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Abstract

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INFRARED SPECTRA OF SOME CYCLOPENTADIENYL TITANIUM COMPOUNDS

On the basis of the formation of ferrocene in the reaction of $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$ with $FeCl_2$, and the ease of hydrolysis of the bond between the cyclopentadienyl ring and the metal in these compounds, we (^{1}) suggested that the bond of the titanium atom with the cyclopentadienyl rings in $C_5H_5Ti(OC_2H_5)_3$ and $(C_5H_5)_2Ti(OCOCH_3)_2$ has, to a considerable extent, an ionic character. The possibility of such a type of bond in cyclopentadienyl titanium compounds is also indicated by the closeness of the excitation energy of the valence state and the ionization potential of the central metal atom (^{2}). On the other hand, we showed (^{1}) that, after replacing two or even one ethoxy group in the molecule $C_5H_5Ti(OC_2H_5)_3$ by chlorine atoms, interaction with $FeCl_2$ no longer leads to the formation of ferrocene. In this reaction $C_5H_5Ti(OC_2H_5)_2Cl$ and $C_5H_5Ti(OC_2H_5)Cl_2$ behave similarly to $(C_5H_5)_2TiCl_2$ and $C_5H_5TiCl_3$. Thus, the character of the titanium—cyclopentadienyl-ring bond depends substantially on the nature of the other ligands attached to the central atom. It is known that the ability of titanium compounds to form complexes at the expense of the vacant 3*d* and 4*p* orbitals of the metal and the unshared pairs of electron donors, as well as the stability of the complexes formed, decreases on going from titanium chlorides to its alkoxy derivatives ($^{3-5}$).

A similar regularity may also be expected for titanium π-complexes with cyclopentadienyl (CPD) rings. With increasing electron-donor properties of the ligands, the donor-acceptor interaction of the central atom with the cyclopentadienyl radicals decreases, which should lead to a decrease in the strength and an increase in the degree of ionicity of the titanium—CPD-ring bond.

Continuing the study of the nature of this bond as a function of the ligands attached to the central atom, we measured the infrared spectra in the region from 400 to 4000 cm^{-1} for a series of mono- and dicyclopentadienyl titanium derivatives of the type $C_5H_5TiX_3$ (where $X = -Cl$, $-OCH_3$, $-OC_2H_5$ and $-OCOCH_3$) and $(C_5H_5)_2TiY_2$ (where $Y = -Cl$, $-OCOCH_3$, $-OCOC_2H_5$, $-OCOCH_2Cl$, $-OCOCF_3$) and their derivatives containing alkyl substituents in the cyclopentadienyl rings. Table 1 gives the most characteristic frequencies in their infrared spectra.

Fritz (^{6}), using a large number of cyclopentadienyl compounds of various metals as examples, observed a shift of the band of out-of-plane deformation vibrations of the C—H bonds of cyclopentadienyl rings in infrared spectra to the low-frequency region with increasing ionicity of the Me—ring bond. In the successive replacement of Cl atoms in the $C_5H_5TiCl_3$ molecule by ethoxy groups, we also observed an analogous shift of this band from 838 cm^{-1} in $C_5H_5TiCl_3$ to 806 cm^{-1} in $C_5H_5Ti(OC_2H_5)_3$ and $C_5H_5Ti(OCH_3)_3$.

At the same time, the 415 cm^{-1} band in the spectrum of $C_5H_5TiCl_3$, assigned by Fritz (^{7}) to antisymmetric vibrations of the Me—ring bond, is also shifted in the series of compounds under consideration to the low-frequency region: in the spectrum of $C_5H_5TiCl_2(OC_2H_5)$ a band is observed at 407 cm^{-1}, in the spectrum of $C_5H_5TiCl(OC_2H_5)_2$ a shoulder at 390 cm^{-1}, while in the spectrum of $C_5H_5Ti(OC_2H_5)_3$ there is no absorption in the region 390-420 cm^{-1}.

The infrared spectra of alkyl orthotitanates have been considered in a number of previous studies (^{8},^{9}). However, the authors of these works did not study the region

Table 1

Some characteristic frequencies in the IR spectra of cyclopentadienyl titanium compounds (cm^{-1})

Compound	Ti—C_5H_5	Frequencies of vibrations of cyclopentadienyl rings	Ti—O—R	Ti—O—COR
$C_5H_5TiCl_3$	415	838; 1020; 1042; 1372; 1440; 3098, 3415	—	—
$C_5H_5TiCl_2(OC_2H_5)$	407	835; 1016—1022; 1382; 1438; 3096, 3415	602—615; 1073	—
$C_5H_5TiCl(OC_2H_5)_2$	390	815; 1019; 1378; 1445; 3100	597—615; 1070	—
$C_5H_5Ti(OC_2H_5)_3$	—	806; 1021; 1379; 1443; 3400, 3410	595—615; 1070	—
$C_5H_5Ti(OCOCH_3)_3$	—	807; 1018—1022; 1375; 1445; 3095, 3420	—	545; 1260, 1440; 1550, 1725

Compound	Ti–C_5H_5	Frequencies of vibrations of cyclopentadienyl rings	Ti–O–R	Ti–O–COR
$(C_5H_5)_2TiCl_2$	415	822; 1017–1028; 1371; 1443; 3107	–	–
$(C_5H_5)_2Ti(OCOCH_3)_2$	417	822–832; 1020; 1375; 1447; 3095, 3107	–	515–525; 1258; 1631–1645
$(C_5H_5)_2Ti(OCOC_2H_5)_2$	415	815–820; 1015–1020; 1378; 1444; 3098, 3405	–	525–570; 1235–1243; 1629
$(C_5H_5)_2Ti(OCOCH_2Cl)_2$	417	835–845; 1015; 1375; 1440; 3095, 3105	–	522; 1228; 1670
$(C_5H_5)_2Ti(OCOCH_3)_2$	417	833; 1017–1023; 1375; 1446; 3120, 3430	–	492–502; 1408; 1700–1711
$CH_3C_5H_4TiCl_3$	415	835; 1055; 1380; 1451; 3095, 3105, 3124	–	–
$C_5H_5H_7TiCl_3$	415	840; 1060; 1382; 1440, 1496; 3100, 3415	595–610; 1075, 1110	–
$CH_3C_5H_4TiCl_2(OC_2H_5)$	407	830–840; 1055; 1380; 1449, 1497; 3090, 3105	600–615; 1073, 1112	–
$CH_3C_5H_4TiCl(OC_2H_5)_2$	–	816; 1053; 1379; 1446, 1500; 3090, 3100	595–615; 1070, 1115	–
$CH_3C_5H_4Ti(OC_2H_5)_3$	–	801; 1046; 1375; 1443, 1502; 3400	590–615; 1072, 1120	–

Compound	Ti–C_5H_5	Frequencies of vibrations of cyclopentadienyl rings	Ti–O–R	Ti–O–COR
$C_2H_5C_5H_4Ti(OC_2H_5)_3$	412	806; 1055; 1379; 1448; 3110	–	–
$(CH_3C_5H_4)_2TiCl_2$	408	828; 1017–1029; 1379; 1446; 3095	–	–

spectra below 660 cm^{-1}, and in them there are no data on the Ti–O-bond absorption bands, which are very important for these compounds. In the spectra of the titanium ethoxy derivatives examined by us, along with intense bands in the region 1070–1120 cm^{-1}, characteristic of the C–O bonds of alkoxyl groups, there is observed a broad band with two maxima at 590 and 615 cm^{-1}, the relative intensity of which increases regularly with an increase in the number of ethoxy groups attached to titanium. In this same region an intense broad band is observed in the spectrum of $Ti(OC_2H_5)_4$, and absorption is absent in the spectra of both simple ethers and $C_5H_5TiCl_3$ and $(C_5H_5)_2TiCl_2$. This makes it possible to assign the 590–615 cm^{-1} band to vibrations of Ti–O bonds.

The position of this band in titanium alkoxy derivatives in the region of lower frequencies, compared with the bands characteristic of Ti–O–Ti bonds in the spectrum of polybutoxytitanoxane (820 and 763 cm^{-1}) (9) and in the spectrum of $(C_5H_5)Cl_2Ti{-}O{-}TiCl_2(C_5H_5)$ (780–800 cm^{-1}) (10), is apparently explained by the more double-bond character of the Ti–O–Ti bonds, which is confirmed by the data of an X-ray structural study of $(C_5H_5)Cl_2Ti{-}O{-}TiCl_2(C_5H_5)$ (11).

Comparison of the spectra of $(C_5H_5)_2Ti(OCOR)_2$ with the spectrum of $(C_5H_5)_2TiCl_2$ shows the absence of any noticeable change in the position of the band of out-of-plane deformation vibrations of the C–H bonds of the cyclopentadienyl rings···

···due to a change in the character of the ligands attached to the central atom. This is apparently explained by the weaker electron-donor properties of the acetoxy groups in comparison with alkoxy groups. In addition, the influence of the ligand in these compounds is distributed over two cyclopentadienyl rings and is manifested more weakly in the vibrations of each C–H bond. However, with an increase in the ionic character of the Ti–OCOR bond one may expect an increase in the covalent character of the titanium–ring bond. Therefore it is of interest to consider the absorption regions characteristic of the Ti–O-and

$$-\mathrm{OC}^{\mathrm{O}}-$$

groups in these compounds. G. A. Razuvaev, V. N. Latyaeva, and L. I. Vyshinskaya (12) assign the 865 cm^{-1} band in the spectra of $(C_5H_5)_2Ti(OCOCH_3)_2$ and $(C_5H_5)_2Ti(OCOC_6H_5)_2$ to vibrations of the Ti–O bond. However, in the spectrum of $(C_5H_5)_2TiCl_2$ there is a band of medium intensity at 872 cm^{-1}, while in the spectra of $(C_5H_5)_2Ti(OCOCH_2Cl)_2$ and $(C_5H_5)_2Ti(OCOCF_3)_2$ there are no absorption bands in the region 850–900 cm^{-1}. Thus, the assignment of the weak 865 cm^{-1} band in the spectrum of $(C_5H_5)_2Ti(OCOCH_3)_2$ to Ti–O bond vibrations is apparently erroneous. It seems more justified to assign to Ti–O bond vibrations in $C_5H_5Ti(OCOR)_3$ and $(C_5H_5)_2Ti(OCOR)_2$ the broad band of medium intensity in the region 550–500 cm^{-1}, observed in the spectra of all compounds of this type that we examined and absent from the spectra of $C_5H_5TiCl_3$ and $(C_5H_5)_2TiCl_2$. With decreasing electron-donor properties of the OCOR group, this absorption band shifts to the low-frequency region from 550–575 cm^{-1} in $(C_5H_5)_2Ti(OCOC_2H_5)_2$ to 490–500 cm^{-1} in $(C_5H_5)_2Ti(OCOCF_3)_2$. At the same time there is a tendency for the absorption bands of the C=O and C–O bonds to approach one another, characteristic of the transition from an ester to an ionized carboxyl group. If the bands 1631–1645 and 1287–1300 cm^{-1} in the spectrum of $(C_5H_5)_2Ti(OCOCH_3)_2$ are still far from the absorption region of the acetate ion (1560 and 1410 cm^{-1}) (13), then the frequencies 1700 –1710 and 1408 cm^{-1} in the spectrum of $(C_5H_5)_2Ti(OCOCF_3)_2$ are close to the positions of the COO$^-$-group bands in sodium trifluoroacetate (1680 and 1457 cm^{-1}) (13). This indicates an increase in the degree of ionicity of the Ti –OCOR bond on going from $(C_5H_5)_2Ti(OCOCH_3)_2$ to $(C_5H_5)_2Ti(OCOCF_3)_2$. At the same time, the covalent character of the Me–ring bond increases; in reaction with $FeCl_2$, $(C_5H_5)_2Ti(OCOCF_3)_2$, unlike $(C_5H_5)_2Ti(OCOCH_3)_2$, does not give ferrocene.

The presence of alkyl substituents in the cyclopentadienyl rings leads to a change in the position of certain absorption bands associated with ring vibrations. Thus, the band 1017–1025 cm^{-1}, observed in the spectra of all investigated compounds containing free cyclopentadienyl rings, shifts upon substitution to the region 1040–1055 cm^{-1}. The presence of a substituent in the ring also in all cases leads to the appearance of a band at 1500 cm^{-1}, the relative intensity of which increases with an increase in the number of substituted rings (comparison of the spectra of $(C_5H_5)_2TiCl_2$, $(C_5H_5) + CH_3C_5H_4)TiCl_2$, and $(CH_3C_5H_4)_2TiCl_2$). Thus, consideration of the IR spectra in the regions 1000–1060 and 1490–1510 cm^{-1} makes it possible reliably to identify substituted cyclopentadienyl rings in the series of compounds considered.

Experimental Part

The IR spectra of the compounds studied were measured on a double-beam UR-10 IR spectrometer with KBr, NaCl, and LiF prisms. Spectra of solid substances were recorded in pastes with Vaseline oil and fluorinated hydrocarbons. Owing to the extreme sensitivity of most of the substances studied to the action of oxygen and atmospheric moisture, preparation of the samples was carried out in an atmosphere of dry argon.

IR spectra:

$CH_3C_5H_4TiCl_3$ * (mp 98–99°): 415(s), 450(s), 592(w), 602(w), 609(w), 635(w), 835(s), 895–900(m), 934(m), 1042(m), 1055(m), 1074(w), 1248(w), 1380(w), 1441–1451(m), 1496(m), 2852(m), 2919(m), 3093(m), 3105(m), 3124(w).

$C_2H_5C_5H_4TiCl_3$ (b.p. 136°/1 mm): 415(s), 428(s), 455(s), 596(w), 708(m), 780(s), 840(s), 895(m), 915(m), 934(m), 1039(m), 1060(m), 1073(m), 1243(w), 1266(w), 1322(w), 1366(w), 1382(w), 1396(w), 1440(m), 1464(m), 1496(m), 2877(m), 2936(m), 2976(m), 3100–3115(m).

$C_5H_5Ti(OC_2H_5)Cl_2$: 407(s), 445(s), 602–615(m), 711(w), 737(w), 806(s), 835(s), 940(m), 1016–1022(m), 1073(s), 1103(s), 1270(w), 1360(w), 1382(w), 1438(m), 1465(m), 1685(w), 1782(w), 2877(m), 2935(m), 2982(m), 3096(m), 3115(m).

$CH_3C_5H_4Ti(OC_2H_5)Cl_2$*: 407(s), 450(s), 595–610(m), 709(m), 790(s), 830–840(s), 880(m), 937(s), 1040(m), 1055(m), 1075(s), 1110(s), 1244(w), 1270(w), 1354(m), 1380(m), 1449(m), 1497(m), 1700(w), 2873(m), 2930(m), 2980(m), 3100(m).

$C_5H_5Ti(OC_2H_5)_2Cl$: 390(m), 425(m), 597–615(s), 735(w), 815(s), 928(s), 1019(m), 1070(s), 1110(s), 1270(w), 1356(m), 1378(m), 1445(m), 1471(m), 1670(w), 1740(w), 2700(w), 2740(w), 2864(m), 2915(m), 2928(m), 2974(m), 3100(w).

$CH_3C_5H_4Ti(OC_2H_5)_2Cl$* (b.p. 143–145°/2 mm, n_D^{20} 1.5730): 430(s), 600–615(s), 735(w), 780(w), 816(s), 845(m), 853(w), 880(w), 928(s), 1039(m), 1053(m), 1073(s), 1112(s), 1242(w), 1272(w), 1356(m), 1379(m), 1446(m), 1472(m), 1500(m), 1710(w), 2700(w), 2740(w), 2864(s), 2890(m), 2915(m), 2927(m), 2974(s), 3090–3105(w).

$C_5H_5Ti(OC_2H_5)_3$: 427(m), 595–615(s), 758(m), 806(s), 920(s), 1021(m), 1070(s), 1110(s), 1274(w), 1357(m), 1379(m), 1445(m), 1477(m), 1720(w), 2700(w), 2740(w), 2860(s), 2925(s), 2980(s), 3100–3110(w).

$CH_3C_5H_4Ti(OC_2H_5)_3$* (b.p. 85–86°/1 mm; n_D^{20} 1.5398; d_4^{20} 1.0809; *MR*: found 76.07; calculated 75.79): 428(m), 590–615(s), 695(w), 757(m), 801(s), 851(w), 917(s), 1040(m), 1050(m), 1070(s), 1115(s), 1240(w), 1274(w), 1354(m), 1375(m), 1443(m), 1472(m), 1502(m), 1710(w), 2698(w), 2735(w), 2852(s), 2918(m), 2928(m), 2970(s), 3090–3100(w).

$C_2H_5C_5H_4Ti(OC_2H_5)_3$* (b.p. 101–102°/1 mm; n_D^{20} 1.5359; d_4^{20} 1.0769; *MR*: found 80.35, calculated 80.41): 430(m), 590–615(s), 703(m), 738(s), 760(s), 806(s), 855–864(w), 920(s), 1038(m), 1055(m), 1072(s), 1120(s), 1272(w),

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* Here and below, substances marked with an asterisk were obtained for the first time. The methods of synthesis and the properties of these substances will be published by us in the near future.

1326(w), 1358(m), 1379(s), 1448(m), 1476(m), 1500(m), 1710(w), 2700(w), 2735(w), 2860(s), 2925(m), 2970(s), 3050(w), 3100(w).

$C_5H_5Ti(OCOCH_3)_3$* (m.p. 115–117°): 430(m), 545(s), 620(m), 692(m), 807(s), 829(m), 846(m), 952(m), 1018–1022, 1053(w), 1260(m), 1295(m), 1355(w), 1360(m), 1375(m), 1410(m), 1445(m), 1475(s), 1550(s), 1677(m), 1725(m), 1750(w), 2850(m), 2930(m), 2970(m), 3095(m), 3120(m).

$C_5H_5Ti(OCH_3)_3$ (recorded in the region 700–4000 cm^{-1}; m.p. 50–52°; b.p. 88/1.5 mm): 700(s), 738(s), 760(s), 806(s), 850(m), 916(w), 1019(m), 1100(s), 1155(s), 1268(m), 1365(w), 1375(w), 1443(m), 1730(w), 2812(s), 2888(m), 2915(m), 3050(w), 3100(w).

$(C_5H_5)_2Ti(OCOCH_3)_2$: 417(w), 515(m), 525(m), 595(w), 610(w), 638(m), 866(w), 877(w), 956(w), 1015–1020(m), 1040(w), 1075(m), 1233(s), 1258(s), 1355(s), 1370(s), 1425(w), 1448(m), 1639(s), 1730(w), 2875(w), 2936(m), 2976(m), 3098–3105(m).

$(C_5H_5)_2Ti(OCOCH_3)_2$: 417(m), 515(m), 525(m), 595(w), 610(w), 638(m), 663(w), 822–832(m), 869(w), 941(m), 1020(m), 1287(s), 1300(s), 1321(m), 1375(m), 1447(m), 1585(w), 1631–1645(s), 1731(w), 2860(w), 2935(m), 2970(w), 3095–3107(m).

$(C_5H_5)_2Ti(OCOCH_2Cl)_2$* (m.p. 98–99°): 417(w), 423(w), 450(m), 522(m), 667(w), 696(m), 781(m), 835–845(s), 880(w), 939–948(m), 1015(m), 1033(w), 1070(w), 1190(m), 1228–1243(s), 1330–1345(s), 1375(m), 1413(m), 1440(m), 1670(s), 1750(w), 1900(w), 2880(w), 2960(w), 3095–3105(m).

$(C_5H_5)_2Ti(OCOCF_3)_2$: 417(w), 430(m), 492(m), 502(m), 600(w), 615(m), 692(m), 721(s), 781(m), 833(s), 956(w), 1017–1023(m), 1072(w), 1147(s), 1200(s), 1286(w), 1375(m), 408(s), 1446(m), 1566(m), 1700–1711(s), 1800(w), 1920(w), 3120–3130(m).

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