showed by thermodynamical computations that the stable species of chromium in seawater should be hexavalent. Sillén<sup>8</sup> suggested that uncharged soluble chromic hydroxide might be present.

Because two contradictory ideas exist about the valency state of chromium in seawater, I have devised a differential method for the determination of the trivalent and hexavalent chromium which occurs in seawater. The principle of the method depends on independent measurements of two equivalent samples from the same sample of water, one treated by direct coprecipitation of chromium with iron hydroxide and the other by a similar coprecipitation after reduction with sodium sulphite in acid medium.

The results obtained by the method for samples of water collected from the Ligurian Sea are summarized in Table 1. It can be seen that hexavalent chromium was found in all the water samples. For some of the samples the trivalent chromium estimated was within the range of analytical sensitivity. These results seem to support the thermodynamical estimation of the valency state of chromium given by Fukai and Huynh-Ngoc<sup>7</sup>. The thermodynamically unstable species, trivalent chromium, however, was detected in many cases. This fact suggests that there

is some process which is working against thermodynamic equilibria.

R. FUKAI

International Laboratory of Marine Radioactivity,  
International Atomic Energy Agency, Monaco.

Received January 24, revised February 1, 1967.

- <sup>1</sup> Osterberg, C., Cutshall, N., and Cronin, J., *Science*, **150**, 1585 (1965).  
<sup>2</sup> Cutshall, N., Johnson, V., and Osterberg, C., *Science*, **152**, 202 (1966).  
<sup>3</sup> Riley, J. P., *Chemical Oceanography*, **2**, 346 (Academic Press, London and New York, 1965).  
<sup>4</sup> Goldschmidt, V. M., *Geochemistry*, 545 (Oxford Univ. Press, London, 1958).  
<sup>5</sup> Krauskopf, K. B., *Geochim. Cosmochim. Acta*, **9**, 1 (1956).  
<sup>6</sup> Arrhenius, G., and Bonatti, E., *Progress in Oceanography*, **3**, 7 (Pergamon Press, London and New York, 1965).  
<sup>7</sup> Fukai, R., and Huynh-Ngoc, L., *Bull. Inst. Oceanogr. Monaco* (in the press).  
<sup>8</sup> Sillén, L. G., *Oceanography, Publ. No. 67*, 549 (Amer. Assoc. Adv. Sci., Washington, D.C., 1961).

## Some Reactions of Triruthenium Dodecacarbonyl

WE have been investigating some reactions of triruthenium dodecacarbonyl  $\text{Ru}_3(\text{CO})_{12}$ . The structure of this compound is well established as an equilateral triangle of three ruthenium atoms with twelve terminal carbonyl groups<sup>1</sup>. The reactivity of this compound towards halogens, thiols, olefines and related compounds is, however, virtually unexplored. Some similarity in its chemical reactivity to that of tri-iron dodecacarbonyl can be expected, but whereas reactions of the iron cluster normally lead to cleavage of the trimeric unit, the ruthenium analogue appears to give stable trinuclear species. This may be correlated with an increase in the stability of metal-metal bonds on going down the transition metal triad<sup>2</sup>. This communication summarizes some of the reactions carried out on ruthenium carbonyl.

*Reaction with halogens.* Oxidation of triruthenium dodecacarbonyl with halogens ( $X_2$ ) ( $X = \text{Cl}, \text{Br}$  or  $\text{I}$ ) has led to the isolation of four classes of ruthenium carbonyl halides, namely: (i) The monomeric  $\text{Ru}(\text{CO})_4X_2$  (ref. 3). (ii) The dimeric  $\text{Ru}_2(\text{CO})_6X_4$ ;  $\text{Fe}(\text{CO})_3\text{Br}_2$  (ref. 4) and  $\text{Os}(\text{CO})_3X_2$  (ref. 5) reported previously may be of a similar type. (iii) The trimeric  $\text{Ru}_3(\text{CO})_{12}X_6$  which to our knowledge represent the first examples of a new class of trimeric carbonyl halide. This class of compound emphasizes that the metal cluster unit appears to behave in a novel way by donating six electrons to available groups. We have previously observed this behaviour in the compound  $\text{Os}_3(\text{CO})_{12}\text{OsO}_4$  (ref. 6). The fact that no analogues of iron are known may be correlated with the enhanced stability of metal-metal bonded compounds in the higher oxidation states of second and third row transition metals. The molecular weights of these compounds (i), (ii) and (iii) are based on the appearance of the parent molecular ions in the mass spectra. (iv) The polymeric carbonyl halides  $(\text{Ru}(\text{CO})_2X_2)_n$  (ref. 7).

*Reaction with thiols.* Reaction of triruthenium dodecacarbonyl with thiols follows a different course from that

Table 1. TRIVALENT AND HEXAVALENT CHROMIUM IN SEAWATER SAMPLES

Sample	Location of sampling	Date of sampling	Chlorinity (per ml.)	Cr <sup>3+</sup> ( $\mu\text{g/l.}$ )	Soluble chromium Cr <sup>6+</sup> ( $\mu\text{g/l.}$ )	Total ( $\mu\text{g/l.}$ )
Surface seawater	Monaco coast	January 12, 1966	—	0.14	0.29	0.43
" "	" "	June 1, 1966	—	0.02 >	0.34 <	0.36
" "	2 km south of Monaco	June 8, 1966	—	0.02 >	0.36 <	0.38
" "	Cap d'All Coast	July 19, 1966	21.15	0.02 >	0.28 <	0.30
" "	Roquebrune Bay	September 13, 1966	20.95	0.18	0.05	0.23
" "	Cap d'All Coast	September 30, 1966	—	0.19	0.19	0.38
Seawater from 5 m depth*	42° 47' N. 7° 29' E.	October 25, 1966	20.92	0.23	0.10	0.39
Seawater from 500 m depth*	" "	" "	21.08	0.19	0.16	0.35
Seawater from 1,000 m depth*	" "	" "	21.03	0.20	0.21	0.41

\* The seawater was not filtered.