

8. *Reactions of Zirconium t-Butoxide with Acetyl Chloride and Zirconium Tetrachloride with t-Butyl Acetate.*

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The reactions of zirconium tetra-t-butoxide with acetyl chloride have been studied. The replacement of the first t-butoxide group is slow, but with further replacement side reactions occur resulting in the formation of acetate derivatives. The conclusion has been confirmed by a detailed study of the reactions between zirconium tetrachloride and t-butyl acetate in different stoichiometric ratios. A plausible mechanism of the reaction has been suggested.

In a detailed study of the reactions of zirconium alkoxides with acetyl chloride, Bradley *et al.*^{1,2} showed that the primary and secondary alkoxides reacted readily with the stoichiometric replacement of the alkoxide groups by chloride, and with excess of acetyl chloride, the tetrachloride (with esters of addition) was the final product. However, the reactions of zirconium tertiary alkoxides with acetyl chloride were complicated and although the replacement of the first tertiary alkoxide group is easy, further replacement becomes slow and does not proceed to completion even at higher temperatures with an excess of acetyl chloride. The exceptional behaviour of the tertiary alkoxides was attributed to steric factors in a general way, although it could also be argued that the steric factors should be most operative in the replacement of the first alkoxide group.

In a recent study³ of the reaction of silicon tetrachloride with t-butyl acetate, it has been found that silicon tetra-acetate is formed at room temperature in quantitative yield and similarly it has been shown⁴ that the reaction of aluminium trichloride with t-butyl acetate under refluxing conditions leads to aluminium triacetate. In view of the above a

¹ Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

² Bradley, Halim, Mehrotra, and Wardlaw, *J.*, 1952, 4609.

³ Mehrotra and Pant, *Tetrahedron Letters*, 1963, 5, 321.

⁴ Mehrotra and Misra, *Canad. J. Chem.*, 1964, 42, 717.

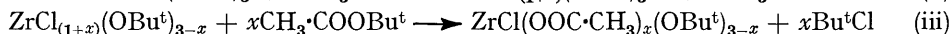
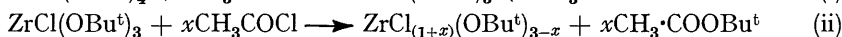
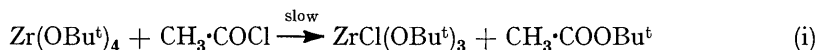
TABLE I.
Reactions between $Zr(OBu^t)_4$ and CH_3COCl .

Molar ratio	Reaction mixture	Conditions	Nature	Analysis						
				Found			Calc.			
				Zr (%)	Cl (%)	Cl/M	Alk. eq.	Zr (%)	Cl (%)	Alk. eq.
1 : 1	$Zr(OBu^t)_4$ (2.37 g.) CH_3COCl (0.48 g.) in benzene (15.6 g.)	Carried at 0—5° shaking well. Kept overnight (27°)	White (foamy) solid (2.20 g.)	26.0	6.8	0.7	0.7	25.5	6.9	0.7
1 : 2	$Zr(OBu^t)_4$ (1.58 g.) CH_3COCl (0.66 g.) in benzene (8.0 g.)	Reaction at 0—5°. Kept overnight (40°)	$ZrCl_{1.7}(OBu^t)_{1.3}$ White solid (crystalline) (1.43 g.)	27.9	13.1	1.2	2.0	27.9	13.0	2.0
1 : 3	$Zr(OBu^t)_4$ (2.02 g.) CH_3COCl (1.25 g.) in benzene (7.20 g.)	Reaction at 0—5°. Kept overnight (27°)	$ZrCl_{1.2}(OAc)_{0.8}(OBu^t)_2$ White (foamy) crystalline solid (1.78 g.)	29.9	12.4	1.09	2.9	28.9	12.4	3.0
1 : 4	$Zr(OBu^t)_4$ (1.17 g.) CH_3COCl (0.96 g.) in benzene (12.9 g.)	Reaction at 0—5° shaking well. Kept overnight (27°)	$ZrCl_{1.1}(OAc)_{1.9}(OBu^t)$ White foamy solid (1.02 g.) $ZrCl_{1.1}(OAc)_{2.3}(OBu^t)_{0.6}$	29.7	12.4	1.09	3.4	29.4	12.6	3.4
1 : 4.5	$Zr(OBu^t)_4$ (2.67 g.) CH_3COCl (2.46 g.) in benzene (14.6 g.)	Reaction at 0—5°. Kept overnight (27°)	Light yellowish white solid (2.32 g.)	29.6	12.5	1.09	3.7	29.8	12.7	3.7
1 : 6	$Zr(OBu^t)_4$ (0.88 g.) CH_3COCl (1.08 g.) in benzene (20.0 g.)	Reaction at 0—5° shaken well, refluxed (90°/3 hr.)	$ZrCl_{1.1}(OAc)_{2.6}(OBu^t)_{1.3}$ Orange yellow crystalline solid (0.709 g.) $ZrCl(OAc)_3$	30.3	11.6	1.0	3.8	30.0	11.6	3.9

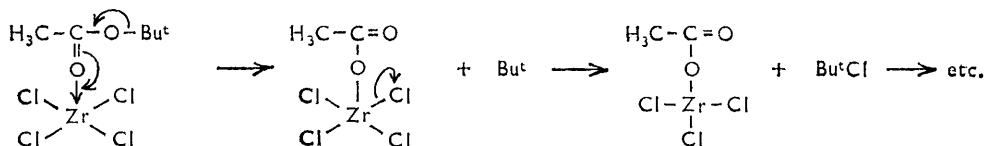
TABLE 2.
Reactions of $ZrCl_4$ and t-BuOAc.

Molar ratio	Reaction mixture	Conditions	Nature	Analysis						
				Found			Calc.			
				Zr (%)	Cl (%)	Cl/M	Alk. eq.	Zr (%)	Cl (%)	Alk. eq.
1 : 1	$ZrCl_4$ (1.00 g.) $tBuOAc$ (0.50 g.) in benzene (17.6 g.)	Reaction at 0—5°. Kept for 4 hr. (25°)	White solid (1.20 g.) $ZrCl_3(OAc)$	34.8	41.6	3.0	4.0	35.5	41.4	3.9
1 : 2	$ZrCl_4$ (1.23 g.) $tBuOAc$ (1.24 g.) in benzene (14.8 g.)	Reaction at 0—5°. Kept overnight (25°)	White crystalline solid (1.55 g.) $ZrCl_3(OAc)_2$	32.2	25.0	2.0	3.8	32.5	25.3	3.9
1 : 3	$ZrCl_4$ (0.87 g.) $tBuOAc$ (1.31 g.) in benzene (18.16 g.)	Reaction at 0—5°. Kept overnight (25°)	White crystalline solid (1.18 g.) $ZrCl_{1.3}(OAc)_{2.7}$	30.7	15.5	1.3	3.8	30.7	15.5	3.9
1 : 4	$ZrCl_4$ (0.57 g.) $tBuOAc$ (1.14 g.) in benzene (19.3 g.)	Reaction at 0—5°. Kept overnight (25°)	White crystalline solid (0.74 g.) $ZrCl(OAc)_3$	31.3	13.3	1.08	4.0	30.0	11.6	3.9
1 : large excess	$ZrCl_4$ (2.14 g.) $tBuOAc$ (33.0 g.) without solvent	Reaction at 0—5°. Kept overnight (25°)	White solid (2.18 g.) $ZrCl_{1.4}(OAc)_{3.6}$	30.1	4.8	0.39	3.8	28.7	4.5	3.9
1 : large excess	$ZrCl_4$ (3.56 g.) $tBuOAc$ (25.0 g.) without solvent	Refluxed 110°/6 hr.	White solid (4.50 g.) $ZrCl_{1.2}(OAc)_{3.8}$	29.5	2.3	0.19	3.8	28.3	2.2	3.9

reinvestigation of the reaction of zirconium tetra-*t*-butoxide with acetyl chloride was undertaken. The results (Table 1) show that the replacement of the first *t*-butoxide group is slow, but with further replacement [eqn. (ii)] a side reaction occurs according to equation (iii):



The correctness of the latter side reaction has been confirmed by a detailed study of the reactions between zirconium tetrachloride and *t*-butyl acetate. The results (Table 2) show that the reaction is exothermic and facile up to the formation of the dichloride diacetate and becomes slow afterwards; the replacement of the last chlorine atom requires refluxing with excess of *t*-butyl ester. The most plausible mechanism of this reaction could be represented as below:



The initial co-ordination is shown through the carbonyl oxygen atom of the organic ester in view of the infrared studies of Lappert.⁵ However, the lower alkoxides have been shown⁶ to react with *t*-butyl acetate with the formation of the *t*-butoxide of zirconium and in such reactions, the co-ordination through the alkoxy-oxygen appears to lead to a more plausible mechanism. It may be that owing to the +*I* inductive effect of the *t*-butyl group the nature of co-ordination becomes different from that in esters of primary alcohols but this point can be decided only after actual physicochemical studies.

Evidence in favour of this mechanism has been derived by collecting the *t*-butyl chloride formed in the reaction between zirconium tetrachloride and excess of *t*-butyl acetate in an almost quantitative yield.

EXPERIMENTAL

All-glass apparatus was used with precautions to exclude moisture. Zirconium *t*-butoxide and *t*-butyl acetate were prepared and purified as described.⁶ Zirconium tetrachloride used was a sublimed (E. Merck) product.

Analysis.—Methods of elemental analysis were as already described.² Acetoxy-group was estimated by back titration. Initially it was tested that zirconium tetrachloride as well as tetra-acetate require 3.9 equiv. of sodium hydroxide with phenolphthalein as indicator. This is not unexpected in view of the earlier observations of Britton⁷ and Kapoor and Mehrotra⁸ that the potentiometric titration of zirconyl chloride (ZrOCl_2) with sodium hydroxide shows an inflexion at 1.8 equiv. of alkali and the pH of the solution assumes a value of about 9–10 with 1.9 equiv. of alkali. In the absence of any acetoxy or chloride group (as in the case of zirconium tetra-*t*-butoxide) the aqueous hydrolysis of the product would not produce any acid, and hence the solution becomes alkaline with the first drop of alkali. This has been tested by titrations with phenolphthalein as indicator. On the basis of these observations, the number of acid (acetoxy + chloride) groups attached per zirconium atom in a particular derivative has been estimated by alkalimetric titrations, as the *t*-butoxide group would not interfere in these titrations; the chloride groups per gram atom of zirconium have been separately determined by gravimetric estimation as silver chloride.

Reactions between Zirconium t-Butoxide and Acetyl Chloride (Table 1).—Since preliminary trials showed that the reaction between acetyl chloride and zirconium tetra-*t*-butoxide is highly

⁵ Lappert, *J.*, 1961, 817; 1962, 542.

⁶ Mehrotra, *J. Amer. Chem. Soc.*, 1954, **76**, 2266.

⁷ Britton, "Hydrogen Ions," Chapman and Hall Ltd. (London), Vol. II, 1956, pp. 77–82.

⁸ Kapoor and Mehrotra, *Z. anorg. allg. Chem.*, 1957, **293**, 100; *J. Sci. Ind. Res. India*, 1957, **16B**, 300; *J. Amer. Chem. Soc.*, 1958, **80**, 3569.

exothermic, these were carried out at lower temperatures to avoid any early side reactions. Acetyl chloride (in required ratio) was admitted in a clear solution of zirconium *t*-butoxide in benzene at 0–5°. After being shaken well, it was either allowed to stand overnight at room temperature (27–30°) or gently refluxed. The solid products were obtained by distilling the volatile fractions from the reaction mixture under reduced pressure. Except for the soluble product obtained in 1 : 1 molar ratio, all were found to be insoluble in benzene but soluble in water with hydrolysis.

Reactions between Zirconium Tetrachloride and t-Butyl Acetate (Table 2).—The general procedure was as described above. All the products were insoluble in benzene. For the isolation of *t*-butyl chloride assumed to be formed in these reactions, zirconium tetrachloride was heated with *t*-butyl acetate (1 : >4) in the absence of any solvent. *t*-Butyl acetate (25.0 g.) was thoroughly shaken with zirconium tetrachloride (4.80 g.) at 0–5°. The colour of the reaction mixture changed from colourless to pink and finally violet as the temperature was gradually raised. A colourless liquid (4.0 g.) was distilled (bath temperature (86–100°) from the reaction mixture. The distillate was further subjected to a careful fractionation in a semimicro variable take-off still-head, when a colourless liquid (3.8 g.) was collected at 51–52° (Found: Cl, 38.30. Calc. for C₄H₉Cl: Cl, 38.37%).

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