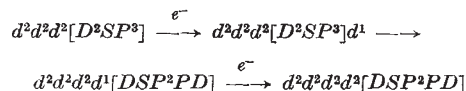


The mechanism of the electron transfer and the electronic configuration for the above reactions are believed to be as follows. The acceptance of the electrons occurs in two stages:



First, the electron is accepted into the 4*d* peripheral orbitals temporarily, where it is held loosely, since the 3*d* atomic orbitals of Co(III) atom are fully occupied. After that the consecutive change of the electronic configuration and the placement of the electron in the stable 3*d* orbitals occur slowly. Therefore, this electrode process requires fairly high overpotential. In the second stage, the electron is accepted into the vacant 3*d* orbital directly. Thus, the difference of the electronic configuration in the oxidized and the reduced forms is considered to be one of the main causes for irreversibility of the electrode reactions.

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Carbonates of Uranium

MILLER and co-workers¹ for the first time isolated uranyl carbonate, prepared by the action of carbon dioxide under pressure on uranium trioxide, ammonium and sodium uranates. A different process was followed by Chernyaev and co-workers², who prepared the compound by the treatment of aqueous and alcoholic solutions of uranyl nitrate with carbon dioxide under pressure or aqueous suspensions of uranium oxide, UO₃, under normal conditions. A simple and convenient method has been developed by us for the preparation of the compound. The hitherto unreported compound uranium (IV) oxycarbonate, the preparation of which is described below, on exposure to dry air undergoes simultaneous oxidation and dehydration, resulting in the formation of the compound UO₂CO₃ · 2.5 H₂O, the progress of the oxidation being indicated by the gradual change of colour from dark green to bright yellow. This hydrated uranyl carbonate, when heated *in vacuo* at 160°, gives the anhydrous compound UO₂CO₃, which is stable up to 500° C.

Uranyl ion undergoes photoreduction when exposed to sunlight in the presence of reducing agents such as alcohol or formic acid. When ammonium carbonate is added to a photochemically reduced solution of uranyl nitrate or formate, a green precipitate is obtained in a fine state, which on washing turns dark green. Analysis of the freshly prepared moist compound was carried out after ammonia had been tested for and found to be absent. The uranium to carbonate ratio was found to be 1 : 1 by semimicro-combustion method. The water content was found to vary from time to time due to the moist compound

being used for analysis. The total uranium content was estimated as U₃O₈ and also by the Jones reductor method. That all the uranium exists as uranium (IV) was proved by directly titrating the solution of the compound in 2*N* sulphuric acid against standard potassium permanganate. On account of the extreme proneness of the compound to oxidation and hydrolysis at high temperature, and also our lack of equipment for isothermal dehydration at low temperature, it has not been possible to get the compound either in the anhydrous state or in a definite state of hydration.

The isolation of uranium (IV) oxycarbonate offers a new route for the syntheses of uranium (IV) compounds³. Investigations are proceeding with the view of preparing some new compounds of uranium as well as the dioxide⁴.

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Photolysis of 1 : 3-Dichlorotetrafluoroacetone

THE primary act in the photolysis of acetone at room temperature has been shown by a number of workers to be the production of an acetyl and a methyl radical¹. It is believed that the photolysis of hexafluoroacetone is a simpler process in which only trifluoromethyl radicals and carbon monoxide are formed². Hexafluoroacetone is thus an unambiguous photochemical source of trifluoromethyl radicals, and the close structural similarity of 1 : 3-dichlorotetrafluoroacetone has prompted an investigation into its suitability as a source of difluorochloromethyl radicals.

The near ultra-violet absorption spectrum of 1 : 3-dichlorotetrafluoroacetone shows a broader and more intense band than does that of acetone (λ_{\max} , 2,900–3,100, ϵ_{\max} , 80, cf. acetone λ_{\max} , 2,700–2,800, ϵ_{\max} , = 16). A preliminary study of the photolysis of this ketone, at room temperature, using a high-pressure mercury lamp, has indicated that the primary step in this case is also dissociation into two identical radicals and a molecule of carbon monoxide. This conclusion is based upon the absence among the secondary products of reaction of any species which could have arisen from the difluorochloroacetyl radical, for example, tetrafluorodichlorodiacyl.

The photodecomposition of dichlorotetrafluoroacetone is, however, more complex than that of hexafluoroacetone because the chlorodifluoromethyl radicals formed in the primary step are capable of abstracting chlorine atoms present in the undissociated ketone. Thus in the products of photolysis there appears, in addition to the *sym.*-dichlorotetrafluoroethane formed by the dimerization of chlorodifluoromethyl radicals, a smaller concentration of dichlorodifluoromethane. These two compounds have been isolated from the reaction products by means of gas chromatography, and their identity has been confirmed by comparison of their properties,