Contribution from the Chemical Laboratories,
University of Rajasthan, Jaipur-4, India

Reactions of Oximes with Zirconium Isopropoxide

A. Singh, A.K. Rai, and R.C. Mehrotra*

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Zirconium isopropoxide isopropanolate reacts with various oximes in refluxing benzene to give complexes of the formula, $Zr(OPr)^i_{4-x}(ON = CR^1R^2)_x$ *(*$x = 1$*-*4*;* $R^1 = Me, Et$*;* $R^2 = Me, Et, Pr^n, Pr^i, Ph$*;* $R^1 = R^2 = (CH_2)_5$*. Ebullioscopic molecular weight measurements in benzene show that some of these derivatives are polymeric in nature. I.r. spectra have been recorded and some probable assignment have been made.*

Introduction

Many zirconium compounds having Zr-O-C[1-3] bonds have been reported. Little is known about compounds containing Zr-O-N bonds. Derivatives of titanium with various oximes[4] have been studied, in these laboratories. Similar studies are also reported in case of Zn[5-6], Sn[7], Si[8], As[9], B, Al Ga, In and Tl[10-11] but there appears to be no reference in the literature to oxime derivatives of zirconium.

Results and Discussion

Zirconium isopropoxide isoproponalate was treated with acetoxime, ethylmethyl, diethyl, isopropyl methyl ketoximes in different stoichiometric ratios (1:1, 1:2, 1:3 and 1:4) and methyl propyl ketoxime, cyclohexanone oxime in molar ratios 1:4 only in anhydrous benzene. Isoproponal produced during the course of the reactions was removed azeotropically with benzene and progress of the reactions was followed by estimating the amount of isoproponal fractionated out:

$$Zr(OPr^i)_4 . Pr^iOH + xR^1R^2C{=}NOH \xrightarrow[\text{Reflux}]{\text{Benzene}} Zr(OPr^i)_{4-x}(ON{=}CR^1R^2)_x + (x+1)Pr^iOH$$

$(x=1\text{-}4,\ R^1=Me, Et;\ R^2=Me, Et, Pr^n, Pr^i, Ph;\ R^1R^2=(CH_2)_5)$

Table I. I.r. spectra (cm^{-1}) of products of the reactions of oximes with zirconium isopropoxide.[a]

$Zr(OPr^i)_3(ON:CMe_2)$ [b]:	3340-3260w,br, 2910s, 2882s, 2828s, 1640w(A), 1612vw(B). 1464s. 1452s, 1378s, 1340m, 1270w, 1165s, 1145s, 1130s, 1083m, 1025s, 1015s, 975m, 954s,br(C), 845m, 825m, 722w, 670sh, 660m, 650m, 625sh, 604m, 560s(D), 535m(D), 505s(D), 483sh(D), 470s, 455s(D), 415s.
$Zr(OPr^i)_2(ON:CMe_2)_2$ [b]:	3400-3200w,br, 2929s, 2897s, 2827s, 1647w(A), 1612w(B), 1463s, 1452s, 1380s, 1270m, 1168s, 1138s, 1125s, 1092m, 1022sh, 1012m, 992s, 976s, 962s, 952s(C), 938s(C), 922s(C), 850w, 825m, 725w, 672sh, 625m, 570s(D), 535m(D), 507s(D), 476s, 452s(D), 422s.
$Zr(OPr^i)(ON:CMe_2)_3$ [b]:	3300-3140w,br, 2930s, 2900s, 2840s, 1647m(A), 1612w(B), 1465s, 1455s, 1380s, 1270m, 1172m, 1136m, 1122s, 1090s, 1075m, 1000s, 975s, 945s(C), 935s(C), 852m, 823w, 723w, 683m, 673m, 642m, 625s, 572s(D), 530m(D), 505s(D), 485s(D), 475s, 450s(D), 420s.
$Zr(ON:CMe_2)_4$ [b]:	3300-3160w,br, 2927s, 2900s, 2830s, 1645w(A), 1614w(B), 1465s, 1455s, 1380s, 1268m, 1170w, 1120w, 1090m, 1075m, 1035w, 1000m, 980s, 948m(C), 850w, 824w, 724w, 680m, 674m, 666w, 644m, 628m, 575w(D), 530 m(D), 510m(D), 492s(D), 480s, 452m(D).
$Zr(OPr^i)_3(ON:CMePr^i)$ [b]:	3400-3266m,br, 2954s, 2919s, 2850s, 1648w(A), 1618w(B), 1448m, 1364m, 1350m, 1260w, 1228w, 1162m, 1126m, 1081m, 1008m,br, 948m(C), 885m, 762w, 606m, 539m(D), 514s(D), 496s(D), 461s(D).
$Zr(OPr^i)_2(ON:CMePr^i)_2$ [b]:	3354-3238m,br, 2955s, 2921s, 2854s, 1653w(A), 1618w(B), 1450m, 1372m, 1354m, 1266w, 1230w, 1161m,br, 1126m, 1081m, 1006s,br, 950s(C), 881m, 811w, 776w, 726w, 670m, 641m, 611m, 500s(D), 451s,br(D).
$Zr(OPr^i)(ON:CMePr^i)_3$ [b]:	3300-3217m,br, 2964s, 2925s, 2864s, 1650w(A), 1622m(B), 1465m, 1450s, 1373m, 1351m, 1260w, 1230w, 1165m, 1150m, 1130m, 1100m, 1083s, 1005s, 965sh, 950s(C), 854m, 816w, 800w, 775w, 720w, 666sh, 645m, 610m, 588m, 500(D), 455s(D).
$Zr(ON:CMePr^i)_4$ [b]:	3275m,br, 2965s, 2919s, 2901s, 2860s, 1619m(A), 1589vw(B), 1464s, 1450s, 1374s, 1356s, 1270w, 1263w, 1230w, 1178w, 1151m, 1123sh, 1086s, 1008s, 961s, 948s(C), 883m, 800w, 774w, 766w, 733w, 718w, 670w, 641m, 613s, 588m,br, 542sh, 500s(D), 462s(D).
$Zr(ON:CEt_2)_4$ [b]:	3305-3255m,br, 2964s, 2919s, 2864s, 1628m(A), 1596w(B), 1455s, 1368s, 1330m, 1271w, 1251w, 1218w, 1201w, 1166w, 1150w, 1132m, 11104s, 1079m, 1048m, 1031s, 1004s, 970s, 936s(C), 886w, 821w, 781m, 759w, 716w, 669s, 621s, 589s, 506s(D), 476s(D), 459s(D), 430s.
$Zr(ON:CMePr^n)_4$(neat):	3315-3230m,br, 2974s, 2940s, 2883s, 1633m(A), 1600w(B), 1460s, 1428s, 1378s, 1360s, 1292w, 1258w, 1158w, 1108m,br, 1048m, 1010s,br, 915s(C), 863w, 813w, 773m, 736m, 671s, 643s, 614s, 591s, 518s(D), 473s,br(D).

[a] Abbreviations: A, terminal ν(C=N); B, bridging ν(C=N); C, ν(N-O); D, ν(Zr-O). [b] Compounds scanned in Nujol unless otherwise indicated.

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Table II. Reactions of Zirconium isopropoxide isopropanolate with various oximes.

	Reactants						Analysis %			
Comp. No.	$Zr(OPr^i)_4 \cdot Pr^iOH$ (g)	Oximes (g) $R^1R^2C{=}NOH$	Molar Ratio	Refluxing hours	Products,* Yield[a] (%), and Nature[b]	Alcohol liberated (g) Found (Calc.)	Found (Calc.) Zr	Found (Calc.) N	Molecular weight[c] Found (Calc.)	Degree of association.
1.	2.76	$Me_2C{=}NOH$ 0.52	1:1	2	$Zr(OPr^i)_3(ON{=}CMe_2)$	0.85 (0.86)	27.33 (26.78)	4.40 (4.10)	1040 (341)	3.0
2.	4.52	$Me_2C{=}NOH$ 1.71	1:2	2	$Zr(OPr^i)_2(ON{=}CMe_2)_2$	2.09 (2.10)	26.58 (25.80)	8.10 (7.90)	843 (354)	2.4
3.	4.76	$Me_2C{=}NOH$ 2.69	1:3	2.5	$Zr(OPr^i)(ON{=}CMe_2)_3$	2.95 (2.95)	25.60 (24.88)	11.40 (11.46)	952 (367)	2.6
4.	4.01	$Me_2C{=}NOH$ 3.02	1:4	4	$Zr(ON{=}CMe_2)_4$	3.06 (3.10)	24.49 (24.04)	14.42 (14.70)	585 (380)	1.5
5.	3.74	$MeEtC{=}NOH$ 0.85	1:1	2	$Zr(OPr^i)_3(ON{=}CMeEt)$	1.16 (1.16)	25.96 (25.60)	3.80 (3.95)	1039 (355)	2.9
6.	4.92	$MeEtC{=}NOH$ 2.23	1:2	2	$Zr(OPr^i)_2(ON{=}CMeEt)_2$	2.28 (2.29)	24.41 (23.90)	7.30 (7.30)	1146 (382)	3.0
7.	4.26	$MeEtC{=}NOH$ 2.88	1:3	2.5	$Zr(OPr^i)(ON{=}CMeEt)_3$	2.64 (2.64)	22.92 (22.33)	10.20 (10.30)	927 (409)	2.3
8.	4.50	$MeEtC{=}NOH$ 4.05	1:4	4	$Zr(ON{=}CMeEt)_4$	3.42 (3.49)	21.24 (20.90)	12.53 (12.80)	563 (436)	1.3
9.	4.65	$Et_2C{=}NOH$ 1.23	1:1	2	$Zr(OPr^i)_3(ON{=}CEt_2)$	1.42 (1.44)	24.83 (24.73)	3.80 (3.80)	1030 (369)	2.8
10.	4.68	$Et_2C{=}NOH$, 2.45	1:2	2	$Zr(OPr^i)_2(ON{=}CEt_2)_2$	2.12 (2.18)	22.40 (22.25)	6.70 (6.80)	960 (410)	2.3
11.	3.44	$Et_2C{=}NOH$, 2.70	1:3	2.5	$Zr(OPr^i)(ON{=}CEt_2)_3$	2.10 (2.13)	20.34 (20.22)	9.20 (9.30)	990 (451)	2.2
12.	4.87	$Et_2C{=}NOH$, 5.10	1:4	4.5	$Zr(ON{=}CEt_2)_4$	3.70 (3.77)	18.68 (18.54)	11.30 (11.40)	569 (492)	1.2
13.	2.81	$MePr^iC{=}NOH$ 0.74	1:1	2	$Zr(OPr^i)_3(ON{=}CMePr^i)$	0.84 (0.87)	24.88 (24.73)	3.70 (3.80)	994 (369)	2.7
14.	4.20	$MePr^iC{=}NOH$ 2.20	1:2	2.5	$Zr(OPr^i)_2(ON{=}CMePr^i)_2$	1.94 (1.96)	22.36 (22.25)	6.80 (6.80)	975 (410)	2.4
15.	5.89	$MePr^iC{=}NOH$ 4.68	1:3	3	$Zr(OPr^i)(ON{=}CMePr^i)_3$	3.64 (3.65)	20.32 (20.22)	9.20 (9.30)	926 (451)	2.0
16.	4.67	$MePr^iC{=}NOH$ 4.89	1:4	4.5	$Zr(ON{=}CMePr^i)_4$	3.58 (3.62)	18.68 (18.54)	11.30 (11.40)	541 (492)	1.1
17.	5.81	$MePr^nC{=}NOH$ 0.06	1:4	4	$Zr(ON{=}CMePr^n)$ highly viscous liquid.	4.46 (4.49)	18.65 (18.54)	11.20 (11.40)	570 (492)	1.2
18.	2.96	$\underline{CH_2(CH_2)_4C}{=}NOH$ 3.46	1:4	4	$Zr(ON{=}\underline{C(CH_2)_4CH_2})_4$	2.26 (2.30)	17.12 (16.90)	10.30 (10.38)	[d]	
19.	1.91	$MePhC{=}NOH$ 2.66	1:4	4	$Zr(ON{=}CMePh)_4$	1.46 (1.48)	14.62 (14.53)	8.80 (8.90)	[d]	

[a] All products were obtained in quantitative yields (i.e. yields >97% in each case). [b] All the compounds are white solids except No. 5 (white pasty solid), No. 9 and 17 (yellowish white solids). [c] Ebulliometrically in benzene. [d] Not determined. * The following abbreviations are used: Me = CH_3, Et = C_2H_5, Pr^n = n-C_3H_7, Pr^i = iso-C_3H_7, Bu^n = n-C_4H_9, Bu^i = iso-C_4H_9, Ph = C_6H_5.

These xirconium oximates are isolated in quantitative yields. These derivatives are generally colourless solids (sometimes with a yellowish tinge), except $Zr(ON = CMePr_n)_4$ which is a highly viscous liquid. All these derivatives are soluble in common organic solvents and are polymeric (degree of polymerisation varies from 1.1 to 3, as determined ebullioscopically in benzene). These tend to decompose on being heated even under reduced pressure and are readily hydrolysed by the atmospheric moisture.

Three features are observed when the molecular weights of zirconium oximates are compared with the corresponding derivatives of titanium[4]: (a) that the molecular complexities of the zirconium oximates are greater than those of corresponding titanium oximates, probably due to greater atomic radius of zirconium and its higher maximum coordination number; (b) that molecular complexity in the titanium series (all titanium oximates are practically monomers) is not affected by chain length, whereas in the zirconium series molecular complexity depends on chain length and ramification and; (c) that same alkyl groups when attached to the imino carbon atom offer more shielding effect than when attached to the carbinol carbon atom.

Ir. spectra. The tentative i.r. assignments for some structurally significant bands (Table I) have been made on the basis of published data about oximes[12-14] and zirconium isopropoxide.[15] Although precautions were taken to avoid contact with atmospheric moisture during sampling, some hydrolysis occurs as evidenced by absorptions in the range 3437-3280 cm^{-1}.

Two weak to medium intensity absorption bands at 1643 ± 10 cm^{-1} and 1609 ± 13 $^{-1}$ are observed in the C=N stretching region in case of all the zirconium oximates studied. In view of the greater association tendency in these derivatives compared to

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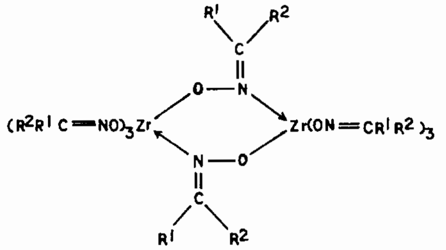
the titanium analogues, and also in view of the presence of two absorptions in the $\nu C=N$ region, the lower $C=N$ absorption occuring yat 1600 ± 13 cm^{-1} in tetra derivatives could be ascribed to the bridging oximino groups in structures of the type:



The higher $C=N$ absorptions at 1643 ± 10 cm^{-1} also are at somewhat lower positions than in the parent oximes themselves, but this lowering is of the same order as observed in the unassociated titanium derivatives. These can, therefore, be assigned to the resonance effects caused by the inductive release of charge from the electropositive zirconium atoms and could thus be assigned to the terminal oximate groups.

Experimental Section

Zirconium isopropoxide isopropanolate was prepared as previously described.[16] Benzene (BDH) was dried over sodium followed by azeotropic fractionation in the presence of ethanol. Oximes were prepared by standard methods. Fractionations were carried out in a column packed with Raschig rings.

Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) using a thermistor sensing.

Nitrogen was estimated by Kjeldahl procedure. Zirconium was estimated gravimetrically as ZrO_2 Isopropanol was estimated by oxidation with N-potassium dichromate in 12.5% sulphuric acid[17] in all cases near quantitative yields were obtained.

I.r. spectra of the above derivatives were recorded in Nujol using KBr optics (Perkin-Elmer 337) in the range of 4000-400 cm^{-1}.

Reactions of Zirconium Isopropoxide Isopropanolate with Oximes. Calculated amounts of oximes are added to the benzene solutions of zirconium isopropoxide. The reaction mixtures were refluxed for six to eight hours and the isopropanol produced was fractionated out azeotropically with benzene. The excess solvent was distilled out and the last traces are removed under reduced pressure, *ca.* 40-50°/0.5-1.0 mm. The alcohol in the azeotrope was estimated. Results of these reactions are summarised in Table II.

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