BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 554 (1969)

Zirconium Ethoxide: A New Method of Preparation

S. K. ANAND, J. J. SINGH, R. K. MULTANI and B. D. JAIN

Department of Chemistry, University of Delhi, Delhi-7, India

(Received May 10, 1968)

Meerwein and Bersin[1] could not obtain zirconium tetraethoxide by the interaction between zirconium tetrachloride and sodium ethoxide in anhydrous alcohol due to the formation of $NaH[Zr(OEt)_6]$ which in the presence of dry HCl gas however gave zirconium tetraethoxide. Bradley and Wardlaw,[2,3] prepared $Zr(OEt)_4$ by the action of dry ammonia on solutions of zirconium tetrachloride in appropriate alcohol. The above methods involve the use of anhydrous alcohol, the preparation of which is quite tedious.

It is well known that most of the alkyl esters of fatty acids react with ammonia and form corresponding alcohols and acid amides. This property of the esters has been utilised for the preparation of a number of metal alkoxides. The present communication deals with the preparation of zirconium tetraethoxide by the interaction of anhydrous zirconium tetrachloride in dry benzene with ethyl formate, ethyl acetate or diethyl oxalate in the presence of dry ammonia, whereby the alcohol which is formed in the above reaction is itself used in the formation of metal alkoxide.

Through benzene dried azeotropically, containing anhydrous zirconium chloride and ester-dried over anhydrous magnesium sulphate (quantities given in Table 1) placed in a two necked one litre quickfit flask fitted with a reflux condenser, dry ammonia was passed. As the reaction was exothermic in all cases, ice bath was used to prevent the loss of benzene and the lower esters. On the completion of the reaction and after the removal of dissolved ammonia under reduced pressure, zirconium tetraethoxide was obtained by distillation at 235°C/5.2 mmHg.

Zirconium in the alkoxide was estimated as ZrO_2 and ethoxy group was determined by the chromic acid method.[4,5]

From the analytical data (given in Table 1), the composition of the compound obtained in all the cases studied above corresponds to $Zr(OC_2H_5)_4$.

Although a large number of workers,[6,7] have prepared metal alkoxides by the ammonia method no definite information regarding the role of ammonia in the reaction has been reported and it is generally believed that it acts as a hydrogen chloride acceptor. Fowles and Pollard[8–10] who have studied in detail the behaviour of a number of transition metal halides towards ammonia have reported the formation of various ammoniates and amido chlorides of these metsls. In order to ascertain the role of ammonia in the above reactions the formation of the above intermediates during the preparation of zirconium tetraethoxide by the present method is also under investigation.

TABLE 1

Ester	Ester taken (g)	$ZrCl_4$ taken (g)	Benzene taken (g)	Yield %	Analysis of Zr-ethoxide found	
					%Zr	$\%OC_2H_5$
Ethyl formate	10.5	1.1	550	60—65	33.52	66.25
Ethyl acetate	16.0	1.5	500	54—57	33.65	66.18
Diethyl oxalate	10.0	0.9	400	49—51	33.55	66.25

Calcd for $Zr(OC_2H_5)_4$: Zr, 33.63; OC_2H_5, 66.37%.

1) H. Meerwein and T. Bersin, *Ann.*, **476**, 113 (1929).
2) D. C. Bradley and W. Wardlaw, *Nature*, **75**, 165 (1950).
3) D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, **1951**, 280.
4) C. A. Adams and J. R. Nicholls, *Analyst*, **54**, 2 (1929).
5) D. C. Bradley, F. M. Abdel Halim and W. Wardlaw, *J. Chem. Soc.*, **1950**, 3450.
6) D. C. Bradley, "Progress in Inorganic Chemistry," Vol. II, ed. by F. A. Cotton, Interscience Publishers, Inc., New York (1960), p. 303.
7) R. C. Mehrotra, Proc. 54th Ind. Sci. Cong. (Hyderabad) Part II, 1967.
8) G. W. A. Fowles and F. H. Pollard, *J. Chem. Soc.*, **1952**, 4938.
9) G. W. A. Fowles and F. H. Pollard, *ibid.*, **1953**, 4128.
10) G. W. A. Fowles and F. H. Pollard, *ibid.*, **1953**, 2588.