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3. TITANIUM

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CONTENTS

INTRODUCTION

This article attempts to cover, as comprehensively as possible, developments of titanium chemistry during the 1982 calendar year, with the emphasis reflecting, by and large, the interests of the authors. As done with the previous review [2], the material is presented in terms of areas of interest which have recently been popular. These include preparation and properties of Ti compounds, catalytic reactions involving oxides and various Ti compounds, as well as uses of Ti species in organic reactions. Once again, solid-state aspects have not been treated directly but will be found in connection with other areas of interest. Here, we have found an increasingly

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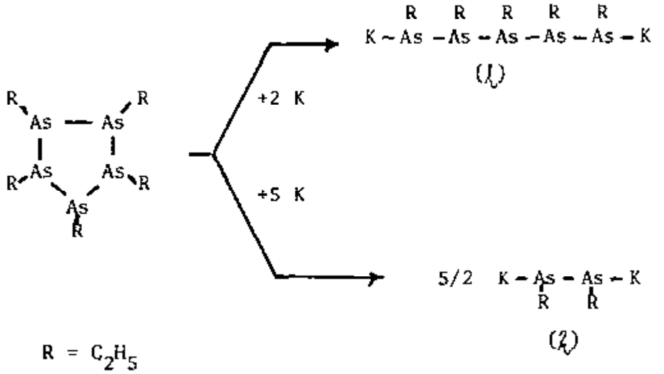
large number of articles. This probably reflects the increased interest in semiconductors and colloids in the catalytic and photocatalytic fields.

Three short reviews have appeared lately. The first deals with properties and applications of metal hydrides in energy conversion systems [3] and the second deals with a brief discussion of the structures, properties, uses, preparation and occurrence of TiO_2 [4], while another deals briefly with optical and paramagnetic properties of titanium in lithium fluoride [5].

We have attempted to cover the material in the major chemical journals, as well as non-chemical journals and the foreign, less well-known journals for the period covered by Chemical Abstracts from Volume 95, number 19 to Volume 97, number 20; in some cases, articles dated pre-1982 and abstracted in these volumes have been considered.

3.1 PREPARATION AND CHARACTERIZATION OF Ti COMPOUNDS

Reaction of cyclopentaarsane, $(AsC_2H_5)_5$, with metallic potassium in THF (1:2 or 1:5 molar ratio) yields $K_2(AsC_2H_5)_5$ (1) or $K_2(AsC_2H_5)_2$ (2), respectively [6]. Both (1) and (2) further react with $(C_5H_5)_2TiCl_2$ in THF to give the dark brown, air-sensitive triarsanato complex $(C_5H_5)_2Ti(AsC_2H_5)_3$(3).

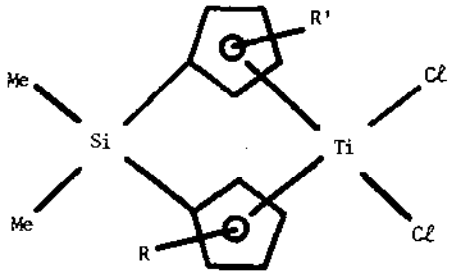


(1)

(2)

(3)

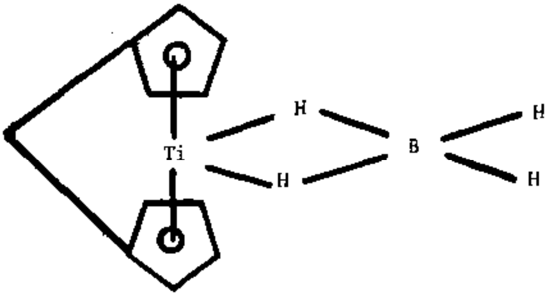
Metallation of $Me_2Si(C_5H_5)(MeC_5H_4)$ or $Me_2Si(MeC_5H_4)_2$ with butyllithium followed by reaction with $TiC\ell_4$ gives ring-substituted titanocenophanes (4) and (5) [7]. Reaction of (5) with NaI produces $Me_2Si(C_5H_4)(MeC_5H_3)TiI_2$.



(4) R = H; R' = Me

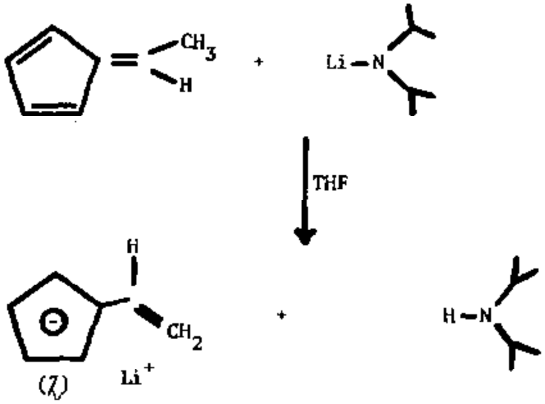
(5) R = R' = Me

The 1,1'-methylenetitanocene tetrahydroborate (6) was synthesized from $CH_2(C_5H_4)_2TiC\ell_2$ with $LiBH_4$ in 78% yield [8]. Exchange of (6) with $LiA\ell H_4$



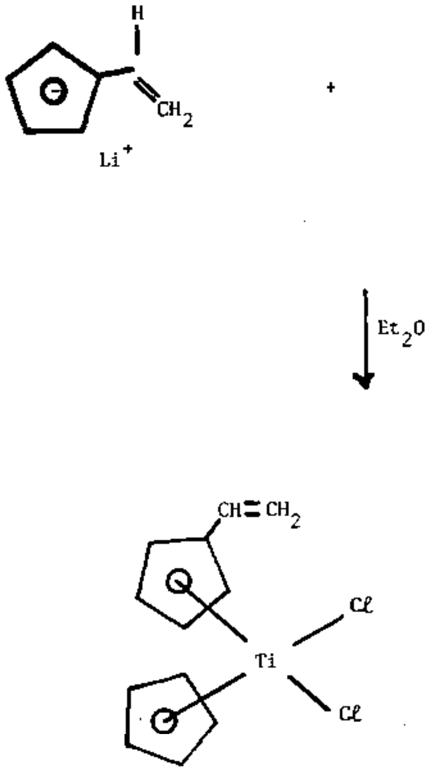
(6)

gives the aluminate analog of (6) in 60% yield. A new convenient method (reactions 4 and 5) has been reported for introducing vinyl substituents directly onto η^5-cyclopentadienyl rings in systems incapable of undergoing



(7)

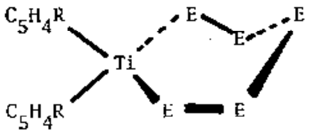
(4)



(5)

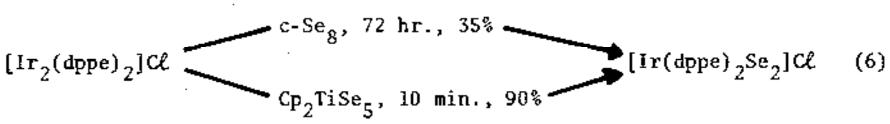
electrophilic aromatic substitution; it uses η^5-cyclopentadienyltrichlorotitanium [9]. For example, 6-methylfulvene reacts with lithium diisopropylamide in THF at 25°C to produce vinylcyclopentadienyllithium (7) in 80-90% yield. Compounds of the type $(\eta^5\text{-}C_5H_5)TiC\ell_2(OC_6H_4X)$, where X = NO_2, Cℓ, CH_3, can be prepared from $CpTiC\ell_3$ and suitable substituted phenols in 1:1 molar ratio in benzene at 353K using Et_3N as a HCℓ-complexing agent [10]. Some of the i.r. and nmr bands of these compounds correlate directly with Hammett σ factors.

$(\eta^5\text{-}C_5Me_5)TiC\ell_3$ reacts with 2-butenylmagnesium bromide at low temperatures to give $(\eta^5\text{-}C_5Me_5)TiL_3$ (L = methallyl), which on heating is readily converted into $(\eta^5\text{-}C_5Me_5)Ti(\eta^3\text{-}L)(\eta^4\text{-}L')$, where L' = butadiene [11]. This compound shows fluxonial behaviour of the η^3-1-methallyl group and is very reactive towards a large variety of organic substrates. Interestingly, $(C_5H_4R)_2TiE_5$ (8,9) (R = H, CH_3;E = S, Se) efficiently transfers a dichalcogenide fragment to $[Ir(Ph_2PCH_2CH_2PPh_2)_2]C\ell$ affording $Ir^{III}E_2$ complexes and in one case $1,4[(C_5H_4CH_3)_2Ti]_2S_4$ [12]. The unique Ti_2S_4 heterocycle can also be prepared *via* the PBu_3 desulfurization of



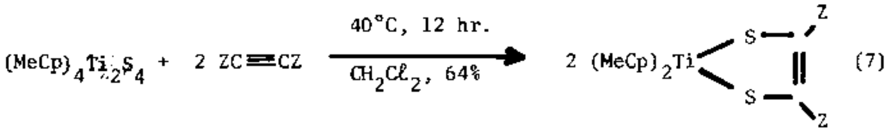
(8a) E = S, R = H
(8b) E = S, R = CH_3
(9a) E = Se, R = H
(9b) E = Se, R = CH_3

$(C_5H_4CH_3)_2TiS_5$. Reaction 6 shows the utility of pentaselenides as conveniently reactive and soluble sources of elemental selenium. Iridium



$$[Ir_2(dppe)_2]C\ell \xrightarrow[Cp_2TiSe_5,\ 10\ min.,\ 90\%]{c\text{-}Se_8,\ 72\ hr.,\ 35\%} [Ir(dppe)_2Se_2]C\ell \qquad (6)$$

desulfurization of (8b) gives $(MeCp)_4Ti_2S_4$ (10), a new compound which reacts with dimethylacetylenedicarboxylate to give (11). Pure, red needles of (10)



(10) $Z = CO_2CH_3$ (11)

can also be obtained in 28% yield by treating (8b) with 3 equivalents of $p(n\text{-}Bu)_3$ in refluxing dichloromethane for 15 minutes [12].

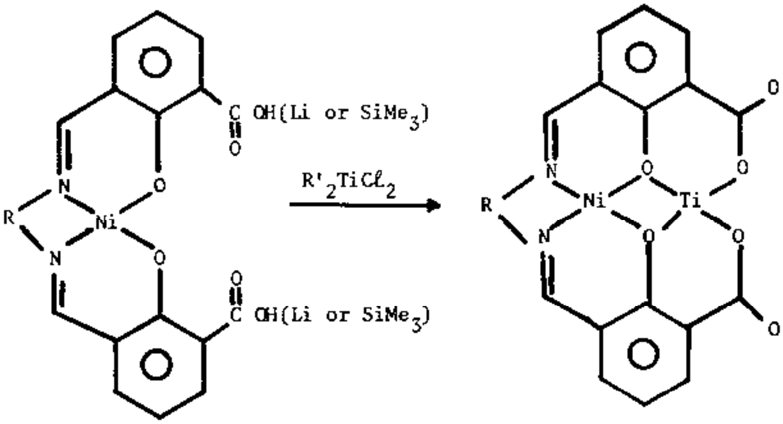
3-buten-1-oxy derivatives of titanium have been synthesized by an alcohol interchange technique [13], reaction 8. These derivatives are

$$Ti(OR)_4 + 4\ CH_2{=}CHCH_2CH_2OH \longrightarrow Ti(OCH_2CH_2CH{=}CH_2)_4 + 4\ ROH \qquad (8)$$
$$R = Et \text{ or } {}^{i}Pr$$

volatile under reduced pressure. They can also be prepared by addition of pyridine to the alkenol before addition of $TiC\ell_4$, followed by treatment with ammonia (reaction 9). A nickel(II) complex of a quadridentate Schiff base,

$$TiC\ell_4 + 4\ CH_2{=}CHCH_2CH_2OH + 4\ NH_3 \longrightarrow Ti(OCH_2CH_2CH{=}CH_2)_4 + 4\ NH_4C\ell \qquad (9)$$

obtained by condensation of 3-formylsalicyclic acid with ethylenediamine $(3\text{-fsaen-}H_4)$, has been employed to prepare a variety of bimetallic-type compounds. For example, 3-fsaen(H_2)M has been successfully silylated and lithiated to obtain 3-fsaen($SiMe_3$)$_2$M and 3-fsaen(Li)M which, in turn, react (reaction 10) with R'TiCℓ_2 to yield compounds of the type 3-fsaenMM'R_2 [14].



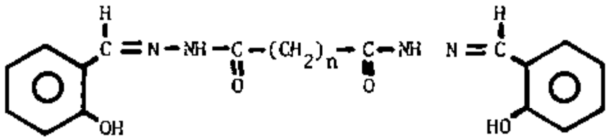
(10)

R' = π-C_5H_5

Compounds of composition $TiC\ell_{4-n}(OPh)_n \cdot 2L$ (n = 1-4) have been prepared by reaction of titanium phenoxides with ligands L (= N-methylacetamide and dimethylacetamide); they are monomeric and non-electrolytes in nitromethane solutions [15]. Based on the magnitude of carbonyl stretching frequency lowering ($\Delta\nu$), the following order of acceptor strength was proposed: $TiC\ell_3(OPh) > TiC\ell_2(OPh)_2 > TiC\ell(OPh)_3 > Ti(OPh)_4$.

Reaction of dichlorobis(η^5-fluorenyl)titanium(IV) with ammonium N-aryldithiocarbamates yields chlorobis(η^5-fluorenyl)-N-aryldithiocarbamato-titanium(IV) compounds of the type $(\eta^5-C_{13}H_9)_2Ti(S_2CNHR)C\ell$, where R is different aryl groups [16]. The diamagnetic compounds are monomeric and non-electrolytes in nitrobenzene; they are stable as solids under an inert atmosphere, and are moisture-sensitive. On the basis of molecular weight, conductance, infrared, and magnetic susceptibility studies, titanium is pentacoordinated with the fluorenyl groups occupying single coordination sites. The monomeric, non-electrolytes chloro(N,N-alkylcyclohexyldithiocarbamato)-bis(η^5-cyclopentadienyl)titanium(IV) compounds, $(\eta^5-Cp)_2Ti(S_2CNRR')C\ell$ (R = Me, Et, ^{i}Pr; R' = cyclohexyl group), can be prepared by reacting stoichiometric amounts of $Cp_2TiC\ell_2$ with sodium salts of dithiocarbamic acids in refluxing dichloromethane [17]; titanium is pentacoordinate and dithiocarbamate acts as a bidentate ligand. Also, reaction of dithiocarbamate salts with $TiC\ell_3$ in ethanol yields a yellow-green solid which shows a 3:1 stoichiometry indicating tris coordination; infrared spectral data indicate the complexes to be bonded through the S atoms and to possess approximate D_{3h} symmetry, with the d^1 state being maintained [18]. The diamagnetic, monomeric and non-electrolyte complexes of the type $Ti(S_2CNRR')_nC\ell_{4-n}$, where R = Et, R' = tolyl and R = H, R' = cyclopentyl and cycloheptyl, have been reported for n = 1-4 in which the coordination is 5, 6, 7 or 8 depending on the value of n [19]. Complexes of titanium(IV) with the methyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid are stereochemically rigid at ambient temperature with respect to the arrangement of the alkoxy groups [20].

Dihydrazones derived from salicylaldehyde and malonodihydrazine ($msdH_2$), succinoyldihydrazine ($ssdH_2$), and adipoyldihydrazine ($asdH_2$) form complexes with titanium(IV) (11a, b, c) which are monomeric and six-coordinate [21].



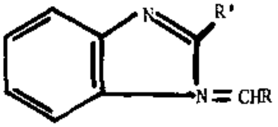
(11) a: n = 1, $msdH_2$
b: n = 2, $ssdH_2$
c: n = 3, $asdH_2$

The *cis*-$TiL_2C\ell_4$ complexes, where L is a Schiff base derived from salicylaldehyde and $PrNH_2$, iso-$PrNH_2$, $BuNH_2$, sec-$BuNH_2$, hexylamine, $PhNH_2$, octylamine, $PhCH_2NH_2$ and *p*-toluidine, have been reported; the Schiff base is monodentate [22]. By contrast, the Schiff bases are bidentate in the complexes $TiLC\ell_4$, where L = Schiff based derived from furfural and $PhNH_2$, iso-$PrNH_2$, $BuNH_2$, sec-$BuNH_2$, hexylamine, octylamine, $PhCH_2NH_2$, $PhNH_2$ and *o*- and *p*-toluidine [23].

The formation of $Ti(OR)_{4-n}L_n$ (R = Et, $^{\underline{i}}$Pr) and $Ti(OR)_{4-n}L_n$ (R = Et, $^{\underline{i}}$Pr) and $TiC\ell_{4-n}L_n$ (n = 1, 2) complexes, where L is 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one and the acyl group is OAc, pyrazonyl, BzO or *p*-$C\ell C_6H_4CO$, has been described; $Ti(OR)_{4-n}L_n$ reacts with t-BuOH to give $Ti(^{\underline{t}}BuO)_{4-n}L_n$ and $Ti(^{\underline{i}}PrO)_2L_2$ reacts with PhNCO to yield $Ti(PhNCO)(^{\underline{i}}PrO)_2L_2$ [24]. $TiBr_4\cdot OP(NCS)_3$ and $TiC\ell_4\cdot 2OP(NCS)_3$ have been prepared by gradual addition of a small excess of the phosphoryl isothiocyanate ligand to the corresponding metal halide, both in $CC\ell_4$ solutions; these compounds are moisture-sensitive and rapidly hydrolyze in air [25]. The heat of solution and heat of adduct formation for $TiC\ell_4$(semicarbazide) have been determined [26]. $TiC\ell_4$(5-aminoindazole) has been reported to possess an octahedral, halogen-bridged structure in which the indazole ligand is unidentate [27]. The synthesis of $TiC\ell_4L$, where L is 2-piperidinomethyl-4-methylphenol and 2-piperidinomethyl-4-tert-butylphenol, has been described [28].

Bromopyrogallol red and cetylpyridinium form mixed ligand complexes with titanium [29]. Cytidine, *p*-phenylenediamine, benzotriazole, ethylenediamine, $PhNH_2$, $PhNMe_2$, and β-picolineurea form $(LH)_2TiF_6$ complexes by reaction of H_2TiO_3 with L in the presence of 45% HF [30]. $TiBr_4$ and TiI_4 in $CC\ell_4$ and benzene, respectively, react with IN_3 solutions at room temperature to give $TiBr_2(N_3)_2$ and TiI_3N_3; dry $TiBr_2(N_3)_2$ is very explosive [31]. $(C_6F_5)_3Ti(THF)_3$ forms in 45% yield by treating $C_6F_5MgC\ell$ in tetrahydrofuran with $TiC\ell_3\cdot 3THF$ (3 hr., 0-5°C); treating the pentafluorophenyl compound with $MeCOCH_2COMe$ gave $Ti(MeCOCH_2COMe)_3$ [32]. The $TiC\ell_3\cdot 3THF$ complex can be prepared by dissolution of $TiC\ell_3$ in THF, while $TiC\ell_4(THF)_2$ is prepared by addition of THF to $TiC\ell_4$ in $CH_2C\ell_2$ [33].

The azomethine ligand (13) forms complexes with titanium [34]. Also, the azomethines $(PhC(OH){:}CHCH{:}N)_2R$ (H_2L; R = CH_2CH_2, *o*-C_6H_4) form the mononuclear complexes $H_2LTiC\ell_4$ in which the ligand is bidentate with coordination through the O atoms [35]. Tetraphenylporphine reacts with $TiC\ell_4$ in dimethylformamide in the presence of pyridine to give TiO(TPP); this porphyrin complex further reacts with $HC\ell$ to give $TiC\ell_2(TPP)$ [36]. In $HOAc$-H_2SO_4 solutions at 50-70°C, dissociation occurs with the protonation of TPP^{2-}. At high concentrations of H_2SO_4 in the solvoprotolytic solutions, $Ti(TPP)^{2+}$ complexes of the type $(H_2SO_4)Ti(TPP)$ are formed.



(13)

R' = H; R = Ph, C_6H_4-*p*-Ph, 2-naphthyl, 3-IC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-HOC_6H_4, 2-HOC_6H_4, 2-HO-5-BrC_6H_3.

R' = Me; R = 4-$NO_2C_6H_4$.

Potentiometric and potentiodynamic techniques have been used to obtain data on the complexing of Ti(IV) with F^- in halide ($NaC\ell$-$KC\ell$) melts; conditional stability constants following the method of Leden were reported [37]. Thermodynamic data for the equilibrium of reaction 11 have been determined [38].

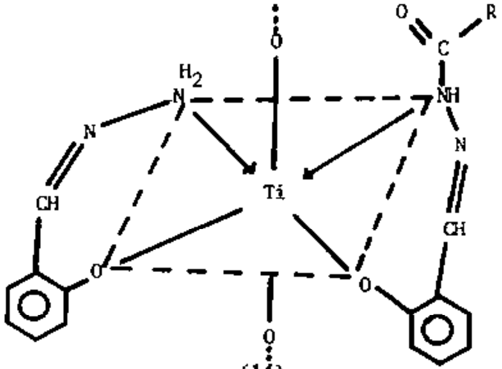
$$TiC\ell_3(s) + 0.5n\ A\ell_2C\ell_6(g) \rightleftharpoons TiC\ell_3 \cdot nA\ell C\ell_3(g) \qquad (11)$$

Titanium(IV) forms complexes with protocatechuic acid (H_3L) and antipyrine with the stoichiometry of 1:2 and 1:3 for Ti:H_3L and 1:3:4 for Ti:H_3L:antipyrine complexes [39]. Ti_5S_8(12R type) was recently prepared in a pure state as a single phase by a chemical transport method [40]. The importance of gaseous TiS_2 for chemical transport and sulfide syntheses has been noted [41].

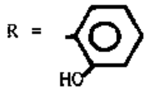
The synthesis of titanium chelates and their properties as colouring materials have been described by Misono and co-workers [42]. Reaction of $Ti(OCHMe_2)_2$ with 2,2'-dihydroxy and 2-hydroxy-2'-carboxy azobenzenes, 1,1'-azonaphthalenes and 1-(phenylazo)naphthalenes gives neutral, water-insoluble 1:2 titanium chelates; they are sparingly soluble in organic solvents and are mahogany brown in colour. The light-fastness and thermal stability of these complexes appear to depend on the structure of the ligands and the nature of the central metal (Ti *vs* Zr).

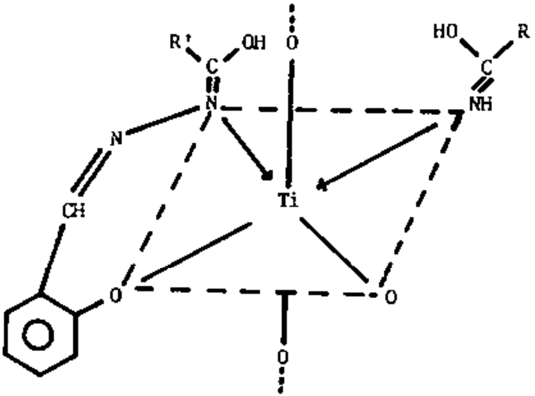
Anchoring of the coordinatively unsaturated complex $TiC\ell_3(C_4H_8O_2)_2$, prepared by thermal decomposition of $TiC\ell_3(C_4H_8O_2)_3$, to the surface of magnesium oxide leads to formation of surface-attached Ti(III) complexes [43]. Anchoring was achieved by reaction of the complex with the basic centres on the surface of magnesium oxide. Aggregation of the surface-bound titanium(III) complexes occurs upon thermal decomposition, while reaction of O_2 with these complexes produces O_2^-, coordinated to Ti(IV).

Polymeric oxotitanium(IV) complexes of the type $TiO(LH)_2$, $TiO(LH_2)$, $TiO(LH)_2 \cdot 2L$, and $TiO(LH_2) \cdot 3L$, where L is N,N'-disalicylaldimine-oxamide, -malonamide, -succinamide, and -anthranilamide, have been prepared and characterized by infrared and electronic spectral studies [44]. The complexes are orange to deep red in colour with high melting decomposition temperatures. Tentative structures are shown as (**14**) through (**16**). It appears that $>C=O$ and/or $>C=N$ and hydroxyl groups of the ligands take part in bonding to titanium; charge transfer bands (350-600 nm) in the uv-visible spectra originate from a $3d^04s^0$ electronic configuration of Ti(IV). Infrared bands have been identified at 1670-1640 cm^{-1} ($>C=O$) and 1610-1604 cm^{-1} ($>C=N$) along with 815-785 cm^{-1} assigned to $Ti-O$. These were taken as suggestive of a polymeric structure for the complexes by comparison with the known polymeric species $K_2[TiO(C_2O_4)_2]$, from which complexes (**14**-**16**) were derived [44]. An inversion in the stability of TiO^{2+}-SO_4^{2-} and TiO^{2+}-$HC_2O_4^-$ bands has been observed on going from $TiO(SO_4)_2^{2-}$ and $TiO(HC_2O_4 \cdot H_2C_2O_4)^+$ to $TiO(SO_4)_2(HC_2O_4 \cdot H_2C_2O_4)^{3-}$; this indicates the existence of interligand bonds [45]. The central atom (Ti) significantly strengthens the $C_2O_4H^-$-SO_4^{2-}

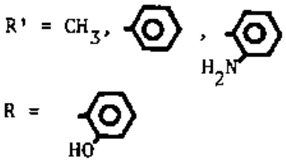

O
H$_2$
N
O
C
R
NH
N
N
CH
Ti
CH
O
O
O

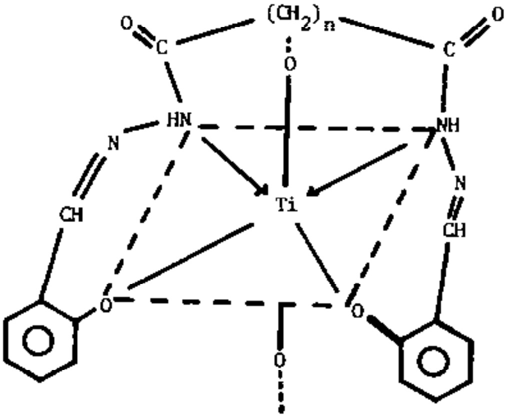
(14)


R =
HO


R'
C
OH
O
HO
C
R
N
NH
N
CH
Ti
O
O
O

(15)


R' = CH$_3$,
H$_2$N
R =
HO


O
C
(CH$_2$)$_n$
C
O
O
HN
NH
N
N
CH
Ti
CH
O
O
O

(16)

n = 0, 1, 2

bond, compared to the free $(H_2C_2O_4 \cdot H_2SO_4)_n$ associates.

The preparation and crystal structure of two barium titanium platinum oxides have been described by Fischer and Tillmanns [46]. $Ba(Ti_{0.88}Pt_{0.12})_3$ is hexagonal, space group $P6_3/mmc$ while $Ba_4(Ti_{1.81}Pt_{0.19})PtO_{10}$ is orthorhombic, space group Cmca. Both structures are closed-packed arrangements of Ba and O atoms with Ti and Pt in octahedral sites. Heating the products of co-precipitation of the metal salts by aqueous NH_3 and $H_2C_2O_4$ forms $La_4Ti_2B^{II}_{2/3}B^{V}_{4/3}O_{14}$, where B^{II} = Mg, Zn and B^{V} = Nb and Ta; the mixed oxide compounds possess a lamellar perovskite type structure with space group $Pna2_1$ or Pnam [47]. Nitric acid solutions containing Ti(IV) and Zr(IV) ions form a polymeric complex containing a 4:1 Zr^{4+}:Ti^{4+} molar ratio and containing OH and O bridges; the composition of the polymeric compound lies between $Ti_2Zr_8(NO_3)_{14}(OH)_{26} \cdot xH_2O$ and $Ti_2Zr_8(NO_3)_{14}O_{13} \cdot yH_2O$ [48]. The synthesis and structural properties of the spinels $Li_2MgTi_3O_8$ and $Li_2Mg_3Ti_4O_{12}$ have also been reported [49]. Mixed hydroxides of Pb and Ti were prepared by the heterophase reactions of hydroxides of Ti with aqueous $Pb(OAc)_2$ from which $PbTiO_3$ crystallizes directly [50].

Formation of anatase precipitates containing Fe(III) occurs by the air oxidation (at 95°C) of strongly acidic titanium(III) chloride solutions containing iron(II) sulfate; the physical properties of these precipitates have been described [51]. It was concluded that the Fe(III) in the product is interposed between the extremely fine particles, whereas the H_2O and SO_4^{2-} are adsorbed in the spherical, polycrystalline particles formed with oxo and hydroxo combination of the fine particles.

The formation of two new heteropolyanions with titanium(IV) and nickel(II) in solution has been reported [52]. More details on the synthesis, analysis and basicity of the heteropolyanions $[H_2ONiTiW_{11}O_{39}]^{6-}$ and $[H_2ONiTiW_5O_{20}]^{4-}$ were later described by the same authors [53].

3.2 STRUCTURAL STUDIES

The titanium metallocene complex μ-(η^1:η^5-cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium, $[\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$, displays a wide range of chemical reactivity with N_2 [54]. For example, in hydrocarbon solvents it reacts reversibly with dinitrogen to give the deep blue complex $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$; also, it reacts with N_2 (10 atm) in 1,2-dimethoxyethane to yield a N_2 complex characterized by a N-N stretching at 1222 cm^{-1}, the lowest N-N vibrational frequency yet observed for any coordinated dinitrogen ligand. Reaction of this N_2 complex with THF yields another N_2 complex with $\nu(N\text{-}N) = 1296\ cm^{-1}$. Successive treatment of $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$ with THF/glyme and diglyme(bis-2-methoxyethyl ether) produces a crystalline dinitrogen complex with $\nu(N\text{-}N) = 1282\ cm^{-1}$ and whose composition and structure (Figure 1) have been determined by x-ray diffraction methods; the complex is $(\mu_3\text{-}N_2)[(\eta^5{:}\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2Ti_2][(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2]\cdot[(\eta\text{-}C_5H_5)_2\text{-}(C_6H_{14}O_3)Ti]\cdot C_6H_{14}O_3$, in which the N_2 ligand is coordinated simultaneously to three titanium atoms. The N_2 is σ-bonded to the one formally divalent Ti atom in $[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)](\eta\text{-}C_5H_5)_3Ti_2$, as well as being coordinated in a σ,π mode to the two Ti atoms in $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(\eta\text{-}C_5H_5)_2Ti_2$. The result of this multiple coordination is a considerably longer N-N bond length [1.301 Å] than in free N_2 [1.0976 Å], and is intermediate between bond lengths found in azo ($-N{=}N-$) and hydrazo ($>N-N<$) compounds. Aqueous hydrolysis of the complex of Figure 1 in diglyme yields mostly NH_3 which has important consequences in the chemistry of N_2-fixation systems [54].

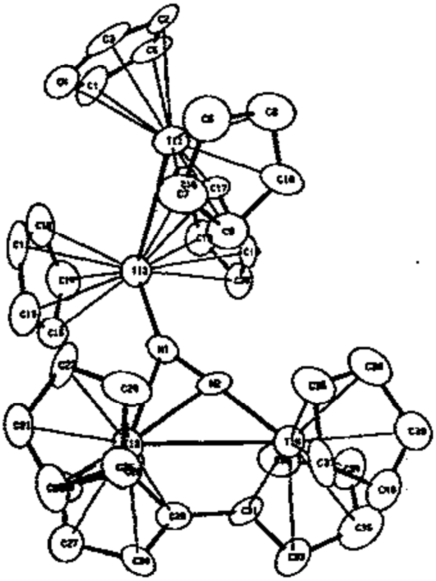
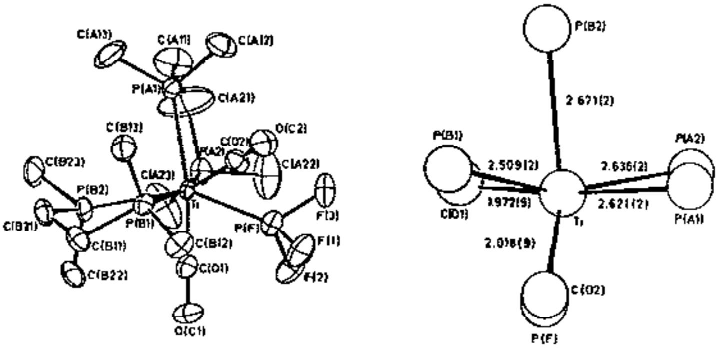


FIGURE 1: ORTEP view of the $(\mu_3\text{-}N_2)[(\eta^5{:}\eta^5\text{-}C_{10}H_8)\text{-}(\eta\text{-}C_5H_5)_2Ti_2][(\eta^1{:}\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2]$ unit with C, Ti, and N atom labels.

Carbonylation of $Ti(\eta\text{-}C_4H_6)_2(dmpe)$ [dmpe = 1,2-bis-dimethylphosphinoethane] or reduction of $TiCl_4\cdot 2THF$ in the presence of dmpe and CO affords

$[Ti(CO)_3(dmpe)_{3/2}]_n$, which further reacts with PF_3 and dmpe to form $Ti(CO)_2(PF_3)(dmpe)_2$, a derivative of the non-existent $Ti(CO)_7$ [55]. The carbonylated dmpe complex is at least a tetramer ($n \geq 4$) as four equally populated ^{31}P nmr resonances were observed at low temperatures. The structure of the trifluorophosphine complex and the inner coordination sphere about Ti are depicted in Figure 2. The complex crystallizes in the monoclinic space group $P2_1/c$, and it is clear from Figure 2 that the coordination geometry about titanium defines an approximate capped trigonal prism. The adduct between $Cp_2TiC\ell_2$ and Arphos [= 1-diphenylphosphino-2-diphenylarsinoethane] has been prepared by reducing the titanocene with manganese powder in the presence of potassium t-butylate using diethyleneglycoldimethylether as solvent and then adding the Arphos ligand [56]. The resulting dimeric complex, μ-1-diphenylphosphino-μ-2-diphenylarsinoethanebis[chlorodicyclopentadienyltitanium(III)], crystallizes in the monoclinic space group $P2_1/n$. The structure, illustrated in Figure 3, shows that the Ti atom is tetrahedrally surrounded by two Cp rings in a staggered configuration, one Cℓ and one P (or As) atom from the centrosymmetrical ligand molecule which joins adjacent coordination polyhedra such that the resulting complex molecule is dimeric. The molecular and crystal structure of 1,1'-dimethylsilylenetitanocene dichloride, $[(CH_3)_2Si(C_5H_4)_2TiC\ell_2]$, shows that this complex is also monoclinic, space group C2/c [57].



(a) (b)

FIGURE 2: Molecular structure (a) and inner coordination sphere (b) of $Ti(CO)_2(PF_3)(dmpe)_2$.

A structure for a simple metallocyclobutane (11) has been proposed from *ab initio* theoretical studies [58]; also reported were relative energetics for the equilibrium with free ethylene plus the metal alkylidene complex (12).

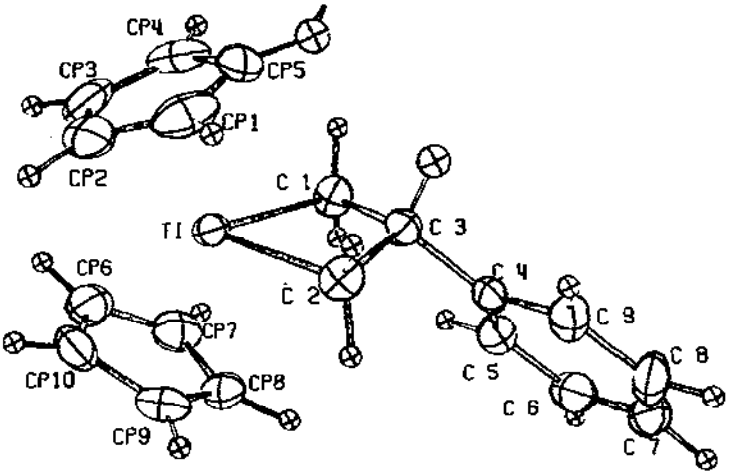
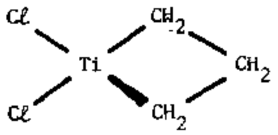
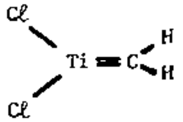


FIGURE 3: ORTEP drawing of the molecular structure of μ-1-diphenylphosphino-μ-2-diphenylarsinoethane-bis[chlorodicyclopentadienyltitanium(III)].

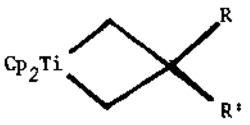


(17)



(18)

Similar structures had also been reported earlier for the titanacyclobutanes (19) [59]. The structure of (19b) is depicted in Figure 4.



a) R = t-butyl, R' = H
b) R = C_6H_5, R' = H
c) R = R' = CH_3

(19)

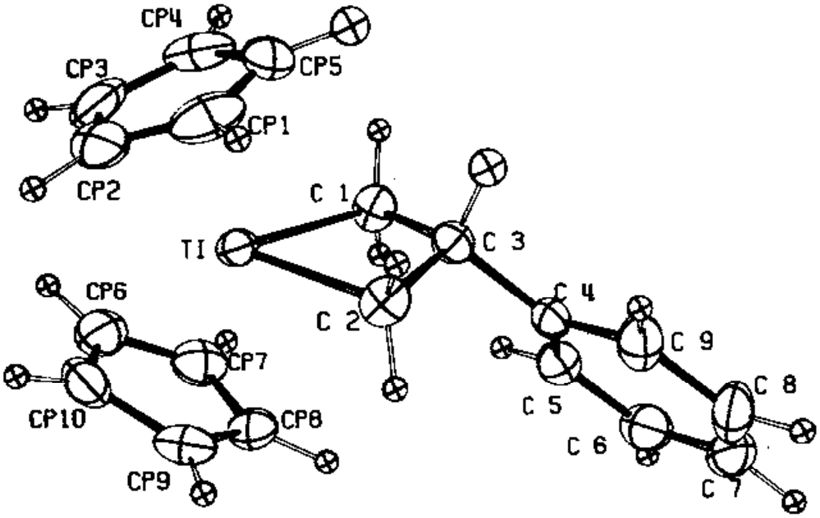
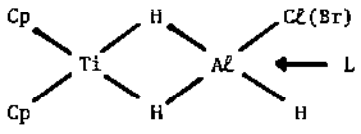


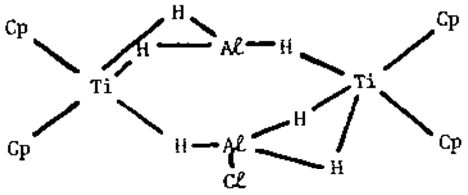
FIGURE 4: ORTEP drawing of the titanacyclobutane (**19b**).

Infrared spectra of the crystalline compounds $Cp_2TiH_2A\ X(X')\cdot L$ (X and X' = H or halogen; L = Et_2O or NEt_3) have been reported [60]. Crystallization from solutions containing the monomeric complexes $Cp_2TiH_2A\ell C\ell H\cdot Et_2O$, $Cp_2TiH_2A\ell HC\ell\cdot NEt_3$, and $Cp_2TiH_2A\ell HBr\cdot Et_2O$ results in splitting off of 0.5L and formation of structures containing ordinary and double hydrogen bridges, terminal H atoms and non-equivalent Ti and Aℓ atoms. Depending on the reaction temperature, monomeric (**20**) or dimeric (**21**) forms of $Cp_2TiA\ell H_3C\ell$ form in Et_2O



(**20**)

solutions, with the dimeric structure (**21**) retained in the crystalline state. During crystallization of $Cp_2TiA\ H_3X$, (**20**) converts to structure (**22**); crystallization of dihalo compounds containing Et_2O appears to involve dimerization *via* ordinary H bridges (**23**). However, in the presence of the stronger base NEt_3, structure (**24**) is obtained because of the stronger



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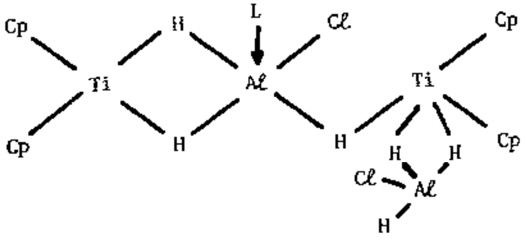

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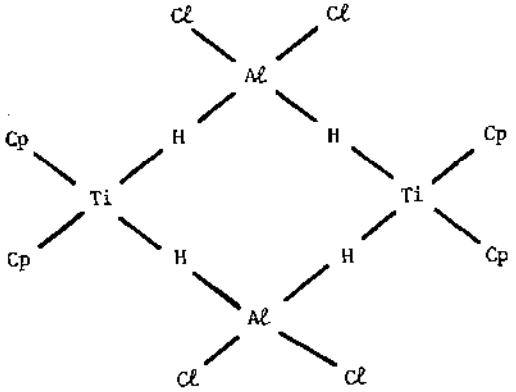

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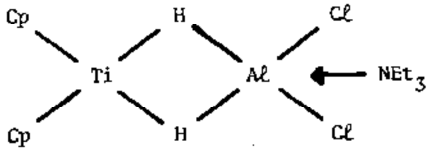


(24)

stabilizing action on $Cp_2TiH_2AlCl_2 \cdot NEt_3$; on crystallization, structure (**24**) is retained [60].

Reaction of $TiCl_4$ with a solution of $MgCl_2$ in dry $CH_3COOC_2H_5$ gives $TiMgCl_6(CH_3COOC_2H_5)_4$, the structure (space group P1) of which is depicted in Figure 5 [61]. The titanium(IV) atom is octahedrally coordinated by six Cl atoms (Ti—Cl_t: 2.293(2) Å and Ti—Cl_b: 2.480(2) Å), while the magnesium atom is coordinated by two Cl atoms (Mg—Cl_b: 2.528(2) Å) and by the carbonyl oxygen atoms of the four ethylacetate residues (Mg—O: 2.038(5) Å). The octahedra share an edge by a double Cl bridge between the Mg and Ti atoms [61].

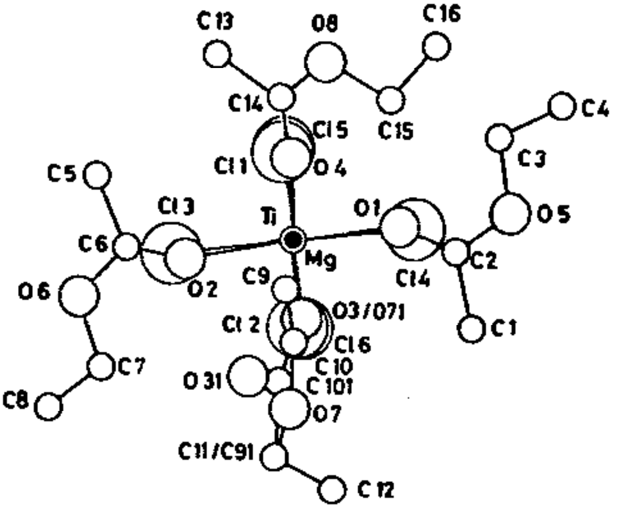


FIGURE 5: View of $TiMgCl_6(CH_3COOC_2H_5)_4$ along the Ti—Mg direction.

X-ray measurements on $CsTiF_4$ crystals show that the crystal is of the $CsFeF_4$ layer-type structure of space group P4/nmm [62]. These results with magnetic susceptibility and EPR linewidth measurements along with neutron diffraction results indicate that $CsTiF_4$ possesses two-dimensional antiferromagnetic character. X-ray measurements have also been carried out on disordered State II Ag_xTiS_2 crystals (x = 0.18 and 0.19) [63], on nonstoichiometric titanium disulfide, $Ti_{1.083}S_2$ [64], on Ti_nO_{2n-1} ($4 \leq n \leq 9$) [65], and on nitride surface films of Ti prepared by reaction with NH_3 gas at high temperature [66].

An x-ray structural study of $Cp_2TiOOCCMe_3$ reveals that the Cp ligands form π bonds with the Ti atom (Ti—C_{mean}: 2.40(1) Å), with the chelate $OOCCMe_3$ ligand located in a bisecting plane with equivalent Ti O bonds equal to

2.13(1) Å [67]. The structure of this titanocene trimethylacetate is depicted in Figure 6.

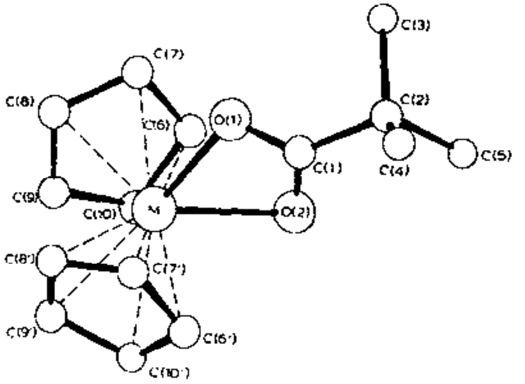


FIGURE 6: The molecular structure of $Cp_2TiOOCCMe_3$, in which only one statistical position of the Cp and t-butyl ligands is shown.

The pentafluorotitanate(IV) ion, $H_3O^+TiF_5^-$, has been prepared from the reaction of H_2O with TiF_4 in HF; a single crystal structural study shows the ion pair to crystallize in the monoclinic space group C2/c [68]. By contrast, the hexafluorotitanate(IV) ion, $(NH_4)_2TiF_6$, crystallizes in the trigonal space group P3m1 [69]. At 153K, the H atoms are ordered but showed large anisotropic thermal motion; at ambient temperature, the greater motion was represented by a disordered model in which the NH_4^+ ion is twisted 19° away from the threefold axis. The TiF_6^{2-} ion consists of a slightly flattened octahedron with Ti–F bond lengths of 1.864 Å. The triclinic structure (P1) of $[Ph_4As]_2[TiCl_4(PO_2Cl_2)]_2$, prepared by reacting $TiCl_4$ with $Ph_4As[PO_2Cl_2]$ in dichloromethane solution, has been determined [70]. The complex anion, $[TiCl_4(PO_2Cl_2)]_2^{2-}$, is dimeric with the dichlorophosphate group bridging through the O atoms as also evidenced by infrared data.

The molecular structure of gaseous $Ti(BH_4)_3$ was determined at ambient temperature by electron diffractometry and ir and UV spectrometry [71]. The structure was solved with a model of the type $Ti(\mu\text{-}H)_3BH]_3$ and is non-planar with C_{3v} symmetry. Electron diffraction techniques were also used to define the structure of TiF_4 at 689 ± 20K; Ti – F = 1.745(3) Å [72]. The force constants and vibrational frequencies [ν_1 = 695(20), ν_2 = 179(8), ν_3 = 787(15), ν_4 = 225(20) cm^{-1}] were calculated using the anharmonic approximation. The evolution of crystal structure and chemical bond characteristics has been studied for a series of isotypical compounds TiX_2 with X = S, Se and Te [73]. Structural studies of $TiTe_2$ and TiSeTe confirm the existence of an increasing trigonal C_{3v} distortion of metal sites when the chalcogen electronegativity decreases. ESCA experiments further showed that this distortion is associated with an increase of the covalent or metallic character of the bond. Structural and spectroscopic differences evident between TiS_2 and $TiSe_2$ were interpreted in terms of an orbital delocalization in $TiSe_2$ and $TiTe_2$, in accord with the semi-metallic behaviour of these TiX_2 compounds [73]. The nature of the chemical bonding in titanium hydrocarbides and carbides, $TiC_{0.6}$, $TiC_{0.6}H$, $TiC_{0.8}$, $TiC_{0.8}H$, $TiC_{0.95}$ and $TiC_{0.95}H$ has been determined from x-ray emission spectra of Ti and C [74].

The unit cell dimensions of $BaTi\ell_6O_{12}$ were determined using x-ray powder diffraction methods [75]. The compound possesses orthorhombic symmetry rather than the previously reported tetragonal symmetry; the space group determined from powder patterns and by electron diffraction is either Pnm2 or Pnnm. $K_{2.38}Sb_{3.62}Ti_{0.38}O_{11}$ crystallizes in the monoclinic space group $P2_1/a$ with the structure closely related to that of $K_2Sb_4O_{11}$; this probably results from having the same M_8O_{22} building units [76].

The system $Fe_{3-x}Ti_xO_4$ $(1.0 \geq x \geq 0)$ is expected to form a continuous solid solution over the entire range of x; Moessbauer measurements taken at various temperatures between 300K and 77K reveal a complex behaviour [77]. The results are understood in terms of disorder and consequent formation of super-paramagnetic clusters which are supported by earlier hysteresis and susceptibility studies. It appears that with increasing Ti content, domain wall formation is inhibited, resulting in effectively monodomain clusters. Moessbauer spectra of $Fe_{2.9}Ti_{0.1}O_4$ and $Fe_{2.8}Ti_{0.2}O_4$ are reported for the first time [77]. The latter system shows hysteresis that is relatively independent of temperature, with small H_c, and that its susceptibility, χ, is independent of temperature below the Hopkinson peak; it has been inferred that $Fe_{2.8}Ti_{0.2}O_4$ exists in the multidomain state. From their studies, Nagarajan and Murtz [77] concluded that:(1) Ti ions in magnetite cause magnetic disorder even though the material may crystallographically be a single phase; (2) the extent of magnetic disorder in $Fe_{2.7}Ti_{0.3}O_4$ inhibits formation of multidomains and the material behaves as a mixture of super-paramagnetic and single domain clusters; (3) Moessbauer spectra of well-formed multidomain material is expected to show narrow, well-resolved lines even close to its T_N; and (4) magnetic materials showing complex and unresolved Moessbauer spectra might in some cases imply bulk super-paramagnetic behaviour and this could be checked by hysteresis and susceptibility measurements at different temperatures.

Iron-57 Moessbauer spectra of monoclinic Fe_2TiO_5 reveal hyperfine patterns belonging to two non-identical iron sites; Fe^{3+} ions are distributed over 4a and 8f sites [78]. The cations are octahedrally coordinated to oxygen with cation-anion distances between 0.201 and 0.203 nm at 4a sites and between 0.189 and 0.226 nm at 8f sites.

Magnetic susceptibilities in the temperature range 3.8-295K of $Ti_7C\ell_{16}$ and Ti_7Br_{16} reveal magnetic ordering points at 15.9 and 13.5K [79]. Determination of oxidation states of the titanium ions and the exchange interactions between them was complicated by the fact that, at room temperature, competing antiferromagnetic intra- and inter-cluster exchange interactions are already present; however, calculations using simple models show that the compounds probably consist of Ti_3 clusters with Ti(II) and isolated Ti(IV) ions.

The orange compound Cs_2TiI_6 has been prepared by reaction of stoichiometric amounts of CsI and TiI_4 in evacuated silica ampoules at 450°C, and crystals were obtained after annealing at 560-600°C for 2-3 days [80]. The compound is moisture-sensitive, thermally decomposes above 600°C to CsI and TiI_4, and crystallizes in the $K_2PtC\ell_6$ structure type. Titanium copper phosphide, $Ti_{11+x}Cu_{1-x}P_8$ where x = 0.34, crystallizes in the space group Pbam; the structure consists of a complex arrangement of PTi_6 trigonal prisms and distorted $CuTi_8$ body-centred-cubic units [81]. Chemical transport reactions of γ-Ti_3O_5, β-Ti_3O_5, Ti_4O_7 and Ti_2O_3 were performed in closed silica ampoules using $TeC\ell_4$ as the transport medium; single crystals of γ-Ti_3O_5 were obtained for the first time [82]. Crystals of the titanium oxides Ti_nO_{2n-1} (n = 2-9) have also been grown by chemical vapour transport with chlorine proving to be the best transporting agent [83].

EXAFS structural parameters have been reported for α-$TiC\ell_3$ and $TiC\ell_2$; Ti—Cℓ distances of 2.46 and 2.42 Å were derived for α-$TiC\ell_3$ and $TiC\ell_2$, respectively, and agree well with the crystallographically-obtained values of 2.46 and 2.50 Å [84].

3.3 PROPERTIES OF TITANIUM COMPOUNDS

Calculations of the electronic structure of octahedral clusters of titanium carbides, nitrides and oxides using the self-consistent multiple scattering method X_α have been reported [85]. The electronic structure of TiH_2 has also been studied using the APW method and LCAO interpolation method [86]. The density of states and its orbital components show that the conduction band is Ti d-like and that the valence band is largely derived from the hydrogen orbitals with small Ti 3d hybridization. Moreover, electronic energy levels in $TiC\ell_3$ and $TiC\ell_4^-$ have been calculated and the effect of ethylene coordination on the d-orbital levels of Ti(III) discussed [87]. A method for calculating the contribution of π-bonding molecular orbitals to the dipole moments of octahedral complexes of the type $M^{III}A_3B_3$ (M = Ti, V, Cr, Fe, Co or Ni(II); A = O or N, B = N, S, or $C\ell$) has been developed [88]. It appears that π-bonding molecular orbitals contribute less than the σ-bonding molecular orbitals, but the π-contribution may not be negligible even for chelate complexes in which delocalization of π electrons is assumed.

Surface properties of metal oxides such as TiO_2 and TiO_2-ZrO_2 have been elucidated using a potentiometric acid-base titration method [89]. A mixture of a titanium compound, 2,7-dichlorochromotropic acid, and a tetraphenyl phosphonium salt in the ratio 1:20:120 in the aqueous phase shows formation of a 1:2:4 complex extractable with nitromethane [90]. A hydrate-solvate mechanism was proposed for titanium extraction from sulfuric acid solutions by petroleum sulfoxides; the extracted solvate, $H_2TiO(SO_4)_2$, tends to polymerize in the organic phase [91]. Extraction of titanium with petroleum sulfoxides from fluoride-sulfate solutions reveals that separation depends on the acid concentration and the relative phase volumes; infrared and nmr studies indicate formation of a series of titanium-fluoro complexes but very little TiF_6^{2-} [92]. The kinetics of anodic oxidation of titanium in 1M chloride solutions have been studied [93].

Bis(cyclopentadienyl)titanium dichloride shows significant antiviral efficiency *in vitro* against representatives of a number of enveloped DNA and RNA viruses [94]. Inhibition of up to 100% of orthopox virus (vaccinia), herpes virus (pseudorabies), orthomyxoviruses (influenze A/ fowl plague [FPV], influenza A/ Victoria 3/75, influenza A/ Jena 48/78, and influenza A/ Johannesburg), paramyxovirus (Newcastle disease), and rhabdovirus (vesicular stomatitis [VSV]) has been observed after direct contact with $Cp_2TiC\ell_2$. Application of this titanocene compound during the replication of vaccinia and influenza viruses A/FPV in cell cultures produced an additional effect of inhibition of virus multiplication [94].

Dielectric relaxation studies of the ionization (reaction 12) and solvation (reaction 13) of $TiC\ell_4$ ester complexes in benzene indicate the

$$(TiC\ell_4\cdot E)_2 \rightleftharpoons (TiC\ell_3\cdot E)^+ + (TiC\ell_5\cdot E) \qquad (12a)$$

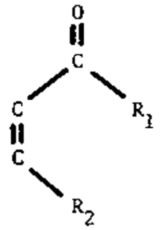
or

$$(TiC\ell_4\cdot 2E)_2 \rightleftharpoons (TiC\ell_3\cdot 3E)^+ + (TiC\ell_5\cdot E)^- \qquad (12b)$$

$$(TiC\ell_3\cdot E)^+ + 2\ C_6H_5 \rightleftharpoons (TiC\ell_3\cdot E\cdot 2C_6H_5)^+ \qquad (13)$$

existence of ellipsoidal and spherical ester complexes [95]. The tendency of the ellipsoidal forms toward association with stretching out of the hydrocarbon chain of the ester increases abruptly as the chain length decreases; the degree of association of these ester complexes varies from 2 to 9. Titanium(IV) chloride complexes with benzo-15-crown-5 or dibenzo-18-crown-6 ethers show an atom ratio of ionically-bound Cℓ to Ti of < 4, while the crown ether to $TiC\ell_4$ ratio lay between 1.02 and 1.62 [96].

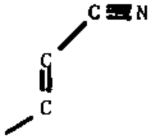
The complex $Ti(OH)(SO_4)^+$ forms at 25°C and ionic strength 0.6<u>M</u> (H_2SO_4 + $HC\ell O_4$) with a stability constant of $\beta_1 = 19 \pm 1$ [97]. Complexation of azo derivatives of pyrocatechol with titanium(IV) has been investigated in aqueous organic mixtures (acetone, DMF, dioxane, EtOH); stability constants for 1:2 Ti:ligand complexes in 40 vol. % aqueous acetone show correlations with ligand ionization constants [98]. Standard enthalpies of formation of $(\eta\text{-}C_5H_5)_2Ti(OR)_2$ complexes (R = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$ and 2-$C\ell C_6H_4$) at 298.15K determined by reaction-solution colorimetry are: R = C_6H_5, -379.2 ± 8.0 kJ mol^{-1}; R = 4-$CH_3C_6H_4$, -416.5 ± 7.8 kJ mol^{-1}; and for R = 2-$C\ell C_6H_4$, -407.6 ± 21.5 kJ mol^{-1} [99]. Enthalpies of complexation of the α,β-unsaturated Lewis bases crotonaldehyde (**25**), methylcrotonate (**26**), mesityl oxide (**27**), and crotononitrile (**28**) with the Lewis acid $TiC\ell_4$ have been measured in $CH_2C\ell_2$ solutions [100]. The enthalpy of reaction of Ti(IV) with salicylate ions (sal) at 25°C and μ = 0.1<u>M</u> is -2.60 ± 0.11 kcal mol^{-1} (calorometrically); the standard enthalpy, free energy, and entropy of formation of TiO(sal) are -301.8 ± 0.9 and -249.5 ± 0.9 kcal mol^{-1} and



(**25**) $R_1 = R_2 = H$; $\Delta H_c = 14.0 \pm 0.6$ kcal mol^{-1}

(**26**) $R_1 = OCH_3$, $R_2 = H$;
$\Delta H_c = 13.6 \pm 0.7$ kcal mol^{-1}

(**27**) $R_1 = R_2 = CH_3$;
$\Delta H_c = 17.9 \pm 0.3$ kcal mol^{-1}



$\Delta H_c = 11.5 \pm 0.3$ kcal mol^{-1}

(**28**)

+29.4 ± 4.1 eu, respectively [101].

Storage of a solution of TiO_2, SO_3, H_2O for long periods (years) led to formation of $TiO(SO_4)\cdot 2H_2O$ which dehydrates at 200-300°C, giving the amorphous $TiO(SO_4)$ complex. Heating this complex to 600-800°C forms anatase and at temperatures > 800°C forms rutile [102]. When a mixture of aqueous $TiC\ell_4$ and aqueous $ZnC\ell_2$ (or $CdC\ell_2$) is slowly added to a hot solution of oxalic acid, zinc titanyl oxalate (ZTO) (or cadmium titanyl oxalate, CTO) forms [103]. Thermogravimetric and differential thermogravimetric studies reveal that thermal decomposition of ZTO and CTO proceeds through three major endothermic steps: (1) dehydration of the oxalate, (2) decomposition of the oxalate to the carbonate, and (3) decomposition of the oxalate to the respective metal titanate.

Titanium dioxide (anatase) reacts with As_2O_5 to form $TiAs_2O_7$, $Ti(AsO_4)_4$, and $3\ TiO_2\cdot AsO_5$, depending on the $TiO_2{:}As_2O_5$ molar ratio; these decompose thermally according to reactions 14a and 14b [104]. Beryllium titanyl oxalate tetrahydrate thermally decomposes under inert and oxidizing conditions (reactions 15a-c) *via* three major steps [106]: (1) loss of water in one step, (2) endothermic decomposition of the dehydrated oxalate in one step, and (3) endothermic decomposition of the carbonate at high temperatures to give the corresponding titanate salt.

$$TiAs_2O_7 \xrightarrow[<860°C]{} Ti_3(AsO_4)_4 \xrightarrow[940°C]{} As_2O_5 + TiO_2(\text{rutile}) \tag{14a}$$

$$3\ TiO_2\cdot As_2O_5 \xrightarrow[940°C]{} TiO_2(\text{rutile}) + As_2O_5 \tag{14b}$$

$$BeTiO(C_2O_4)_2\cdot 4H_2O \longrightarrow BeTiO(C_2O_4)_2 + 4\ H_2O \tag{15a}$$

$$2\ BeTiO(C_2O_4)_2 \longrightarrow Be_2Ti_2O_5CO_3 + 4\ CO + 3\ CO_2 \tag{15b}$$

$$Be_2Ti_2O_5CO_3 \longrightarrow 2\ BeTiO_3 + CO_2 \tag{15c}$$

The magnetic properties of mixed ligand chlorotitanium(III) compounds with composition $TiC\ell_3(C_4H_8O)_2(CH_3CN)$, $TiC\ell_3(CH_3CN)(C_4H_8O)_2$, $TiC\ell_3(C_4H_8O)(CH_3CN)_2$, and $TiC\ell_3(C_4H_8O)(CH_3CN)$ were reported [106]. The first three of these are six-coordinate monomers possessing a distorted octahedral geometry, while the latter compound is polymeric with antiferromagnetic interactions between the Ti(III) ions. Magnetic properties have also been used as a means of characterizing the importance of non-stoichiometry in the dichalcogenide

$FeTiS_4$ in the preparation of the rigorously stoichiometric compound which has well reproducible magnetic properties [107]. Magnetic studies and crystal structural studies of $CsVTiF_6$ have also been carried out [108].

Electronic absorption spectra of $TiC\ell_3$ and $TiC\ell_4$ dissolved in alkali metal chloride melts have been obtained as a function of temperature, concentration, and redox potential. Relationships were determined which characterized quantitatively the relations of the spectral shifts to the concentration of the Ti^{3+} and Ti^{4+}, respectively, as well as to their ratio (degree of oxidation) controlled by the value of the redox potential [109]. Optical spectra of the nickel(II) salt, $NiTiF_6 \cdot 6H_2O$ or $\cdot 6D_2O$, were taken at 77K; these reveal a superposition of asymmetric O—H vibrational modes on the excited electronic states [110]. A progression of M—O stretching vibration is present as fine structure on the main band of the $^3A_{2g} \longrightarrow {^3T_{1g}}(F)$ transitions in the nickel(II) salt. Addition of a $Ti(SO_4)_2$ solution in H_2SO_4 (~9N) to a reaction mixture containing glucose oxidase permits the instantaneous inactivation of the enzyme and the measurement of its activity by means of the formation of the coloured complex between Ti^{4+} ions and the H_2O_2 produced. The complex has an absorbance maximum at 415 nm and a stability of at least 12 hrs. at 25°C [111].

The general quadratic valence force field was applied to the octahedral hexahalide $TiC\ell_6{}^{2-}$ and $TiBr_6{}^{2-}$ anions using molecular constants and the Wilson FG matrix method. These studies [112] reveal that the Ti—Cℓ bond strength is larger than Ti—Br and that the ionic character of a bond is an important factor in determining force constants. The normal coordinate analysis of the adduct $TiC\ell_4 \cdot 2POC\ell_3$ has been re-examined and the results analyzed in terms of a potential energy (PE) distribution [113]. From this PE distribution, the phosphoryl ligand vibrations were found to be not so effectively coupled with the $TiC\ell_4O_2$ skeletal vibrations. This fact infers that the ligand fundamental bands are less sensitive to the differences among the metal halides as an acceptor. $PC\ell_3$ rocking modes of $TiC\ell_4 \cdot 2POC\ell_3$ give considerable mode mixing with $Ti-C\ell_{eq}$ symmetric and $Ti-C\ell_{ax}$ asymmetric stretching modes. The Ti—O stretching force constant is 0.337 mdyne $\mathring{A}^{-1}$; this indicates that the bonding interaction between $TiC\ell_4$ and $POC\ell_3$ is rather weak even as a coordination bond [113]. Infrared studies on suspensions in polyethylene mulls of precipitates from the system $TiC\ell_4/A\ell(^{i}Bu)_3/T\ell C\ell_3/Mg(C_6H_5)_2$ indicate that Ti—C and Tℓ—C bonds are formed in the system; ν(Ti—C) occur at 540-549 cm^{-1} and 420 cm^{-1}, while ν(Tℓ—C) was assigned to the broad band at 437-600 cm^{-1} [114]. The large width of this latter band was attributed to Tℓ being present as mixed Tℓ(I) and Tℓ(III) oxidation states.

Comparison of infrared spectra of crystalline $RTiC\ell_3$ compounds ($R = CH_3$, C_2H_5, i-C_4H_9) over the range 1200-200 cm^{-1} at temperatures -70 to -30°C, and spectra of $RTiC\ell_3$ in the vapour phase containing THF (-30°C), reveal the formation of stable adducts of the type $RTiC\ell_3 \cdot 2THF$ [115]. X-ray structural studies of $(\eta^5\text{-}C_5H_5)Ti(\eta^8\text{-}C_8H_8)$ and $(\eta^5\text{-}C_5D_5)Ti(\eta^8\text{-}C_8H_8)$ indicate that the two organic ligands lie in parallel planes; the C_8H_8 planar ring is η^8-bonded to the central Ti atom (local symmetry C_{8v}) and the other coordination site is occupied by the $\eta^5\text{-}C_5H_5$ ring (local symmetry C_{5v}) [116]. A detailed vibrational spectral analysis of these two organometallic compounds has been made [117].

Complex formation between N-methylated lactams (L) with 11- and 13-membered rings, which in the liquid state assume both the *cis* and the *trans* structures of the amide bond, and $TiC\ell_4$ (M) in 1,1,2,2-tetrachloroethane and $CDC\ell_3$ solutions has been studied by analysis of ^1H and ^{13}C-nmr and Raman spectra [118]. Free energies of activation for the exchange processes in the *cis*-ML_2 complexes have been estimated from the temperature dependence of ^1H-nmr spectra and it appears that the barrier to rotation about the amide bond is increased by complex formation. Also, the effect of $TiC\ell_4$ on the *cis*-*trans* isomerization equilibrium as well as the composition and structure of the complexes have been established [118]. Raman spectra of solutions of lactam with $TiC\ell_4$ in $CDC\ell_3$ were measured at molar ratios 2.9, 5.2 and 10.1; the high intensities of the bands of the $C=O$ group of complexed lactam and of the band at 348 cm^{-1} assigned to a $Ti \leftarrow O$ stretching vibration indicate that Ti is coordinated to the amide bond *via* the carbonyl oxygen [118].

TiO_2 powder, in the form of a pressed pellet, was dried and exposed to silane vapour while mounted in a vacuum infrared cell;infrared spectra indicate that the TiO_2 substrate surface reacts with methylsilanes $Me_{4-x}SiX_x$ ($x = 1\text{-}4$, $X = C\ell$, OMe) and hexamethyldisilazane [119]. The surface is covered by a monolayer of the silane, and, moreover, the surface terminal OH groups appear to react more facilely than bridging OH groups.

The dissociative ionization of TiO and TiO_2 gas into Ti^+ and TiO^+ has been studied by mass spectroscopic methods at high temperatures employing either a single conventional diffusion cell or a multiple effusion cell [120]. The ionization efficiency curves of Ti^+ and TiO^+ were simultaneously recorded for molecules originating from different samples, namely solid TiO, $TiO_{1.965}$, TiN, Ti and liquid Ti_3O_5. The first fragmentation threshholds correspond to the processes shown in reactions 16-18. Two other breaks that occur at higher

$$TiO + e^- \longrightarrow Ti^+ + O + 2e^-;\quad 12.8 \pm 0.4\ eV \qquad (16)$$

$$TiO_2 + e^- \longrightarrow Ti^+ + O_2 + 2e^-; \quad 14.6 \pm 0.5 \text{ eV} \qquad (17)$$

$$TiO_2 + e^- \longrightarrow TiO^+ + O + 2e^-; \quad 13.7 \pm 0.5 \text{ eV} \qquad (18)$$

energies (41.6 eV on the Ti^+ curve and 36.7 eV on the TiO^+ curve) could not be explained unambiguously as a single fragmentation process. Nevertheless, at energies greater than 50 eV, the principal fragmentation process for TiO_2 appears to be (reactions 19, 20):

$$TiO_2 + e^- \longrightarrow Ti^+ + 2\,O^+ + 4\,e^- \qquad (19)$$

$$TiO_2 + e^- \longrightarrow TiO^+ + O^{2+} + 4\,e^- \qquad (20)$$

Secondary ion mass spectrometry was used to study defect formation in TiO_2(rutile) powders irradiated by electrons [121].

A study [122] of the electronic structure of β-FeTiH and $FeTiH_2$ by Moessbauer spectroscopy using the augmented plane wave method has been employed to interpret the Isomer Shift data of Swartzendruber and co-workers [123]. In agreement with experiment, Gupta [122] obtained a decrease of the s-like contact density at the iron site with increasing hydrogen concentration; the physical origin of the phenomenon was described in light of the band structure results. Nuclear Quadrupole Resonance methods on $^{35}C\ell$ nuclei have been used to determine structures and features of donor-acceptor interactions in the complexes $TiC\ell_4 \cdot nL$, where n = 1,2, L = CH_3CN, pyridine, $POC\ell_3$, THF, DMF, hexamethylphosphoramide, $C\ell^-$, and for n = 1, L = $MeNO_2$, MeCOOEt, and for n = 2, L = Ph_2CO [124].

The proton nmr relaxation times T_2, T_1,... were reported for hydrous titania ($TiO_2 \cdot nH_2O$) in the temperature range $135K < T < 336K$ at 60 and 20 MHz [125]. The data demonstrate proton transport including exchange between three environments: (a) surface hydroxyl groups, (b) "acid solution" in micropores (dia. < 100 Å), and (c) "acid solution" in macropores (dia. > 1000 Å).

Exposure of $Cp_2TiC\ell_2$ in various media to ^{60}Co γ-rays at 77K gives the corresponding titanium(III) anionic complex, $Cp_2TiC\ell_2^-$, which was characterized by its ESR spectrum [126]. Warming the methanolic glassy solutions, $Cp_2TiC\ell_2^-$ changes irreversibly into a second titanium(III) complex believed to be $Cp_2TiC\ell$. A similar treatment of $CpTiC\ell_3$ produces the anion $CpTiC\ell_3^-$, the ESR features of which suggest a major contribution from a $\underline{d}_{x^2-y^2}$ configuration rather than a $\underline{d}^1_{z^2}$ configuration as observed for the complexes $Cp_2TiC\ell_2^-$ and $Cp_2TiC\ell$. Irradiation of $TiC\ell_4$ in the pure state at 77K forms $TiC\ell_4^+$ ions which have an ESR spectrum comparable with that for $C\ell_2^-$, together with $TiC\ell_4^-$ ions which possess a distorted structure with the extra electron in a predominantly d_{z^2} orbital [126].

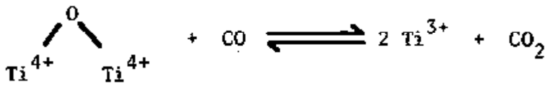
Titanyl oxalates decompose with release of H_2O, NH_3 (in their ammonium compound), CO and CO_2 in several steps. In the initial stages of the decomposition process, there appears to be an important CO/CO_2 proportion that leads to formation of one or two intermediate carbonates [127]. Thermogravimetric data confirm the formation of the corresponding alkali or alkaline-earth titanates [or TiO_2 in the case of $TiOC_2O_4\cdot 2H_2O$ and $(NH_4)_2TiO(C_2O_4)_2\cdot H_2O$] at the end of the decomposition, with deposited carbon traces produced from CO disproportionation. On the basis of electron paramagnetic resonance and thermogravimetric results, Gabelica and co-workers [127] proposed the following scheme (reactions 21-25) for the vacuum decomposition process of alkali and alkaline-earth titanyl oxalates:

A) $$A_xTiO(C_2O_4)_2\cdot yH_2O \longrightarrow A_xTiO(C_2O_4)_2 + yH_2O \qquad (21)$$

$$A_xTiO(C_2O_4)_2 \longrightarrow \underset{\text{(in several steps)}}{A_xTiO_3 + 2\ CO + 2\ CO_2} \qquad (22)$$

B) $$2\ CO \rightleftharpoons C + CO_2 \qquad (23)$$

C)



$$Ti^{4+}\!-\!O\!-\!Ti^{4+} + CO \rightleftharpoons 2\ Ti^{3+} + CO_2 \qquad (24)$$

D) $Ti^{4+}\!-\!O + C$

EPR signal: Ti(III)

$$Ti^{4+}\!-\!O\cdots C \ ;\ \text{carbon} \qquad (25a)$$

$$Ti^{(4-x)+}\text{- -}O\text{- -}C^{x+} \ ;\ CO^{\delta+} \qquad (25b)$$

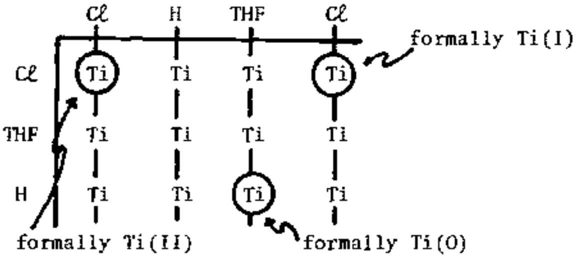
$$Ti^{3+}\cdots\cdots O\!-\!C^{+} \ ;\ CO^{+} \qquad (25c)$$

Low-valent titanium compounds prepared by the action of strong reducing agents on $TiC\ell_3$ or $TiC\ell_4$ can reductively couple ketones and aldehydes to give alkenes (McMurry's synthesis) according to reactions 26 and 27 [128]. Dams and co-workers [128] have discussed a model (see model next page) for the titanium species [M] and they present evidence for the presence of $A\ell(0)$ in [M], generated in the $TiC\ell_3/LiA\ell H_4$ system. Reactions of [M] with alcohols show *inter alia* titanium(III) signals with superimposed aluminum splittings in the EPR spectra, thereby proving the existence of mixed $Ti/A\ell$ compounds in

$$TiC\ell_3 \;+\; \begin{matrix} LiA\ell H_4 \\ \text{-or-} \\ Mg \\ \text{-or-} \\ K,\ Li \end{matrix} \;+\; \begin{matrix} THF \\ \text{-or-} \\ \text{glyme} \\ \text{-or-} \\ \text{diglyme} \end{matrix} \xrightarrow{Ar} [M] \qquad (26)$$

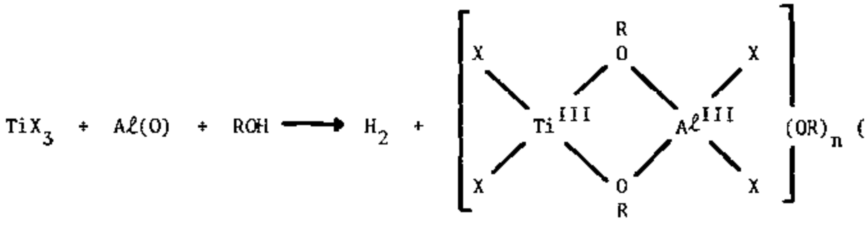
$$[M] \;+\; \text{ketone} \xrightarrow[Ar,\ \text{solvent}]{} [M,O] \;+\; \text{alkene} \qquad (27)$$

Model of Titanium Particle in [M]:

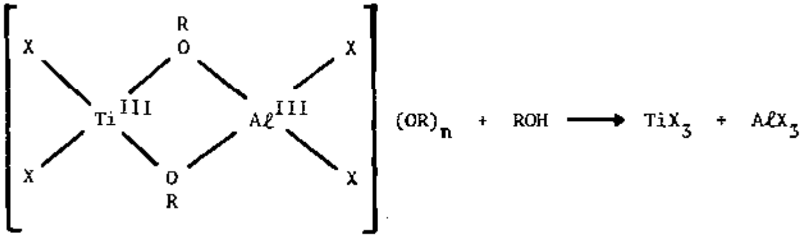


the $TiC\ell_3/LiA\ell H_4/ROH$ system; three stages have been distinguished (reactions 28-30) [128]:

$$M \;+\; ROH \xrightarrow[X\,=\,OR,\ C\ell,\ H]{} H_2 \;+\; Ti^{III}X_3 \qquad (28)$$

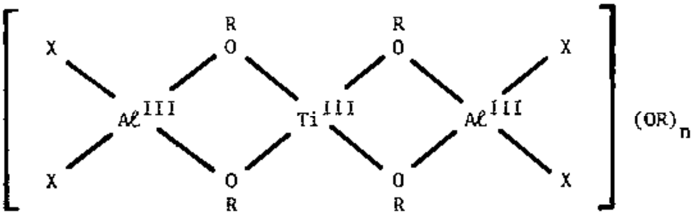


(29)



(30)

When sufficient aluminum is available, two Aℓ nuclei can interact with one Ti to form compounds of the type (22).



(22)

Electron paramagnetic resonance studies on single crystals of copper hexafluorotitanate(IV) tetrahydrate, $CuTiF_6 \cdot 4H_2O$, have been performed between 77 and 485K in the frequency ranges 23-25 and 34-36 GHz [129]. The monoclinic lattice of $CuTiF_6 \cdot 4H_2O$ has two magnetically distinct Cu^{2+} sites, but (except at 4.2K) only one resonance line was observed at all the crystal orientations; using a tetragonal symmetry at each Cu^{2+} site, the single ion parameters at 77K are $g_{\parallel} = 2.403 \pm 0.005$ and $g_{\perp} = 2.082 \pm 0.002$. Linewidth data in the ac plane of the monoclinic system were rationalized in terms of the exchange narrowing of the line broadened by the dipolar and unresolved hyperfine interactions.

Two types (I' and I) of Mo^{5+} ions were observed by EPR methods in Ti/Mo heteropolyacids (HPA) supported on TiO_2; these correspond to stabilization of the heteropoly blue with various degrees of interactions of the HPA with the surface of the solid support [130]. Ions of the type I' possess weak molybdenyl bonds and a slightly distorted HPA structure; in type I, there is a significant distortion in the HPA structure with formation of stronger molybdenyl bonds.

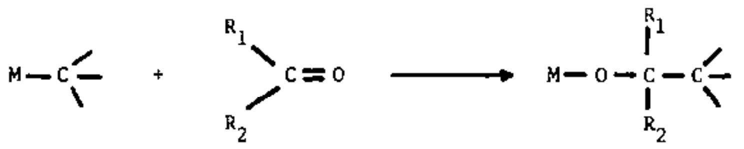
Calculations with the SCF-Xα-SW method indicate that the bonding in $TiC\ell_4$ occurs essentially between Ti $\underline{d}$ orbitals and Cℓ $\underline{p}$ orbitals [131]. Electronic structures, ionization potentials, and energies of electronic transitions have been calculated for $TiC\ell_4$ and $TiBr_4$ by the X_α scattering-wave method by Onopko and Titov [132]. Moreover, SCF-X_α-MO calculations for $TiC\ell_4$ and TiI_4 reveal that ligand $\underline{p} \rightarrow$ titanium $\underline{d}$ orbital excitations will generate metal core photoemission satellites having small intensities (∿5-10% of that of the main peak) and low energies (<5 eV from the main peak) [132]. The energies and intensities so calculated are in reasonable agreement with experiment for $TiC\ell_4$ and $TiBr_4$. The high intensity of the higher-energy (>7 eV) satellites observed for the titanium compounds were not reproduced by the calculations, in which bound empty orbitals of Rydberg character were employed. Gupta and co-workers [133] suggest that the final-state orbital in the high-energy satellite case is actually a continuum orbital of "shape-resonance" type which is localized in the interior of the molecule.

The electronic structure of stoichiometric and sub-stoichiometric titanium nitride, TiN, was studied by ultraviolet and x-ray photoelectron spectroscopy [134]. The valence-bond spectrum of stoichiometric TiN was compared with calculations of the density of states; peak positions and widths agreed well, while photon-energy-dependent intensity variations did not seem to follow the trends expected from atomic photo-ionization cross-sections. Photoelectron spectroscopy of titanium boronitride, titanium diboride, and titanium nitride compounds has also provided binding energies of the Ti $2p_{3/2}$, B 1*s* and N 1*s* core levels [135]: 455.2 eV, 187.9 eV, and 397.3 eV, respectively.

Both rutile and anatase have been the object of an extended x-ray absorption fine structure (EXAFS) study at the K threshhold of Ti [136]. Using the theoretical phases, Ti—O bond distances of 1.93(1) Å were derived for rutile and anatase, as compared with the crystallographically-obtained values of 1.948-1.980(1) Å (rutile) and 1.934-1.980(1) Å (anatase).

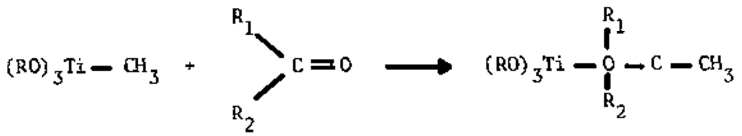
3.4 REACTIONS OF TITANIUM COMPOUNDS

Insertion reactions of the carbonyl group into a metal-carbon bond has been known for some time (reaction 31) [137]. Selective insertion of carbonyl



(31)

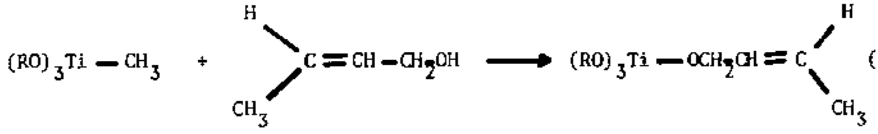
groups of aldehydes and ketones, such as acetaldehyde or acetone, into the Ti—C bond of $CH_3Ti(OR)_3$, where R is C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$, produces mixed tetra-alkoxy titanium complexes [138]. Using stoichiometric amounts of the appropriate carbonyl derivative, alkoxy ($R_1 = CH_3$) or alkenoxy (R_1 = vinyl) groups have been generated in clean processes described by reaction 32. Alkenoxy derivatives have also been obtained by a more classical substitution reaction using vinylic alcohol (reaction 33) [138]. This reaction was followed by measuring the volume of methane or by the disappearance of the


(32)

R = Et, ^{i}Pr, ^{t}Bu;

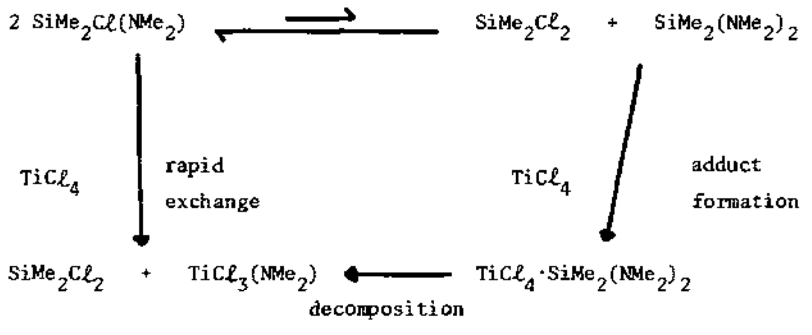
R_1 = Me, vinyl;

R_2 = H, Me,


(33)

$Ti-CH_3$ peak in the proton nmr spectrum.

Reaction of $Cp_2TiC\ell$ with one equivalent of *trans*-2-butenyl-2-lithium yields the green crystalline $Cp_2Ti($*trans*-$CH(CH_3)=CHCH_3)$ in 55% yeild. This complex reversibly adds dinitrogen, and also reductively couples with acetone to give an alkoxy compound as well as undergoing insertion reactions with CO_2, 2,6-xylylisocyanide, phenylisocyanate, CS_2, CO and diphenylacetylene [139]. Reactions of $CH_2(NMe_2)_2$ (30), $SiMe_2(NMe_2)_2$ (31), and $CpTi(NMe_2)_3$ (32) with the covalent metal halides $MC\ell_4$ (M = Ti, Zr, Hf, Si, Ge or Sn) and $MC\ell_3$ (M = Ti, V or Cr) fall into two categories [140]: (a) N-donor chelation leading to complex formation and (b) halide--NMe_2 exchange. (30) gives 1:1 adducts with $TiC\ell_4$ and $SnC\ell_4$, while (31) provodes 1:1 complexes with $MC\ell_4$ (M = Ti, Zr, Hf and Sn). The compound $TiC\ell_4\cdot SiMe_2(NMe_2)_2$ invariably decomposes to $TiC\ell_3(NMe_2)$ (reaction scheme 34) both in the solid state and in solution. Interestingly,



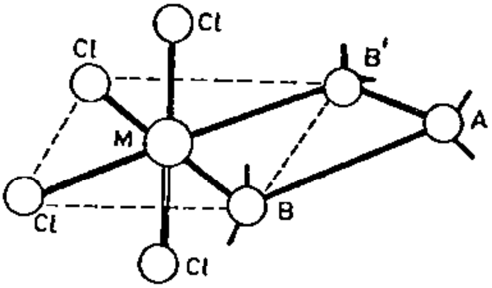
(34)

(31) does not react with metal(III) chlorides. Reactions of $CpTi(NMe_2)_3$ with

$MC\ell_4$ (M = Si, Ge, Sn, Ti, Zr or Hf) (reaction 35) consistently featured halide--NMe_2 exchange rather than adduct formation [140]. The possible

$$Cp\underline{Ti}(NMe_2)_3 \quad + \quad TiC\ell_4 \quad \rightleftharpoons \quad Cp\underline{Ti}C\ell_3 \quad + \quad TiC\ell(NMe_2)_3 \qquad (35)$$

geometries of the six-coordinate $MC\ell_4 \cdot ABB'$ and of the five-coordinate geometry of $MC\ell_4 \cdot SiMe_2(NMe_2)$ are shown in Figures 7 and 8, respectively.



A = CH_2, B = B' = NMe_2, M = Ti, Sn

A = CH_2, B = B' = PPh_2, M = Ti

A = $SiMe_2$, B = B' = NMe_2, M = Ti, Zr, Hf, Sn.

FIGURE 7: Six-coordinate geometry of the $MC\ell_4 \cdot ABB'$ compounds.

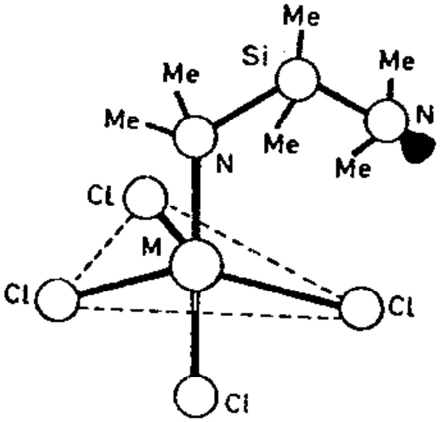
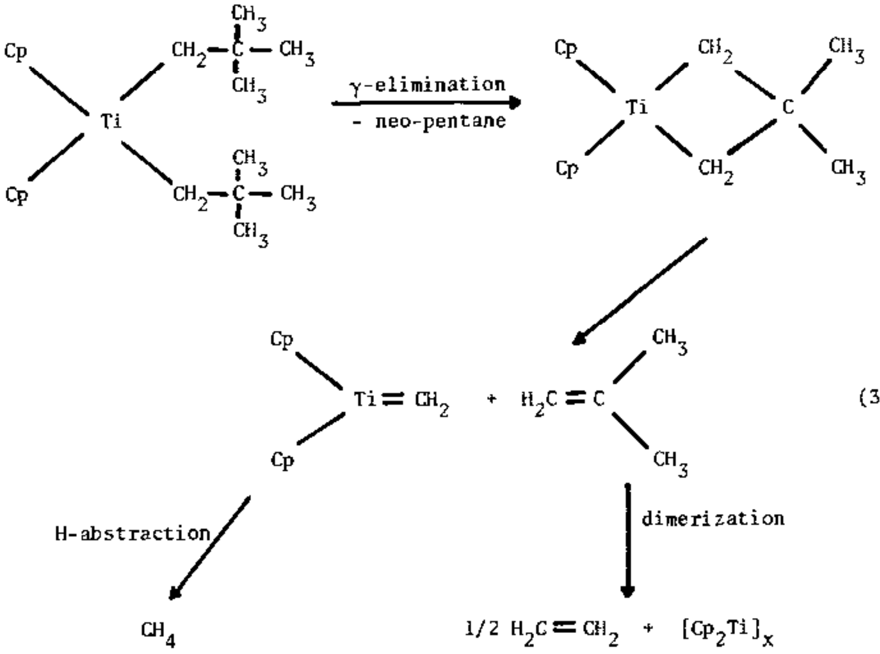


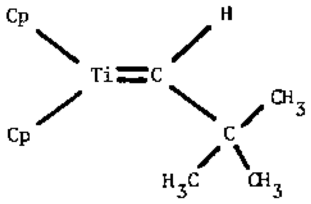
FIGURE 8: Five-coordinate geometry of the $MC\ell_4 \cdot SiMe_2(NMe_2)_2$ compounds.

Alkyl lithium (alkyl = n-propyl, n-butyl, n-amyl, neo-pentyl, and neo-hexyl) reacts with a suspension of $Cp_2TiC\ell_2$ in Et_2O at -78°C for several hours to form Cp_2TiR_2; these thermally decompose in pentane and toluene solutions at 60-80°C to give, in addition to the expected alkanes and alkenes, some CH_4, $H_2C{=}CH_2$, and other hydrocarbons [141]. Formation of minor products was rationalized in terms of δ- and γ-H elimination and metal-carbene formation. The γ-elimination is shown in the reaction sequence 36 for $Cp_2Ti(\text{neo-pentyl})_2$. The $(\eta^5\text{-}C_5Me_5)_2Ti(\text{neo-pentyl})_2$ was also studied [141];



(36)

in this case, α- and γ-hydrogen elimination are the only two possible pathways besides homolytic cleavage of the Ti—C bond. Alpha-hydrogen elimination leads to the Ti-carbene intermediate (33). Irradiation of solutions



(33)

containing $Cp_2Ti(CH_3)_2$ or $Cp_2Ti(CH_3)C\ell$ in the presence of another transition metal compound leads to methyl group transfer from Ti to the transition metal [142]. Titanocene derivatives with an interannular ethylene bridge do not follow reaction paths observed for unbridged titanocene in reactions such as formation of a Ti^{II}-dinitrogen complex, isotope exchange of the cyclopentadienyl ring ligands with deuterium, or formation of a Ti(III) hydride compound, and this in spite of strong resemblances to unbridged titanocene species in transformation reactions involving Ti(IV) or Ti(III) oxidation stages [143]. Apparently, reactions of the interannular-bridged titanocene compounds are blocked by the unavailability of a free titanocene species, $[(CH_2)_2(C_5H_4)_2Ti^{II}]_n$, as an intermediate in such systems.

The stoichiometry and kinetics of oxidation of Ti(III)/EDTA by $HOC\ell$ in the presence and absence of free radical acceptors (e.g., MeOH, EtOH, i-PrOH and methyl methacrylate) have been studied by Kozlov and co-workers [144]. A one-electron pathway was proposed for reduction of $HOC\ell$ by Ti(III)/EDTA. Reduction of $TiC\ell_4$ by $R_3A\ell$, $R_2A\ell C\ell \cdot Et_2O$, $R_{1.5}A\ell C\ell_{1.5} \cdot Et_2O$, and $RA\ell C\ell_2 \cdot Et_2O$ (R = cyclohexyl) in dry argon at 20°C and at a molar ratio of $A\ell/TiC\ell_4 = 0.5$ gave 93, 26, 19 and 16% degree of reduction, respectively [145]. Also, $Et_3A\ell$ reduces $TiC\ell_4$ to an extent of 48%, but $Et_3A\ell \cdot Et_2O$ is ineffective. A mechanism involving a bridged $A\ell$—Ti complex was proposed. Reactions of $TiC\ell_4$ with silicas has been studied at 180-200°C in dry air saturated with $TiC\ell_4$ vapour; the surface was subsequently treated with water vapour and then dried in air [146]. On cyclic repetition of this process, the concentration of Ti on silica decreased until it reached a constant value. This layered-type method of TiO_2 film formation on Silochrome-type silica decreased the film thickness, whereas it increased the thickness on Aerosil-hydrogel surface. The high tendency of Silochrome-80 OH surface groups toward ionization suggested that this silica can be used as an ion-exchanger at high pH values [146].

Diphenyl telluroxide reacts with titanium(IV) chlorides to give diphenyl tellurium dichloride (reaction 37), but with organotellurium trichlorides

$$(C_6H_5)_2TeO \quad + \quad TiC\ell_4 \xrightarrow[CHC\ell_3]{} (C_6H_5)TeC\ell_2 \quad + \quad TiOC\ell_2 \qquad (37)$$

(R = Me, *p*-MeOPh, *p*-PhOPh) it forms 2:1 addition products [147]. Reactions of $TiC\ell_4$ with $R_2P(S)P(S)R_2$ compounds (R = Me, Et) yield the hexa-coordinate species $TiC\ell_4 \cdot R_2P(S)P(S)R_2$; these were characterized by elemental analyses, infrared, visible and EPR spectra which indicate the *cis*-chelating character of these ligands [148]. In the compounds containing $Et_4P_2S_2$, the infrared spectral data show that the *gauche* conformation of the ligand is implicated in bonding to titanium.

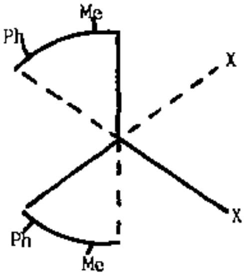
Small gas molecules can be activated by transition metal compounds, the reaction depending principally on the nature of the transition metal compound, the atmosphere and the $Mg/MC\ell_n$ ratio [149]. There appear to be many characteristics common to all systems, such as in the hydrolysis of the products of the reaction under an argon atmosphere to produce saturated hydrocarbons (e.g., methane, ethane, propane, butane, pentane). Presumably, the transition metal compound $MC\ell_n$ is first reduced to form the metal clusters M_x ($x \geq 2$), which then react with THF to form metallacyclic species; hydrolysis of these species by H_2O, D_2O, $DC\ell$ or NaOD gave hydrocarbons identifiable by mass spectroscopy.

Spectrophotometric and anion exchange studies of Ti(IV) solutions in $\leq 8\underline{M}$ H_2SO_4 ($8\underline{M} = H_2SO_4 + HC\ell O_4$) indicate that in $[H_2SO_4] = 5\text{-}8\underline{M}$, 35% of the titanium exists in dimeric form [150]. The reactivity of titanium(IV), determined by using H_2O_2, decreases upon addition of $A\ell_2(SO_4)_3$ for $A\ell_2O_3/Ti$ ratios ≤ 0.3 [151]. In dilute solutions ($\leq 0.1\underline{M}$ Ti), passivation of Ti(IV) is almost independent of $A\ell$ content; but for $0.1\text{-}0.7\underline{M}$ Ti, passivation increases as the $A\ell/Ti$ ratio increases. This passivation process is believed to involve breaking $Ti - SO_4$ bonds and forming $Ti - OH$ and $Ti - O$ bonds [151]. The kinetics of hydrolysis of titanium(IV) sulfate in concentrated solutions at the coagulation stage have been reported by Gornikova and co-workers [152]. The yield of titanium hydroxide in precipitates after prolonged heating of solutions at the boiling point, and the influence of solution concentration and the amount of crystal nuclei of TiO_2 on the kinetic parameters were examined. The hydrolysis rate constant increases as the number of TiO_2 crystal nuclei increases, and the effect appears more noticeable in dilute solutions of titanium sulfate. In concentrated solutions, the coagulation kinetics are determined by changes in the overall titanium concentration and not by the content of colloidal titanium hydroxide [152]. A similar study on the kinetics of Ti(IV) hydrolysis in sulfate solutions has been carried out by Danenko and co-workers [153].

The hydrolytic precipitation of titanium(IV) in $2.0\underline{M}$ (Na, H)$C\ell$ aqueous solutions at 25°C has been studied by measuring the free H^+ concentration potentiometrically and the aqueous concentration of Ti(IV) by a spectrophotometric method [154]. Under conditions where the solution is saturated with regard to precipitated titanyl(IV) hydroxide, monomeric and polycationic species such as TiO_2^{+}, $TiO(OH)_2$ and $[(TiO)_8(OH)_{12}]^{4+}$ may be present in the solution. However, in the presence of 1.3-5.4 times (molar ratio) as much phosphate, only the mono-orthophosphate complex, $TiO(HPO_4)$, forms [155]. A scheme of complex formation and precipitation equilibria was presented [154, 155].

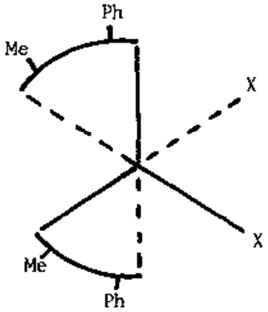
Reaction of ammonium hexafluorotitanate(IV) with excess xenon difluoride gives the corresponding xenon(II) hexafluorotitanate [156].

Diastereotopic probes have been incorporated on the X ligands of $Ti(bzac)_2X_2$ complexes [X = i-C_3H_7O (34) and 2,6-i-$Pr_2C_6H_3O$ (35)] to follow the course of configurational rearrangement processes [157]. (34) was prepared by reacting stoichiometric amounts of benxoylacetone (Hbzac) with $Ti(^{i}C_3H_7O)_4$ in dichloromethane; (35) was obtained from a reaction of (34) with 2,6-diisopropylphenol. Both complexes were characterized by variable temperature nmr techniques which revealed that the complexes possess the *cis* stereochemistry, although the studies did not delineate between bond rupture and twist modes for the configurational rearrangement process, which scrambles the methyl groups of the bzac ligand amongst all 4 sites (see 36-38).



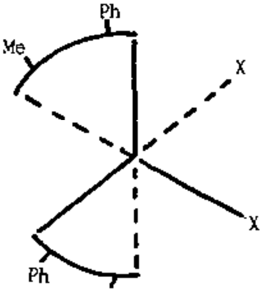
cis(X)-*cis*(Ph)-*trans*(Me)
1-Me site

(36)



cis(X)-*trans*(Ph)-*cis*(Me)
1-Me site

(37)



cis(X)-*cis*(Ph)-*cis*(Me)
2-Me sites

(38)

Infrared absorption spectra of methylsilanes, $Me_{4-n}SiX_n$ (n = 1-4; X = Cl, OMe) and hexamethyldisilazane, bonded to a TiO_2 powder confirm the presence of a bonded silane layer [158]; terminal surface OH groups react more readily than bridging OH groups. The various silanes show only small differences in their ability to sequester surface OH groups. Two TiO_2 samples (anatase) were treated with $C_nH_{2n+1}NH_2$ (n = 3, 4, 6, 8, 12, 14, 16 and 18) and with several carboxylic acids (HOAc, CF_3COOH and BzOH) at 80°C for 1 hr. in benzene [159]. Except for octadecylamine, the amounts of amine reacted with TiO_2 heat-treated at 300°C were 0.84-0.99 mmol/g TiO_2, regardless of the number of carbon atoms in the molecule; the surface area of TiO_2 occupied by amines, as a monolayer, was *ca.* 110 m^2/g TiO_2. The TiO_2 treated with amines possessing a hydrocarbon chain longer than $BuNH_2$ was dispersed in benzene more preferentially than in H_2O, indicating that the hydrophilic surface of TiO_2 was changed to lipophilic by the amine treatment. For the carboxylic acid treatments, only benzoic acid was effective in modifying the TiO_2 surface [159].

The phase compositions of $TiO_2 \cdot nH_2O$, $SrCO_3 \cdot mH_2O$, and their mixtures at a SrO/TiO_2 ratio of 1 at 100-1150°C were studied by differential thermogravimetry, x-ray phase analysis, and by microscopy [160]. At 1150°C, the mixture is converted to $SrTiO_3$ in 99.8% yield.

In a study of the products from the reaction of zinc oxide with titanium tetrachloride, Avrutina and co-workers [161] found that the amount of chemisorbed Ti depends on the synthesis temperature and the Ti-containing product contains a significant amount of $C\ell^-$ ions, while the maximum amount of Ti in the sample of the reaction products was observed at 200-300°C. Kinetic studies of the decomposition behaviour of $A\ell_2TiO_5$ have been reported [162]. Also, in the reaction of hydrated TiO_2 with sulfuric acid, it appears that sulfuration of $TiO_2 \cdot nH_2O$ results from dissolution in H_2SO_4 and may not be the result of a surface reaction [163]. Chlorination kinetics of Fe_2O_3, MgO, TiO_2, and (Fe, Mg)TiO_3 have been studied using $C\ell_2$/CO and $C\ell_2$/C at 400-500°C [164].

Formation of the non-active phase, $NiTiO_3$, during the preparation of NiO/TiO_2 catalysts was prevented by impregnating TiO_2 with a $Ni(NO_3)_2$ solution, drying and calcining for 6 hr. at 600°C [165]. The catalysts were subsequently obtained by reduction at 200-800°C in a H_2/Ar atmosphere. A mechanism of the initial stages of the carbon reduction of TiO_2, Ti_3O_5, Ti_2O_3, and TiO has been suggested [166]. The higher oxides are reduced to lower oxides, whereas TiO_2 disproportionates to Ti_2O_3 and Ti; disproportionation of CO on the oxide surface was also proposed.

pH has a significant influence on the nature of the products from the reduction of N_2 by the hydroxide systems $Ti(OH)_3/Mo(OH)_3$, $Cr(OH)_2/Mo(OH)_3$, and $Mg(OH)_2/Ti(OH)_3/Mo(OH)_3$ [167]. For weakly alkaline solutions, dinitrogen is directly reduced to NH_3; but in strongly alkaline solutions, NH_4 acts as an intermediate. For the three-component hydroxide mixture, direct reduction to NH_3 occurs only at large concentrations of molybdenum; a mechanism was proposed [167] whereby N_2 is reduced through complexation to Mo. The heterogeneous reaction of Ti with alkaline-earth metal oxides in metal chloride melts has been investigated [168].

Reactions between TiP_2O_7 and CuO mixtures containing 10-90 mol % CuO at 900°C for 200 hrs yield $CuTi(PO_4)_6$, $Cu_2P_2O_7$, $5TiO_2 \cdot 2P_2O_5$, TiO_2(rutile), $Cu_3(PO_4)_3$, $4CuO \cdot P_2O_5$, and $5CuO \cdot P_2O_5$ [169].

3.5 ELECTRODE REACTIONS AND ELECTROCHEMISTRY OF TITANIUM COMPOUNDS

In the last year the vast majority of electrochemical studies have centred on the preparation and characterization of TiO_2 semiconductor electrodes, owing to their potential application in photoelectrolysis of water and as photocatalysts. Ahlgren [170] has made a theoretical analysis of the current-voltage characteristics of photoelectrolysis cells; the analysis was subsequently used to rationalize experimental data for cells incorporating n-type titanium oxide and tungsten oxide semiconductor electrodes in acidic media with a platinum counter-electrode. Optimum cell voltages, quantum yields, maximum electrode efficiencies, kinetic parameters (valence and conduction band transfer coefficients and exchange current densities), minority current densities and diffusion lengths were derived.

Several preparative techniques have been evaluated. Photocurrent spectroscopy has been utilized to study the early stages of anodic film growth on titanium. Photocurrent conversion efficiency data as a function of wavelength for films prepared at various potentials show that the film is essentially pure TiO_2 above ~1.5 V *vs* SCE at pH 0 [171]. This technique is also used to follow changes in film structure and thickness during breakdown at higher voltages. Thermally-formed polycrystalline TiO_2 electrodes have been prepared by heating titanium substrates in an oxidizing flame of a gas burner or in an electrical furnace. The open-circuit voltage of the photoelectrochemical cell incorporating this electrode is 600 ± 20 mV. Other data were collected, including, among others, space-charge layer capacitance at various pH and potentials, film thickness; a structure-type model was proposed [172]. Titanium oxide electrodes can be prepared *via* the oxidation of pure titanium laminae in a CO_2 atmosphere at 300-700°C, and used for the photodecomposition of H_2O. X-ray diffraction and an interference indicator method were used to characterize the initial stages of the oxidation of titanium. The presence and influence of metallic interstitial titanium suboxides were revealed and found to promote the efficiency of an overlaying non-stoichiometric rutile scale [173]. A combined ellipsometric-electrochemical study by Krasil'nikova and co-workers [174] of the formation of an anodic oxide film on Ti at 20°C in 5N KOH showed good agreement with a two-layer model: a denser inner TiO_2 layer possessing a highly defective structure with semiconducting properties, and a less dense outer layer of hydrated TiO_2 that is virtually nonabsorbent. Furthermore, most of the film formation occurs rapidly up to a given thickness, followed by a slow growth period during which the optical character of the film may change.

Doped polycrystalline TiO_2 films in metal substrates have been prepared in various electrolytes by anodic oxidation accompanied by sparking [175]. Cationic species present in the electrolyte are doped into the oxide film during oxidation; the TiO_2 film thus prepared at 100 V proved a good photoanode, with a relatively high photocurrent under visible irradiation. It was suggested that the dopant and the interstitial metal $\underline{d}$ bands (or states) which are responsible for the visible response of these films also served as centres for recombination.

The method of preparation appears to have important consequences on the electrode's behaviour. Titanium oxide-coated electrodes have been prepared by (i) anodizing Ti substrates by vacuum heating to convert the surface oxides into semiconducting material, and by (ii) chemical vapour deposition in air on glass plates, followed by vacuum heating [176]. The electrodes prepared in this manner exhibit different degrees of photoanodic current, though the decomposition was was the major anodic reaction. Photoanodic current densities were found to depend on the preparative method used: those electrodes formed at 900°C and vacuum-heated at 600°C yield high photoanodic currents as well as dark currents, while those formed at 700°C over shorter periods of time also gave high photoanodic currents but much lower dark currents. The temperature dependence of the electrical and photoelectrochemical characteristics of TiO_2 films, obtained by vapour decomposition of ethyl titanate, have also been described [177]. It was shown that the electrical properties of these films depend primarily on the deposition temperature, with lower conductivity and higher photosensitivity exhibited by films deposited at higher temperatures. Additionally, the deposition temperature had an effect on the anodic photocurrent-potential character and spectral dependence of anodic photocurrents. Some doping effects (by $A\ell$, Cr and Fe) on these properties were also described [177]. The effects of heat treatment and of the concentration of uncontrolled impurities on the performance of various TiO_2 electrodes were investigated. For optimally heat-treated TiO_2 electrodes, a 1.2% conversion efficiency has been reported [178].

A theoretical/experimental description of the time dependence of pulse photocurrents and experiments on detection of transient intermediates in photoelectrolytic processes involving single-crystal and polycrystalline n-TiO_2 semiconductor materials has been reported [179]. Controlled-potential chronoamperometric techniques permit selective monitoring of various potential regions, while photocoulostatic potentiometric techniques provide for faster time resolution of photo-induced events. The polycrystalline electrode yielded better time resolution data because of lower ohmic resistance. The limitations of the time-resolved measurements and the nature and significance of transient photo-induced events are discussed [179]. Handley and co-workers [180] have measured the interband transitions in single-crystal n-TiO_2 semiconductor electrodes using a stress modulation technique based on optical absorption. The modulated stress was applied to the semiconductor by modulating the strain of an attached piezoelectric transducer. The photoelectrochemical spectrum obtained in the region of minimum inter-band gap was given [180]. A photoelectrochemical study of the reaction of valence-band holes generated upon 347-nm irradiation of aqueous TiO_2(anatase) solutions with halide ions (I^-, Br^-, $C\ell^-$) revealed that hole transfer occurs within the duration of the laser pulse employed (10 nsec), and yielded anion radicals [181]. A comparison of the electroluminescence and photo-luminescence spectra of various semiconductor electrodes (TiO_2, GaP, CdS and ZnO) reveals luminescence bands attributed to surface-trapped holes, which presumably act as precursors to the photoanodic reaction [182].

The presence of various species in solution has been investigated in an effort to elucidate their effects on the electrochemistry of TiO_2 electrodes [183]. The presence of flaws in the surface of TiO_2(rutile) electrodes in the anodic oxidation of several reducing agents [$Fe(CN)_6{}^{4-}$, I^-, Br^- and $C\ell^-$] revealed the following behaviour: the current efficiency decreases with increasing anodic potential up to a critical potential [183]. The results were interpreted in terms of the different behaviour of surface hydroxyl radicals involved in the electrode reaction. Studies on the role of surface states on TiO_2 electrodes in the cathodic reduction of dissolved and/or photogenerated O_2 at pH 3 and 14 reveal support for a model in which these bandgap surface states mediate electron transfer from the conduction band to chemisorbed O_2 molecules [184]. The proposed models in acidic (reaction 38) and basic (reactions 39-41) media are shown. In basic media, the surface states are localized on the $TiOH_b^-$ basic hydroxyl groups.

i) at pH 3:

$$\mathrm{Ti{-}OH^-} + e^- \longrightarrow \mathrm{Ti{-}O^{2-}\cdots H} \tag{38}$$

ii) at basic pH:

$$2\ \mathrm{Ti{-}OH_b^-} + \mathrm{O_2} \longrightarrow 2\ \mathrm{Ti{-}OH^-\cdots O} \tag{39}$$

$$2\ \mathrm{Ti{-}OH_b^-\cdots O} + 4\ e^- \longrightarrow 2\ \mathrm{Ti{-}O^{2-}} + 2\ \mathrm{OH^-} \tag{40}$$

$$2\ \mathrm{Ti{-}O^{2-}} + 2\ \mathrm{H_2O} \longrightarrow 2\ \mathrm{Ti{-}OH_b^-} + 2\ \mathrm{OH^-} \tag{41}$$

The photoprocesses which occur on n-TiO_2 and n-$SrTiO_3$ electrodes in the presence of reducible species generated by pre-illumination under reverse bias conditions have been discussed by Sprünken and co-workers [185]. The amounts of such species formed were found to depend on the negative charge needed to reduce them, which is related to the voltage at which the anodic-cathodic photocurrent transition occurs. The occurrence of the cathodic photoprocesses was interpreted in terms of an electron-tunnelling mechanism. A recent report on the effect of electrolytes and electrolyte concentration on the flat-band potential of n-TiO_2 electrodes has appeared [186]. Using a photoresponse method, it was shown that the presence of compounds such as $NaC\ell$, $KC\ell$, NaI, KNO_3, Na_2SO_4, K_2SO_4 and $NaC\ell O_4$ do not affect the flat-band potential; however, the presence of EDTA and 8-hydroxyquinoline appears to have a pronounced effect, ascribed to complexation with surface ions. The adsorptive characteristics due to the presence of HSO_4^-, $C\ell^-$, $H_2PO_4^-$ and $C\ell O_4^-$ acid anions on TiO_2 electrode surfaces have been investigated with respect to their dependence on electrode potential, anion concentration, adsorption time and solution pH[187]. The solution pH was found to play a major role in the anion adsorption process. The proposed adsorbability sequence is: $C\ell O_4^- < C\ell^- < HSO_4^- < H_2PO_4^-$. Interface energetics of n-TiO_2 and n-$SrTiO_3$ in acetonitrile containing 1$\underline{M}$ $(n\text{-}Bu_4N)C\ell O_4$ and various redox reagents have been studied by cyclic voltammetry [188]. Reversible dark electrochemistry was observed for redox couples with sufficiently negative $E^{o\prime}$ values (<-1.3 V for $SrTiO_3$ and <-0.9 V for TiO_2). Results of photocorrosion studies were also discussed.

The characterization of mixed metal oxides as well as platinized TiO_2 electrodes has received increased attention. A dynamic potential sweep method has been used to investigate and compare the photoelectrodic processes of TiO_2 and platinized TiO_2 materials [189]. The results indicate that the surface energy states of TiO_2 are greatly enriched upon deposition of platinum, which promotes electron transfer across the electrode/solution interface and facilitates catalyst-reactant interaction. Also, cyclic voltammetric and XPS techniques have been employed to characterize the electrochemical and surface behaviour of polycrystalline TiO_2(anatase) which was partially or completely platinized [190].

Anode coatings composed of RuO_2 (30 mol %) and TiO_2 (70 mol %) show increased service life in NaCℓ solutions, as monitored by polarization curves obtained during chlorine evolution experiments [191]. The effect of SO_4^{2-} and pH on the selectivity and corrosion resistance of this electrode system in NaCℓ at 87°C has been reported [192]. The operating effectiveness of active layers of RuO_2 in potassium biphthalate, alkali and H_2SO_4 solutions, and that of RuO_2/TiO_2 mixtures in chloride solutions have also been evaluated [193]. Oxygen evolution occurs on RuO_2/TiO_2 anodes in $1\underline{M}$ $HC\ell O_4$, $0.5\underline{M}$ H_2SO_4 and $1\underline{M}$ $NaC\ell O_4$ on rotating disc electrodes, in $1\underline{M}$ $HC\ell O_4$ on plate electrodes, and in NaOH solutions [194]. The results of this study have allowed for the evaluation of the number of electrons taking part in the $OH^- \rightarrow O_2$ conversion, of the order of reaction with respect to $[OH^-]$, and reaction mechanisms in both alkaline and acidic media.

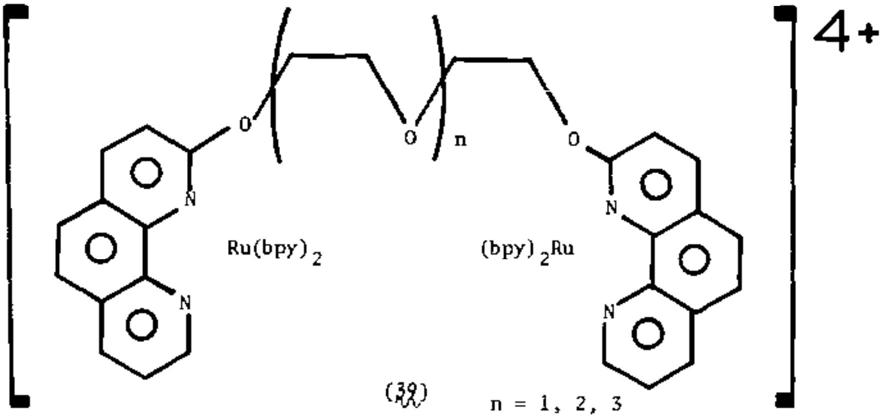
$Ti/Au/PbO_2$ electrodes can be prepared by etching Ti with 20% HCℓ, followed by electroplating of a Au film and deposition of PbO_2 [195]. The electrochemical decomposition of $MnSO_4$ using the $Ti/Au/PbO_2$ electrode system revealed a decrease in electrode resistance ascribed to the presence of the gold layer, as well as to temperature and to electricity yield effects on electrochemical stability. ESR studies of the effect of phase transition (50-250°C) in Mn^{2+} containing $BaTiO_3$ on adsorption of oxygen and carbon monoxide and on the kinetics of CO oxidation were reported and interpreted in terms of changes in the electronic band structure of $BaTiO_3$ during phase transition [196]. Results of surface doping experiments suggest that TiO_2 and $SrTiO_3$ crystals doped with Cr_2O_3 (but not $LaCrO_3$) may have increased efficiencies for photoelectrolysis with visible radiation, as compared to undoped crystals [197]. The photoelectrochemical response of a number of perovskite oxide anodes has been evaluated [198]. Titanium-supported photoanodes, prepared by heating Ti-coated discs with a paste of La_2O_3 with each of the oxides Cr_2O_3, RuO_2, PtO_2, Au_2O_3 and Co_2O_3, showed reasonable photoactivity for oxygen evolution. The specific La_2O_3-Cr_2O_3/Ti photoanodic system was also studied by high-resolution x-ray photoelectron spectroscopy. Photocurrents of n-TiO_2 in aqueous electrolyte solutions can be improved by deposition of an oxygen-evolution catalyst, such as Pt or Rh, onto the semiconductor surface [199].

Gutierrez and co-workers [200] have investigated the electrochemical character of the mixed metal oxide, $NiTiO_3$, for possible incorporation in solar energy conversion schemes. This oxide system undergoes irreversible anodic oxidation and exhibits stirring-independent Cottrell behaviour owing to the current limitation by diffusion of a reaction product far removed from the $NiTiO_3$ surface. Also, $NiTiO_3$ was found to age, most probably due to porous film formation of an irreducible higher oxide. Photoelectrolysis studies at Fe_2O_3/TiO_2 heterojunction electrodes revealed that an energy barrier to the movement of holes from the Fe_2O_3 to the TiO_2 is created by discontinuity at the conduction bands [201]. This energy barrier may be reduced by using a thin TiO_2 film (∿1000 Å), thereby favouring movement of the holes in Fe_2O_3 toward the heterojunction *via* upward band bending. Application of a small anodic bias may aid the holes in overcoming the energy barrier at the heterojunction and contribute to the electrode reaction at the TiO_2/electrolyte surface.

Semiconductor materials with appropriate band gap energies are currently the focus of a great deal of attention with regard to the photo-assisted splitting of water to produce dihydrogen and oxygen. Photodecomposition of H_2O occurs in a photocell equipped with a semiconductor (n-TiO_2)/redox electrolyte/semiconductor junction. Considerable gas evolution was observed at both n-TiO_2 and Pt counter electrodes, though the system is sensitive only to ultraviolet light [202]. Hydrogen production ($\Phi = 0.088$) was observed [203] upon ultraviolet irradiation of a suspension of TiO_2 and Pt in 1N H_2SO_4. The system was also studied in the presence of electron donor species (Co^{2+}, Fe^{2+}, hydroquinone and a Fe^{2+}-EDTA complex), as well as in the presence of various dyes (eosin, Rhodamine and Rose Bengal) and an electron donor species (EDTA or oxalic acid) [203].

Ruthenium(II) polypyridyl complexes have been shown to act as good photosensitizers in the photo-assisted decomposition of H_2O. The photoelectrolysis of H_2O, employing single-crystal $SrTiO_3$ as the photoanode, has been investigated [204]. The photosensitizer species utilized were thin films of water-insoluble ruthenium(II) surfactant dyes of the type $[Ru(bpy)_2(4,4'\text{-}R_2\text{-}bpy)]^{2+}$, where R = n-$C_{19}H_{39}$ or COO-n-$C_{18}H_{37}$ and bpy = 2,2'-bipyridine, or the binuclear type complexes (39). These films are capable of electron donation to the $SrTiO_3$, producing an anodic photocurrent of 60-100 nA/cm^2 [204]. A similar system incorporated the photosensitization of n-TiO_2 and n-$SrTiO_3$ with chemically-attached $[Ru(bpy)_2(bpca)]$ (bpca = 2,2'-bipyridine-4,4'-dicarboxylic acid) [205]. The photolysis of a natural aqueous system with platinized TiO_2 suspended in a $Rh(bpy)_3{}^{3+}$ solution has also been carried out [206].

The anodic and cathodic behaviour of sintered TiN in acidic and alkaline media under anodic polarization, as well as cathodic H evolution, have been reported [207]. TiN films deposited on Si were prepared by reactive evaporation and rf sputtering methods, and were characterized by optical,



(39) n = 1, 2, 3

electrochemical, chemical and structural techniques.

The characterization of the potential dependence of alkali metal ion (Li^+, Na^+, K^+) intercalation has been carried out by cyclic voltammetry of titanium disulfide electrodes in nonaqueous media [209]. The non-Nernstian behaviour of the intercalation reaction in these systems was attributed to slow solid-state diffusion, as indicated by MPSDC experiments. Long-time chronoamperometry experiments have further elucidated the solid-state diffusion coefficient, as well as heterogeneous rate constants and effective electrode area [210]. The intercalation reaction 42, where M = Li, Na or K, occurs in a K-TiS_2 battery cell in dry dioxalane [211].

$$\mathrm{MSCN} + \mathrm{B(C_6H_5)_3} \xrightarrow[\text{dioxalane}]{} \mathrm{M^+[(C_6H_5)_3BSCN]^-} \qquad (42)$$

A solid β"-alumina electrolyte was employed in the electrochemical study of TiS_2 and TiS_3 electrodes in a Na cell at 230-280°C [212]. The reaction of TiS_2 is reversible, while TiS_3 decomposes. Side reactions of the electrode were minimized by use of a solid electrolyte.

Electrochemical reduction of $TiC\ell_4$ in DMSO was carried out in an effort to determine the effect of solvent type on the reduction kinetics and mechanism [213, 214]. Two techniques were employed: (i) cyclic voltammetry [213] and (ii) rotating disc electrodes [213, 214]. These methods suggest a two-step cathodic process, reduction of Ti(IV) to Ti(III) followed by a secondary chemical reaction to produce Ti(II) and Ti(O) [213].

The formal redox potentials of several quinone/hydroquinone couples in $HC\ell$, H_2SO_4 and HOAc media were reported; the quinones include tetrachloro-1,2-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone, and methyl-1,4-benzoquinone [215]. This study incorporated both potentiometric and visual titration methods using $TiC\ell_3$ in $HC\ell$ and H_2SO_4 media. Electroreduction of aromatic nitro compounds (nitrobenzene, dinitrobenzenes, nitrotoluenes, phenols, nitrochlorobenzenes and nitroxylenes) takes place using a Cu cathode, a Pb anode and a porous pot diaphragm [216]. The diaphragm consisted of a 2-3 % $Ti(SO_4)_2$ catholyte and a 30-40 % H_2SO_4 anolyte.

Reduction of nitrate ions in a variety of solvent systems occurs on a rotating disc electrode of VT-1 titanium in a cell with separate anodic and cathodic chambers [217]. The relation between the nature of the reactions products, their concentration and the change in specific rate of dissolution (effective valency) of Ti was established.

In situ formation of polymeric phthalocyanine coatings results from the gas-phase reaction of 1,2,4,5-tetracyanobenzene with metal sheets of Ti, Cu, Ni, Co,and Fe [218]. The coatings have been characterized with respect to layer thickness, electrical resistance and electrochemistry (cyclic voltammetry).

The electrochemical synthesis of $Cp_2Ti(CO)_2$ was accomplished with a titanium metal anode, cyclopentadiene monomer and CO [219]. The same method was used to prepare Cp_2M (M = Fe, Co), $[CpFe(CO)_2]$, $CpCo(CO)_2$ and $CpV(CO)_4$, although attempts to prepare the analogous Ni complexes proved unsuccessful [219].

High yields of bromoanisole were obtained in the photo-assisted bromination of anisole with an n-TiO_2 electrode at 0-0.7 V, while no appreciable bromination at a Pt electrode was observed at such potentials [220]. Furthermore, at potentials less than 0 V, product yield decreased due to low Br_2 production efficiency; whereas, at potentials greater than 0.7 V, the current efficiency decreased because of preferential H_2O and anisole oxidative processes.

Reaction 43 was investigated voltammetrically with n-TiO_2 and Pt electrodes in aqueous electrolytes under dark and illuminated conditions [221].

$$Fe(CN)_4^{3-} + e \rightleftharpoons Fe(CN)_6^{4-} \qquad (43)$$

In the dark, the reaction is reversible at the Pt electrode and irreversible at the n-TiO_2 electrode. The rectifier nature of the latter electrode was attributed to the bonding of H^+ to surface O atoms. Photo-oxidation of $Fe(CN)_6^{4-}$ occurs at *ca.* -0.9 V (*vs* SCE) at the n-TiO_2 electrode [221].

The electrosynthesis of a sebacic acid diester was performed using Pt and Pt oxide/Ti oxide anodes in methanolic and aqueous methanolic media [222]. The results indicate similar kinetics and mechanisms for both electrode systems, with a somewhat higher product yield for the Pt oxide/Ti oxide electrode. Photoelectrochemical reactions of HCHO in aqueous $SrTiO_3$ suspensions containing transition metal oxide deposits reveal that oxidation of HCHO to HCO_2H and then to CO_2 predominates [223]. Reduction of HCHO to yield MeOH, EtOH, MeCHO and traces of C_1-C_3 hydrocarbons accounted for less than 15% of the reaction products [223]. The products and their mechanisms of formation were similar to those of the photo-assisted water-gas shift reaction.

3.6 TITANIUM COMPOUNDS AS CATALYSTS

The use of titanium compounds as catalysts continues to be an active field of study. A kinetic study of the polymerization of acetylene [224] and of the polymerization of ethylene [225] have been reported. The kinetic curves for polymerization of C_2H_2 using soluble $Ti(OBu)_4$-$A\ell Et_3$ as a catalyst showed a rapid consumption of C_2H_2 followed by a slowing of the rate as a polyacetylene film formed. The polymerization rate was a maximum at an $A\ell$/Ti ratio of 4:1. The kinetics of the polymerization of ethylene in the presence of chlorobis(cyclopentadienyl)propyltitanium-$EtA\ell C\ell_2$ suggests that the polymerization active species is formed in two successive dynamic equilibria. A complete reactive scheme for the polyreaction was suggested [225].

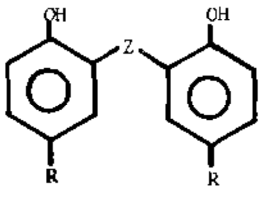
Polymerization of butadiene in the presence of $TiC\ell_4$-$A\ell Et_2C\ell$-$MgPh_2$ at Ti:$A\ell$:Mg molar ratios of 1:10:5 and 1:20:3 produced butadiene rubber with 30-38% 1,4-*cis*- and 56-62% 1,4-*trans*- units [226]. Addition of catalytic amounts of iodine increased the polymer with 1,4-*cis*-configuration to 77%. The rubber produced by this catalyst has good physicomechanical properties without vulcanization. The effects of lubricating oil, carbon black and Neozine D antioxidant on polymerization were examined. Lubricating oil decreased the physicomechanical properties of the rubber. Carbon black and the antioxidant stabilized the rubber without affecting its quality [227].

The effect of the composition of catalysts of the type iso-$Bu_3A\ell$-ketone-$TiC\ell_4$ in the structure of the alternating copolymer of butadiene-propylene in toluene at -40 ± 2°C has been reported [228]. Infrared studies indicated that in toluene $TiC\ell_4$ forms 1:1 or 1:2 complexes with the ketone, but only the 1:1 compounds were active in starting polymerization. The content of the 1,4-*cis*-butadiene units ranged from 86% in AcPh to 94% in MEK. $TiC\ell_4$ also forms complexes with Et_2O, iso-Pr_2O, THF, dioxane and PhCHO, but not with Ph_2O and MeOPh [228].

The polymerization of propylene at 70°C and 20 atmospheres in ligroin, containing $\mathrm{Et_2A\ell C\ell{-}TiC\ell_3}$ modified with 10-15% $\mathrm{Et_3A\ell}$, in the presence of hydrogen increases the polymerization rate by a factor of 1.6 to 1.7 [229]. The use of $\mathrm{Et_2A\ell C\ell{-}TiC\ell_4}$ in hexane to polymerize dimethylbutadiene and $\mathrm{Me_2C{=}CH_2}$ for 8 hrs at -60°C gives 73% copolymer [230]. In the presence of $\mathrm{EtA\ell C\ell_2{-}CpTiEtC\ell}$, the polymerization of ethylene is activated by the presence of Lewis acids ($\mathrm{A\ell C\ell_3}$, $\mathrm{A\ell_2OC\ell_4}$) formed from the reaction of $\mathrm{EtA\ell C\ell_2}$ with donor molecules or with H_2O [231].

A re-evaluation of the experimental data produced in the last twenty years on the number of active sites in $\mathrm{TiC\ell_3}$-propylene polymerization catalysts has led to the conclusion that the number of active centres is in the range of 2-10% of the total $\mathrm{TiC\ell_3}$ after an initial reaction period [232]. The number of active sites increases with increasing temperature.

New linear and cyclic isoprene dimers have been prepared using Ti complexes with $\mathrm{A\ell Et_3}$ activators [233]. Treating ligands (40) (R = H, Z = O, S; R = Br, Z = S) with $\mathrm{TiC\ell_4}$ gave the complexes (41). (41) (R = H, Z = O, S; R = Br, Z = S) with $\mathrm{A\ell Et_3}$ and isoprene in an ampoule at 120°C for 20 hr gave a little α-limonene and traces of 1,4-dimethyl-4-vinyl-1-cyclohexene and 10% polymer. For R = H, Br, and Z = S, (41) gave mostly dimers; specifically, when R is Br and Z is S, (41) gave 55-62% dimers [233].



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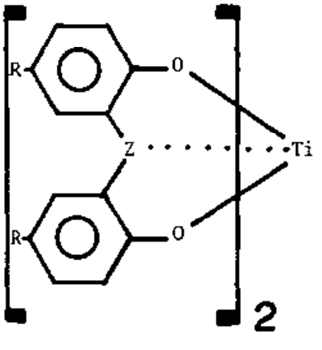


(41)

The rate of hydrogenation of cyclohexene is 10-70 times faster with titanocene on polymer supports than with homogeneous titanocene [234]. The rates with supported catalyst differed with the polymer support employed, the degree of cross-linking and the physical state of the heterogeneous catalyst. The rate of hydrogenation increased when better site isolation was provided. Even uncrossed-linked polymer supports increased the hydrogenation rate over the homogeneous catalyst. The enhanced activity may be due to protection of the titanocene sites [234].

A study of the structure and growth of polymer chains resulting from the polymerization of *trans*-1,3-pentadiene in the presence of trimethylaluminum-tetrabutoxy titainium catalyst shows the stereoregularity of the macromolecule is a growing function of the molecular weight. Long times of polymerization or high concentrations of catalyst apparently result in gel formation [235].

The kinetics of the oxidation of di-n-butylsulfide, *p*-methylphenylmethylsulfide, and *p*-chlorophenyl metal sulfide with t-butylhydroperoxide in toluene with catalytic amounts of $TiO(acac)_2$ and $Ti(OPr)_4$ indicate the reaction is first order in hydroperoxide and catalyst and a positive but fractional order in substrate. It was suggested that the sulfides coordinate with Ti(IV) in solution; a mechanism is proposed [236].

A study of the oxidation of some dialkyl sulfides and some aryl alkyl sulfides with hydrogen peroxide in ethanol catalysed by $TiO(acac)_2$ shows a rate law which is first-order in catalyst and almost zero-order in hydrogen peroxide. A side-bonded peroxytitanium(IV) species was proposed, formed from H_2O_2 and Ti(IV) [237].

The support material for Pd acting as a catalyst for the formation of methane from hydrogen and CO causes a wide variation in the specific activity of the catalyst. TiO_2-supported Pd is the most active catalyst reported, and Pd on SiO_2 the least active [238].

An investigation of reaction 44 catalysed by 10% by weight metal oxides

$$4\ NO + 4\ NH_3 + O_2 \longrightarrow 4\ N_2 + 6\ H_2O \qquad (44)$$

(V_2O_5, Cr_2O_3, Fe_2O_3) supported on TiO_2 and $A\ell_2O_3$ showed TiO_2-supported catalysts to be more active than the $A\ell_2O_3$-supported one. Catalysts impregnated on TiO_2 were less effective than chemically-mixed catalysts at 125°C]239].

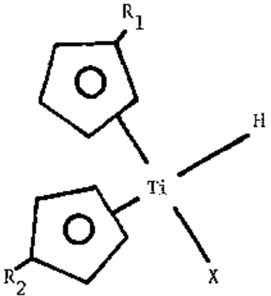
The kinetics of the catalytic oxidation of CO over perovskite oxides have been studied [240]. The oxidation of hydrogen on TiO_2 is described by the same rate law for both continuous and pulse flow conditions. The reaction involves a Langmuir-Hinshelwood absorption mechanism and not surface reduction of the catalyst [241]. A kinetic analysis of the effect of promoters on vanadium-titanium catalysts used in the oxidation of *o*-xylene has appeared in the Russian literature [242]. The addition of 0.3% TiO_2 to a palladium-aluminum catalyst used in the hydrogenation of benzene does not appear to affect its activity after calcining at 500-700°C under one atmosphere of hydrogen [243].

The physical characterization of Fe/TiO_2 model supported catalysts has been extensively studied by electron microscopy. X-ray photoelectron microscopy and conversion electron Moessbauer spectroscopy following hydrogen and oxygen treatments at progressively higher temperatures from 608-707K were employed. Initially iron overlayers undergo reduction to metallic iron at temperatures from 608-707K. At 875°C, iron facilitates the reduction of TiO_2. Subsequent treatment with oxygen at high temperatures converts iron to $FeTi_2O_5$ [244-246].

Fast pyrolysis of $Co_2(CO)_8$ on TiO_2 resulted in the formation of dispersed supermagnetic cobalt particles characterized by a narrow ferromagnetic resonance signal. The catalyst thus prepared showed an increased activity in the hydrogenation of CO [247]. The use of TiO_2 as a support material enhances the specific activity for the hydrogenation of CO over metal catalysts which tend to possess more completely filled *d* bands, such as Ni, Pd, Pt, Rh and Ir [248].

$TiC\ell_3$ has been shown to poison Ru/Rh catalysts used in the hydrogenation of benzene. The poisonous species have been shown to be TiO_2 and titanate ions [249]. Metalloporphyrins show catalytic activity for the reduction of nitric oxide into nitrogen, N_2O and ammonia. The activity of the cobalt porphyrin CoTPP is enhanced greatly if supported on titanium dioxide [250].

An investigation of Ti(IV) catalysts, carrying the chiral ligands menthyl- or neomenthyl-cyclopentadienyl (MCp), used in the homogeneous catalytic reduction of a prochiral olefin such as 2-phenyl-1-butene, hydrogenated to (R)-(-)- or (S)-(+)-2-phenyl-1-butane with acceptable optical yields, has been reported [251]. Bis-CpTi(IV) derivatives of the type $(\eta^5\text{-}C_5H_5)_2TiX_2$ (X = halogen, OPh, OR) act as homogeneous catalysts for the reduction of olefins in the presence of co-catalysts. The higher optical yields were obtained by complexes carrying the (R)-(-)-MCp ligand when two ligands are bound to Ti. Optical yields were lower with neomenthyl-cyclopentadienyl ligands. Optical yields differed only slightly when one or two ligand units were bound to titanium. This, plus the fact that the absolute configuration of the hydrogenated hydrocarbon is determined by the absolute configuration of the carbon atom directly attaching the chiral substituent to the Cp ring, was taken as an indication that the asymmetric induction is related to the crowding about the metal atom in the Ti(IV) monohydride catalytic intermediate (**42**) [251].



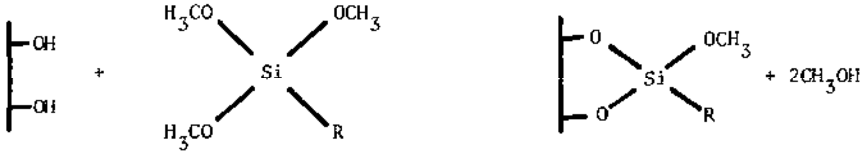
(42)

X = Cℓ, CℓAℓH(OR)$_2$;
R$_1$ = H, CH$_3$;
R$_2$ = (S)-(+)-neomenthyl or
(R)-(-)-menthyl.

Infrared spectroscopy on titanium-molybdenum oxide catalysts, prepared from ammonium paramolybdate on TiO_2, has revealed the presence of heteropoly acids [252,253], while catalysts prepared by the addition of ammonium paramolybdate to titanium hydroxide show, in their ESR structures, the presence of a solid solution of Mo^{5+} ion in TiO_2, a highly dispersed phase of MoO_3, and a partially dehydrogenated titanium-molybdenum heteropoly acid bound to the TiO_2 surface [254]. Further studies on this system could be of interest.

Other studies have been made on the characterization and effect of various supports for catalyst systems. Many indicate that TiO_2 as a support tends to increase the activity of a catalyst. Characterization of the support has been studied by infrared spectroscopy and ESCA [255], x-ray photoelectron spectroscopy, strong metal-surface interaction behaviour [256], and by using CO as a probe molecule for chemisorption [257]. The increased catalytic effect due to the presence of the support has been interpreted in terms of interaction between the catalyst and the support [258-261].

A rapid method for evaluating the amount and reactivity of surface hydroxy groups on TiO_2 surfaces has been reported. It is based on the determination of the extent of reaction between propantrimethylsilane and the TiO_2 surface carried out in an infrared gas cell (reaction 45) [262].



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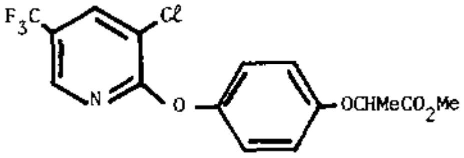
SbO_4-TiO_2 catalysts for the ammoxidation of propylene appear to be most effective when the two oxides are present in equimolar amounts [263]. TiO_2, $TiC\ell_4$ and $Ti(OR)_4$ (R = alkyl) have been reported as efficient catalysts for the transesterification of (43) with minimal amounts of pyridyl ether cleavage [264].



(43)

The interaction of Cp_2TiH containing catalyst with C_{10} and C_{12} cycloalkadienes yielded n-cycloalken-1-yl bis(cyclopentadienyl)Ti(III) compounds (n = 2-6) [265]. Only stable allyl compounds were characterized by ESR and electronic absorption spectra. All of them cooperate in the transformation of the substrate by stepwise double-bond shifts into the equilibrium mixture of isomers. Conjugated cycloalkadienes were minor constituents in the C_{10} and C_{12} equilibrium mixtures. In the C_8-diene, it was the only product. The catalyst appears to be a mixture of Cp_2TiH and $A\ell H_3$ in agglomerates of unknown structure. The catalysis of stepwise-double-bond shifts was reported to proceed by an olefin displacement mechanism (reaction 46) rather than by a dissociation equilibrium (reaction 47) [265].

$$Cp_2Ti\text{-}C\text{-}\overset{*}{C}\text{-}H \quad + \quad C{=}C \longrightarrow Cp_2Ti\text{-}C\text{-}C\text{-}H \quad + \quad C{=}\overset{*}{C} \tag{46}$$

$$Cp_2TiH \quad + \quad C{=}C \rightleftharpoons Cp_2Ti\text{-}C\text{-}C\text{-}H \rightleftharpoons Cp_2TiH \quad + \quad C{=}\overset{*}{C} \tag{47}$$

The use of titanium-containing catalysts in a variety of specific reactions have been studied: oxidation of 2-propanol [267]; dimerization of ethylene [268]; the water-gas shift reaction [269]; and the oxidative dehydrogenation of 1-butene [270].

The catalytic activity of titanium oxide-vanadium oxide catalysts was reported by several workers. The nature of surface vanadium oxygen bonds has been examined and some reactions were found to be structure-insensitive, while others were structure-sensitive [271]. The oxidation of SO_2 was reported to be controlled by the oxygen adsorbed onto the catalyst surface [272]. Other workers reported that the oxidation of SO_2 in real flue gases was more efficient if vanadium were present in the stack exhaust [273].

The addition of α-$TiCl_3$ to $VOCl_3$ or VCl_3 catalysts for the 1,4-*trans*-polymerization of isoprene resulted in increased catalytic activity by causing changes in the catalytically-active centre [274].

Preparation of a catalyst with a monolayer of vanadium species on anatase for selective oxidation of *o*-xylene has been described [275]. An ion exchange method for preparing highly dispersed rhodium on anatase has also been reported [276]. The effect of the nature of various ions on the catalytic properties of $LnATiCuO_6$ (Ln = La, Pr or Nd; A =Ca, Sr, or Ba) has been investigated [277], and it was found that the compounds where Ln and A have large radii have high activities.

The ortho-para conversion of hydrogen and the oxidation of CO in the presence of titanium carbides and nitrides was found to be more effective with increasing defect concentration in either the carbon or nitrogen lattices [278]. The selectivity of vanadium-containing catalysts of the type Ti_xVO_{2-x} ($x = 0$-0.2) in the selective oxidation of methanol has been correlated with the relatively facile electron exchange between active-site cations. Variations in activity in oxygen adsorption do not appear to explain the selectivity [279].

A study on the possibility of quantitative characterization of the catalytic properties of ionic pairs of halides of Group III and IV elements in complex esters has been carried out [280]. The catalytic activity of cation esterates is a maximum with $[TiCl_3{\cdot}3EtOAc]^+$, while the inhibiting effect of the anion is a maximum with $[TiCl_5{\cdot}EtOAc]^-$.

Reports of adsorption and desorption on catalysts have appeared: hydrogen [281], hydrogen and carbon monoxide [282], and formic acid [283].

Molecular orbital energy levels and wave functions have been calculated for the $MeTi(OMe)_nCl_{4-n}$/ethylene (n = 1-4) catalyst systems [284]. An increasing difference between the highest occupied MO and the lowest unoccupied MO occurs with increasing n. This results in a more difficult $\underline{d} \longrightarrow \underline{d}$ transition and decreased catalytic activity, as verified by experimental results.

Titanium compounds as catalysts in photolysis reactions continue to be an active field of investigation. Current studies have dealt largely with preparation and properties of the catalytic material. For the photolysis of water, highly dispersed platinum on TiO_2 produced by the photocatalytic deposition of platinum was effective if the platinum content were maintained at 2-5% [285]. A highly efficient catalyst consists of platinum or ruthenium dioxide supported on colloidal TiO_2 [286]. This showed high activity in a cyclic system using tris(2,2'-bipyridine)ruthenium(II) as the sensitizer. The mechanism probably involves an electron transfer from the excited-state sensitizer to the conduction band of the semiconductor material. The electron is then channeled to a Pt site where hydrogen evolution occurs; N,N'-dimethyl-4,4'-bipyridine was utilized as an electron-relay species [286].

In the presence of TiO_2, oxygen evolved from aqueous solutions of BrO_3^- and IO_3^- on irradiation (> 300 nm) at room temperature [287]. No O_2 was formed in the absence of TiO_2. The reaction probably occurred through the electrons in the conduction band and the holes in the valence band, generated by photo-excitation of the TiO_2. The reaction was presumed to proceed by the reactions 48-50 [287].

$$TiO_2 \xrightarrow{h\nu} 6\ e^- + 6\ p^+ \tag{48}$$

$$6\ e^- + XO_3^- + 3\ H_2O \longrightarrow X^- + 6\ OH^- \tag{49}$$

$$6\ p^+ + 6\ OH^- \longrightarrow 3\ H_2O + 3/2\ O_2 \tag{50}$$

Platinized $SrTiO_3$ catalyses the dissociation of water. The rate of dissociation increases in alkali hydroxide solutions [288]. The decomposition of water on $SrTiO_3$ impregnated with NiO_2 increased by pretreatment *via* reduction of the catalyst followed by re-oxidation with O_2. In the gas phase, the rate of decomposition depends upon the water vapour pressure, indicating that the adsorption of water molecules is necessary for the decomposition into hydrogen and oxygen. A plausible mechanism was described and is summarized in reactions 51-55 [289].

$$H_2O(g) \rightleftharpoons H_2O(ads) \rightleftharpoons H^+(ads) + OH^-(ads) \tag{51}$$

$$SrTiO_3 + h\nu \longrightarrow h^+ + e^- \tag{52}$$

<u>On NiO</u>:

$$2\ H^+(ads) + 2\ e^- \longrightarrow 2\ H^\cdot(ads) \longrightarrow H_2(ads) \longrightarrow H_2(g) \tag{53}$$

<u>On $SrTiO_3$</u>:

$$h^+ + OH^- \longrightarrow OH^\cdot \tag{54}$$

$$4\ OH^\cdot \longrightarrow O_2(ads) + H_2O(ads) \longrightarrow O_2(g) \tag{55}$$

A development of a practical process for the photocleavage of water into hydrogen and oxygen has been reported [290].

A comparison by x-ray photoelectron spectroscopy of Pt/TiO_2 and Pt/ZnO catalysts for the decomposition of methanol by irradiation with a mercury vapour lamp showed no action with the Pt/ZnO catalyst. A comparison of the x-ray photoelectron spectra showed no difference in the valence band structure of the two catalysts. The suggestion was made that the anodic oxidation process on the semiconductor side, and not the cathodic reduction on the loaded platinum, is responsible for the large difference in activity between the two catalysts [291].

The photocatalytic production of hydrogen from linear C_1 to C_4 aliphatic alcohols and propan-2-ol using a 4.85% Pt/anatase catalyst has been studied [292]. Both constituents were necessary for the reaction to be photocatalytic. In the absence of platinum, the anatase became inactive and turned blue. Relatively high quantum yields were obtained: $\sim$0.45 for methanol, $\sim$0.2 for ethanol, and $\sim$0.1 for other alcohols [292].

The ultraviolet irradiation of NO over anatase produces N_2 and N_2O. In the presence of an alcohol, decomposition is increased and an aldehyde or ketone is produced [293]. The photocatalytic decomposition of 2-propanol over a series of TiO_2-loaded catalysts resulted in the activity order $Pt/TiO_2 > Rh/TiO_2 > Pd/TiO_2 > Ru/TiO_2 > Ir/TiO_2 > TiO_2$ [294]. Irradiation of some alcohols in the presence of $TiC\ell_4$ yields products with carbon-carbon formation between two molecules. The reaction between formic esters and alcohols results in formylation of the α-carbon of the alcohol [295].

The kinetics of the conversion of propan-2-ol and butan-2-ol to ketones, lower aldehydes and alkenes on TiO_2 has been investigated. The proposed mechanism for the dehydrogenation process accounts for the dependence on the square root of the incident light intensity, alcohol pressure and oxygen pressure [296]. The suggested overall mechanism was proposed to take into account the elementary processes within n-type semiconductors or at the interface between them and the (alcohol + O_2) reactant.

Ultraviolet irradiation of a mixture of oxygen and olefins over porous Vycor glass resulted in the formation of dienes and oxygen-containing compounds. On the basis of ESR measurements, it was suggested than an O_3^- species was responsible for the photo-oxidation. With a TiO_2-butene system, the formation of 1,3-butadiene predominates [297].

By a combination of the photoelectrochemical production of H_2O_2 on TiO_2 with the Fenton reaction, it has been possible to photocatalytically oxidize aromatic hydrocarbons. By controlling pH and adding Cu^{2+}, both the H_2O_2 and HO produced are used more efficiently [298]. The effect of pH and added Cu^{2+} ions have been studied further. At low and high pH, the total amounts of product increased. In aqueous H_2SO_4, side-chain oxidation prevailed over cresol formation. Benzaldehyde was formed selectively at pH 1. Oxidation of the side chain also occurred at high pH. In the presence of Cu^{2+} at pH 1 and 2, the yield of benzaldehyde increased and cresols, benzyl alcohol and bibenzyl were formed. At high Cu^{2+} concentrations and pH 2, cresol formation occurred in preference to the side-chain oxidation. Addition of large amounts of chloride to the Cu^{2+}-H_2SO_4 aqueous system resulted in no oxidation of toluene [299].

The oxidation of toluene has been studied using TiO_2 powders under nitrogen and air. Four forms of TiO_2 were employed: (a) anatase, (b) updoped, (c) doped and (d) photochemically platinized. The results were: in the presence of oxygen, selective oxidation occurred with the platinized anatase and the undoped anatase;in the absence of water, the main anodic reaction was the one-electron oxidation of the aromatic hydrocarbons to corresponding cations; in the presence of water, the main anodic reaction was the oxidation of OH^- or H_2O to $OH^\cdot$; in the absence of oxygen, the cathodic reaction was the reduction of protons to hydrogen. An explanation was proposed, and suggested mechanisms for the reactions of benzene and toluene were also given [300].

EPR studies of the radicals involved in the photo-oxidation of ethylene on TiO_2 indicate the presence of two radicals, depending upon whether the rutile is chlorinated or chlorine-free. The nature of the alkyl portions of the radicals was discussed [301]. Titanium oxide species prepared on silica gel have been found to be active for the photocatalytic oxidation of isobutene to acetone [302]. The reaction is more selective with TiO_2 grafted on silica gel than with bulk TiO_2 [303]. Infrared data have indicated that the photo-oxidation of C_2-C_4 hydrocarbons on TiO_2 does not proceed by surface carboxylate intermediates. The data suggest that the rate-determining step in the case of alkanes is photoadsorption, and product desorption in the case of alkenes [304].

Various titanium oxide-iron oxide catalysts supported on γ-alumina were tested by a nitrogen-water mixture. All the catalysts used resulted in the formation of ammonia according to the reaction sequence 56-58 [305]. Also,

$$6\ \mathrm{Ti}^{4+}\text{—}\mathrm{OH}^- \xrightarrow{\quad 6\ h\nu \quad} 6\ \mathrm{Ti}^{3+}\text{—}\mathrm{OH}^\cdot \tag{56}$$

$$6\ \mathrm{Ti}^{3+}\text{—}\mathrm{OH}^\cdot \longrightarrow 6\ \mathrm{Ti}^{3+}\square + 3\ \mathrm{H_2O(ads)} + 1.5\ \mathrm{O_2} \tag{57}$$

$$6\ \mathrm{Ti}^{3+}\square + \mathrm{N_2(ads)} + 6\ \mathrm{H_2O(ads)} \longrightarrow 6\ \mathrm{Ti}^{4+}\text{—}\mathrm{OH}^- + 2\ \mathrm{NH_3} \tag{58}$$

the role of the irradiation and of the water was discussed [305].

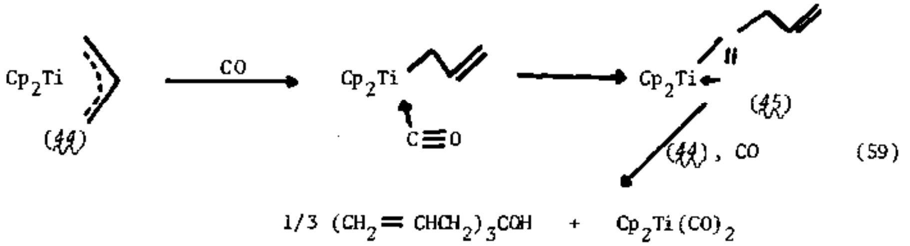
A number of free radical reactions have been observed upon illumination of TiO_2 sols with near-ultraviolet light [306]. Halide ions are oxidized to radical anions and propanol-2 to the 1-hydroxy-1-methylethyl radical. An analysis of studies on the photocatalytic oxidation of various compounds has been reported that included mechanistic information. The main conclusions were that such oxidation reactions proceed in an adsorbed phase and that dissociated oxygen species play an essential role [307].

The photo-reduction of silver ions on a TiO_2 sruface in aqueous solutions has been attributed to transfer of electrons produced in the conduction band of TiO_2 to silver ions adsorbed on the TiO_2 surface [308, 309]. Studies on isotopic exchange reactions involving TiO_2 have also been reported [310, 311]. Radiation-induced reactions of carbon monoxide and hydrogen gas mixtures [312], the $TiC\ell_4$-catalysed photoreaction of 2-acetyl-1,3-dicarbonyl compounds in methanol [313], and the photocatalysed oxidation of polyundecanamides on TiO_2 [314] have been investigated.

A possible pathway to photo-oxychlorinations has been suggested [315]. The interaction of $CC\ell_4$ vapour with dehydroxylated anatase leads to chlorinated surfaces on which photoadsorption of oxygen is enhanced; the formation of $C\ell OO^\cdot$ radicals was detected by ESR spectroscopy. The photocatalytic properties of a powdered semiconductor loaded with metal have been discussed [316].

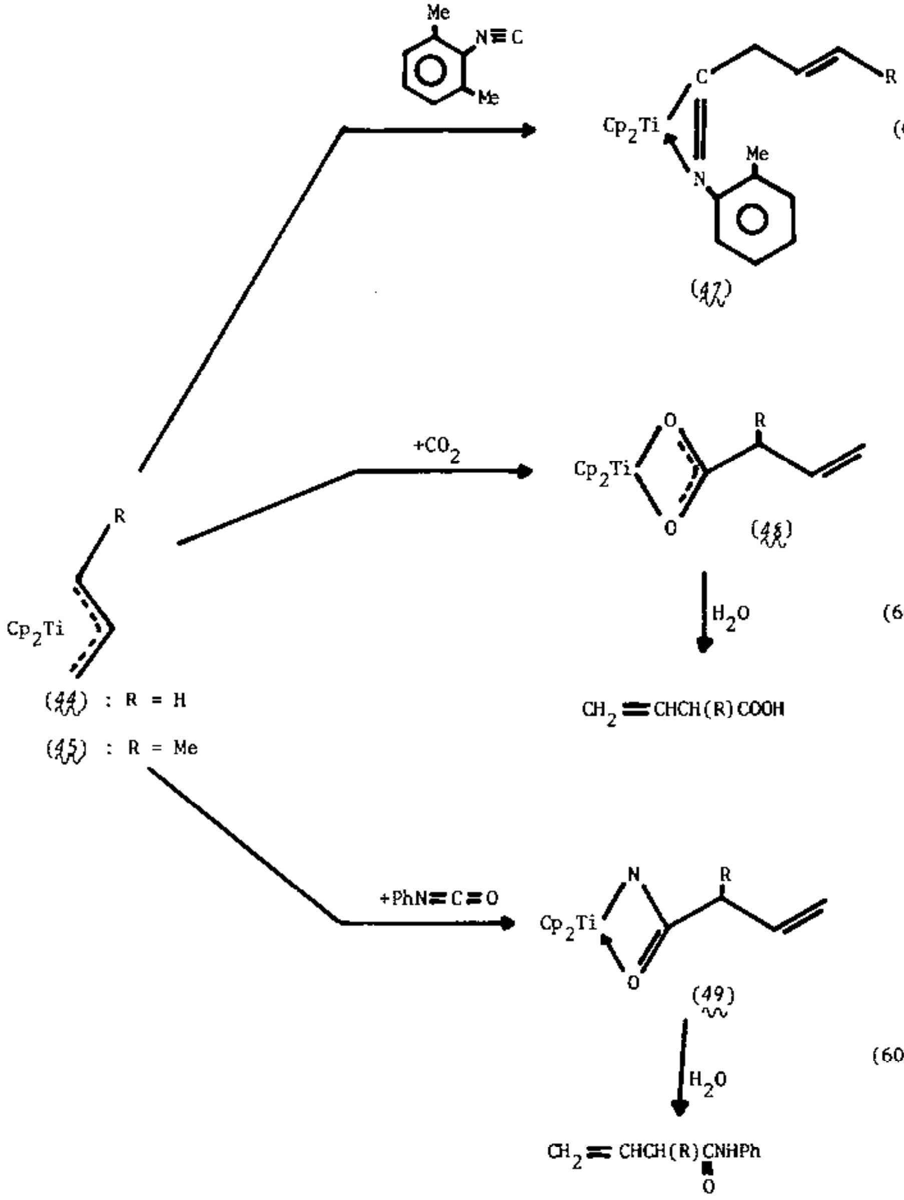
3.7 APPLICATIONS OF TITANIUM COMPOUNDS IN ORGANIC REACTIONS

Carbonylation of $Cp_2Ti(\pi\text{-allyl})$ (44) in pentane gave $Cp_2Ti(CO)_2$ in 65% yield and triallylmethanol in 30-50% yield (reaction 59) [317]. The methanol



(59)

was thought to be generated *via* diallyl-ketone formation by alkylation of the acyl intermediate (45) by $Cp_2Ti(\pi\text{-allyl})$. This is the first case in which insertion of CO into a Ti — C bond is followed by reaction of the intermediate η^2-acyl with other Ti — C bonds to give C — C bond formation. The methyl substituted analogue of (44), $Cp_2Ti(\pi\text{-methylallyl})$ (46) behaved similarly; some of its reactions are summarized in reactions 60a-f [317]. These insertion-type reactions are highly regioselective and proceed essentially quantitatively. Another type of reaction between (44) and ligands like CS_2 and PhC≡CPh is allyl-elimination (reaction 61a,b). CS_2 induces allyl coupling to hexa-1,5-diene to give $Cp_2Ti(\eta^2\text{-}CS_2)$ (53), whereas diphenylacetylene reductively



(47)

(60a)

(48)

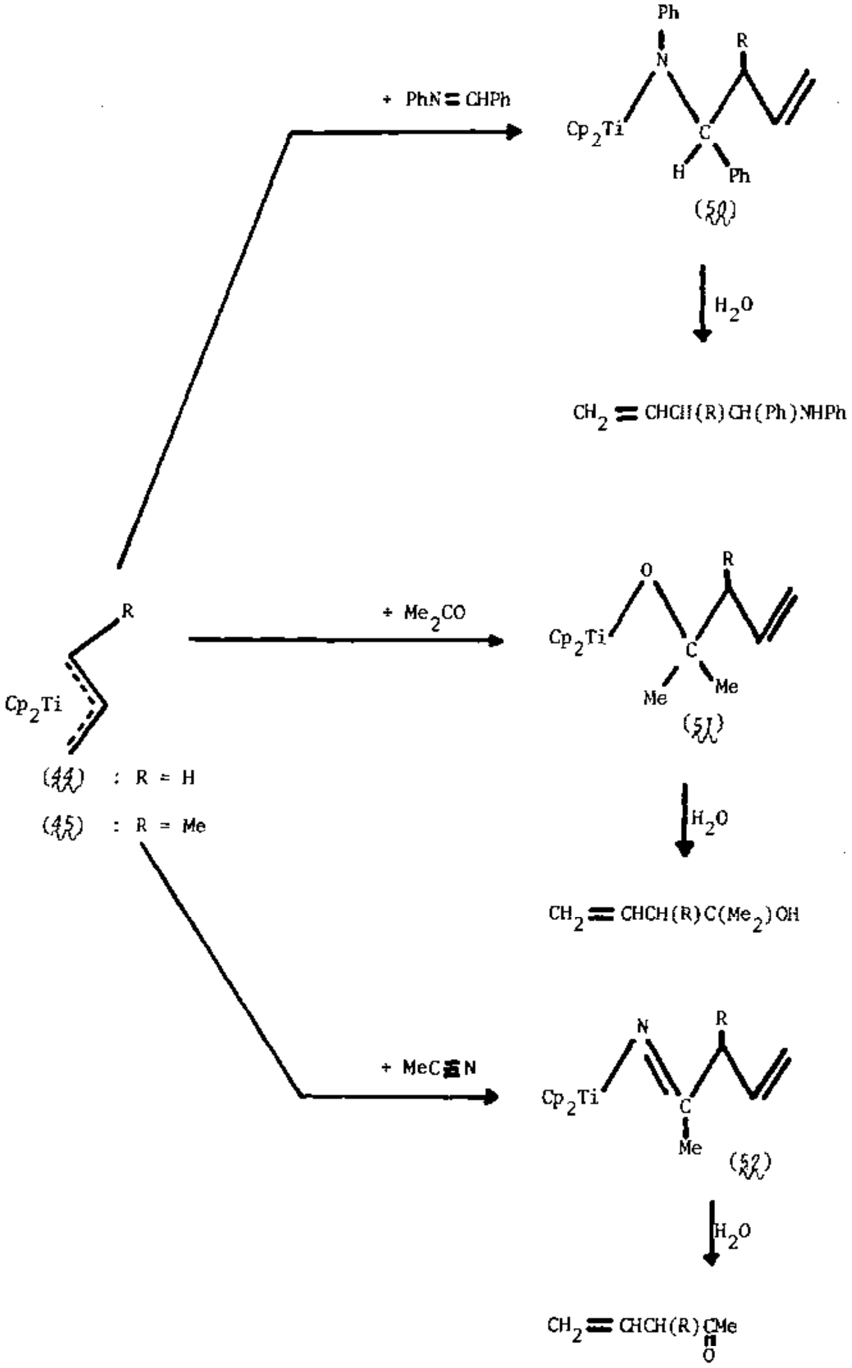
(60b)

(44) : R = H

(45) : R = Me

(49)

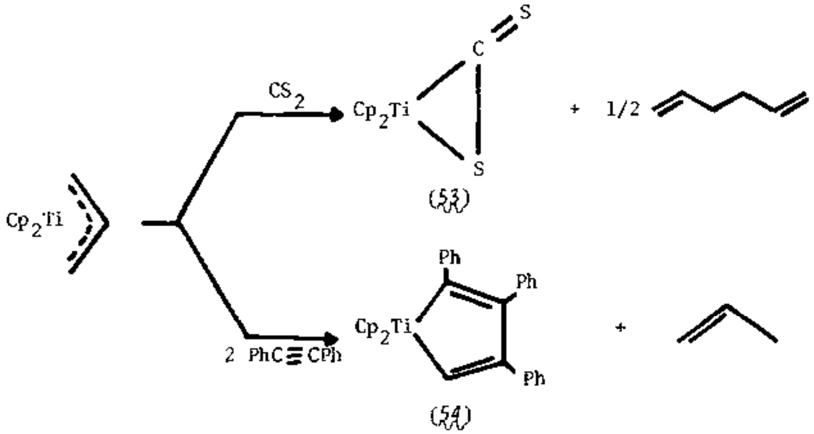
(60c)


+ PhN=CHPh
Ph
N
R
Cp2Ti
C
H
Ph
(50)
H2O
CH2=CHCH(R)CH(Ph)NHPh
+ Me2CO
O
R
Cp2Ti
C
Me
Me
(51)
H2O
CH2=CHCH(R)C(Me2)OH
R
Cp2Ti
(44) : R = H
(45) : R = Me
+ MeC≡N
N
R
Cp2Ti
C
Me
(52)
H2O
CH2=CHCH(R)CMe
O

(60d)

(60e)

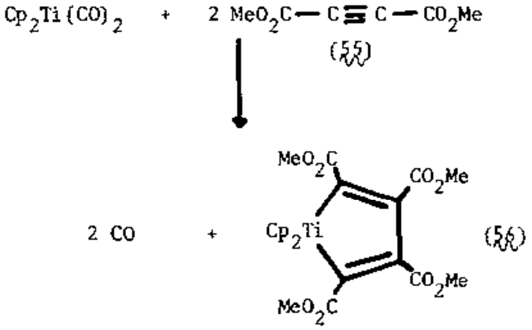
(60f)



(61a)

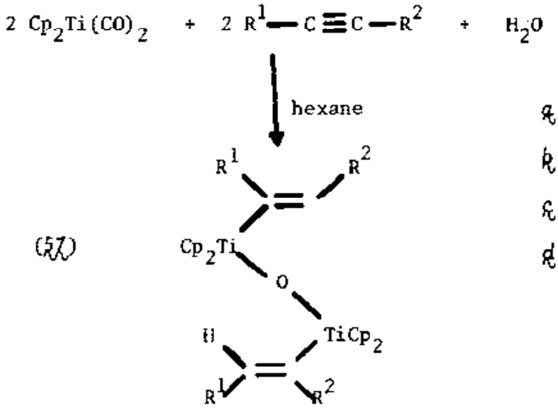
(61b)

coupled to $Cp_2TiC_4Ph_4$ to form propene. Reaction of $Cp_2Ti(CO)_2$ and freshly-distilled dimethylacetylene-dicarboxylate (55) in dry hexane at room



(62)

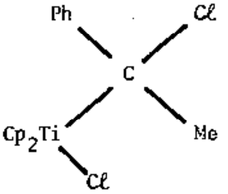
temperature gave the red metallocene (56) (reaction 62) [318]. The same reaction as 62 but in excess H_2O led after 1 day to the evolution of 1.9 mol CO/Ti atom and to the formation of the yellow compound (57a); other derivatives (57b,c) have also been prepared (reaction 63). Further treatment



(63)

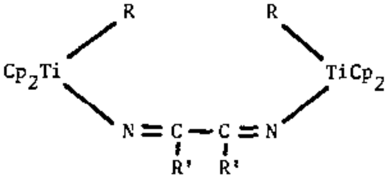
a: $R^1 = R^2 = CO_2Me$
b: $R^1 = R^2 = CO_2Et$
c: $R^1 = R^2 = Ph$
d: $R^1 = Ph$, $R^2 = H$

of (57) in dichloromethane with excess aqueous $HC\ell$ led to formation of *cis*-olefins; for example, (57b) afforded $Cp_2Ti(C\ell)C(CO_2Et){=}CH(CO_2Et)$, (57c) gave $Cp_2TiC\ell_2$ (50%) and *cis*-stilbene (60%), and (57d) gave the red product (58) from reaction with $HC\ell$. A possible pathway for these reactions of $Cp_2Ti(CO)_2$



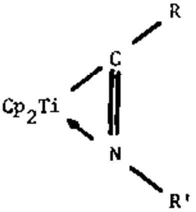
(58)

has been discussed [318]. Carbon monoxide can also be activated by Ti(III) metallocenes, Cp_2TiR, to give $Cp_2Ti(CO)R$, where R = $C\ell$, C_6F_5, as well as the η^2-acyl complexes Cp_2TiCOR, where R = C_6H_5, o-$CH_3C_6H_4$ and $CH(CH_3){=}C(H)CH_3$ [319]. Formation of the ketones RCOR and diketones RCOCOR reveal formation of new C—C bonds in these systems, probably through the radical character induced on the ligands by back donation of the unpaired electron of titanium in Ti(III). Interestingly, Cp_2TiR (R = aryl) reacts with cyanides R'CN, in which coupling of the ligands occurs *via* the cyanide C atom (59); with



(59)

isocyanides, R'CN inserts into the Ti—C bond to give the η^2-iminoacyl complex (60) [319].



(60)

An attractive alternative to the use of Li/$MeNH_2$, thexylborane, or bis(4-methylpiperazinyl)aluminum hydride has recently been reported for the reduction of carboxylic acids to aldehydes [320]. This involves treating carboxylic acids with a mixture of 2 mol of isobutylmagnesium bromide and catalytic amounts of $Cp_2TiC\ell_2$ in ether for 4 hrs at room temperature under an argon atmosphere; subsequent hydrolysis leads to the aldehyde (reaction 64).

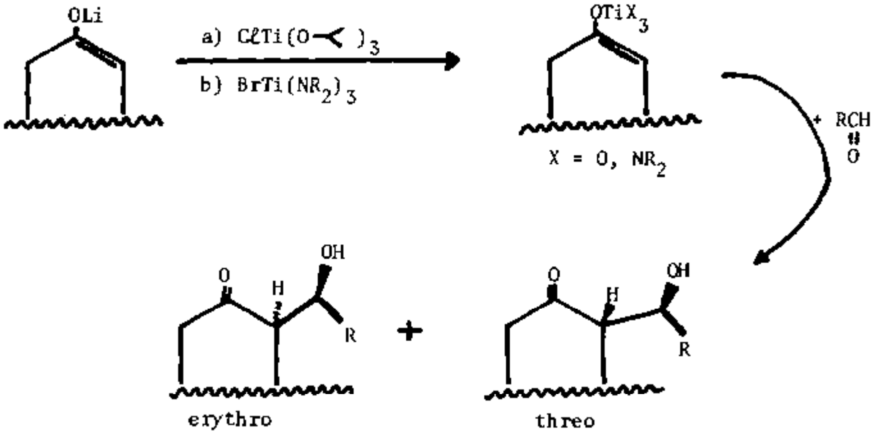
$$RCOOH \ + \ 2\ {}^{\underline{i}}C_3H_7CH_2MgBr \xrightarrow[\text{b) } H_2O]{\text{a) } Cp_2TiC\ell_2} RC(H)=O \qquad (64)$$

A mechanism was also proposed to account for this reduction.

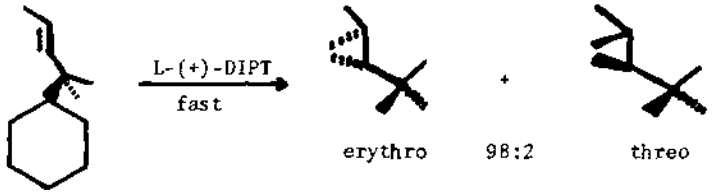
The preparation of conjugated dienes from their 1,5-isomers using two easily obtainable titanocene-derived catalysts has been described by Mach and co-workers [321]. In the first instance, the catalytically active species Cp_2TiR (R = allyl, alkenyl, alkyl) was generated by reduction of $Cp_2TiC\ell_2$ with lithium alanate in the boiling olefin to be isomerized. In the second method, the catalyst was obtained by the decomposition of pre-formed (η^5: η^5-fulvalene)-di-μ-hydrido-bis[cyclopentadienyltitanium(III)], $(C_{10}H_8)(H)_2(CpTi)_2$, at 150-180°C. Both catalytic systems were found to possess comparable isomerization selectivities in spite of marked differences in the required reaction temperature [321]. The synthesis of the five-membered heterocycle (61) containing Ti in the ring has been described by Zakharkin and Shemyakin [322].

(61)

Various titanium enolates, accessible using cheap reagents and which are distillable and miscible in ether, THF, dichloromethane or pentane, display pronounced erythro selectivity in Aldol condensation reactions with aldehydes (reaction 65) [323]. Diastereoselection appears to be better than when using Zr or Sn enolates. Titanium alkoxide tartrate is a highly effective epoxidation catalyst and shows a high degree of sensitivity to pre-existing chirality in allylic alcohol substrates [324]. The outcome for racemic (E)-cyclohexylpropenylcarbinol (62) using L-(+)-diisopropyl tartrate (DIPT)



is shown in reactions 66 and 67 for the (S)-enantiomer of (62) and (R)-enantiomer of (62), respectively. Clearly the titanium alkoxide tartrate



(66)

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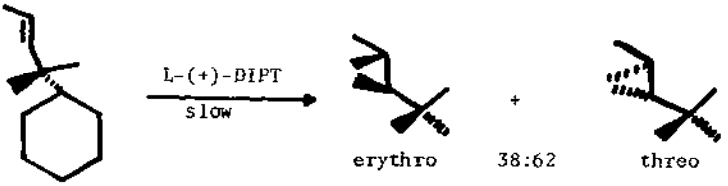
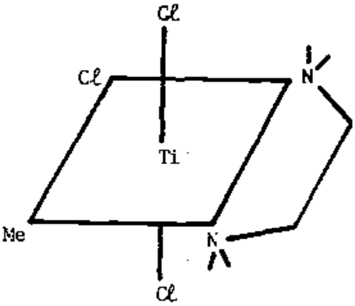


(67)

(62)

strongly favours erythro products. It was also noted that preference for α attack and erythro selectivity are consonant for the (S)-enantiomer, but are dissonant for the (R)-enantiomers. Increasing the size of the alkyl group in the tartrate ester significantly increased the rate difference for epoxidation of the S and R enantiomers [324].

Stable six-coordinate complexes of MeTiCℓ_3 are diastereo- and enantio-selective methylating reagents [325]. Reaction of tetramethylethylenediamine, glyme, THF, or (-)-sparteine with an equivalent amount of MeTiCℓ_3 in dichloromethane produced the compounds (63-66), respectively. When these compounds reacted *in situ* with 2-phenylpropionaldehyde (67) at -50°C in $CH_2C\ell_2$ for 2 hrs, product (68) formed preferentially (reaction 68) [325]. Addition of (66) to heptanal yields a mixture of R- and S-2-octanol with the



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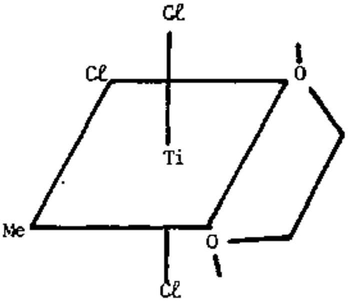

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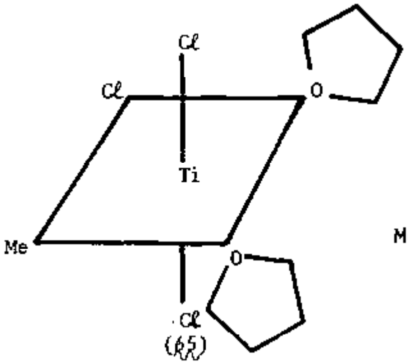

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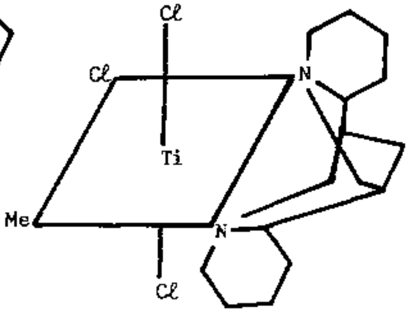

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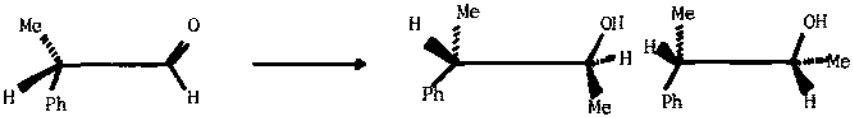
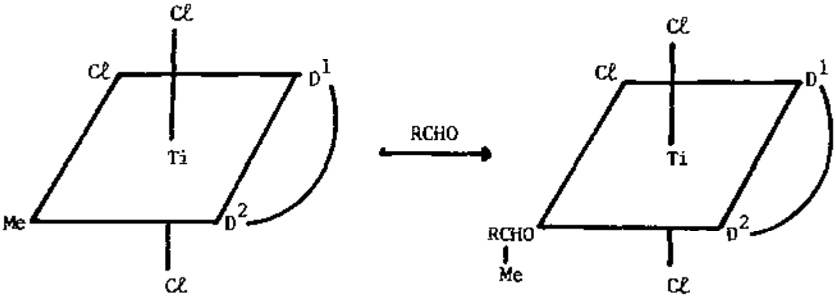


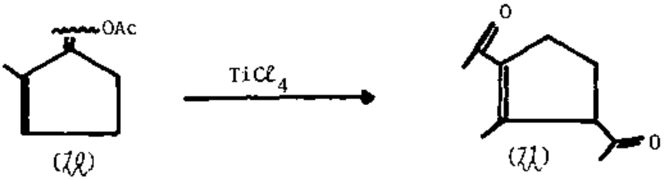
(67) (68) (69)

R-enantiomer dominating. The mechanism of addition appears to involve a ligand exchange reaction (reaction 69) in an octahedral complex in which the methyl group in the meridional position is displaced by an alkoxy ligand prior



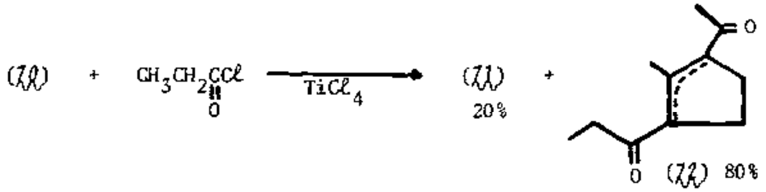
(69)

to aqueous workup [325]. Rearrangement of the O-acylated dienolate (70) in the presence of $TiCl_4$ in CH_2Cl_2 at -40°C takes place cleanly to give the diketone 1,3-diacetyl-2-methylcyclopentene (71) (reaction 70) [326]. The



(70) (71)

possibility of an intramolecular process was ruled out by a cross-over experiment with propionyl chloride (reaction 71). However, when the reaction was carried out with 1.5 mol equivalent of crotonyl chloride (73), then (71) was the major product. No rearrangement was observed for a mixture of O-acetylated dienolates of (+)-pulgeone (76) and (77) (reaction 73).



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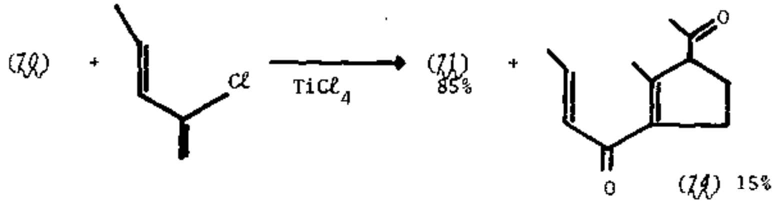

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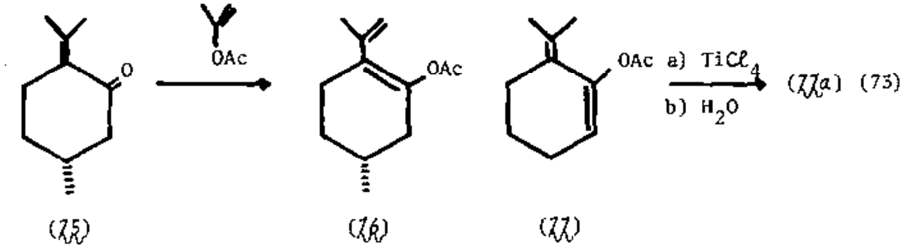
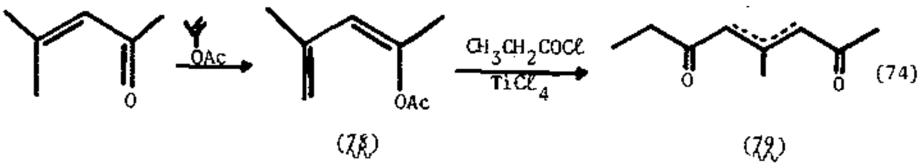


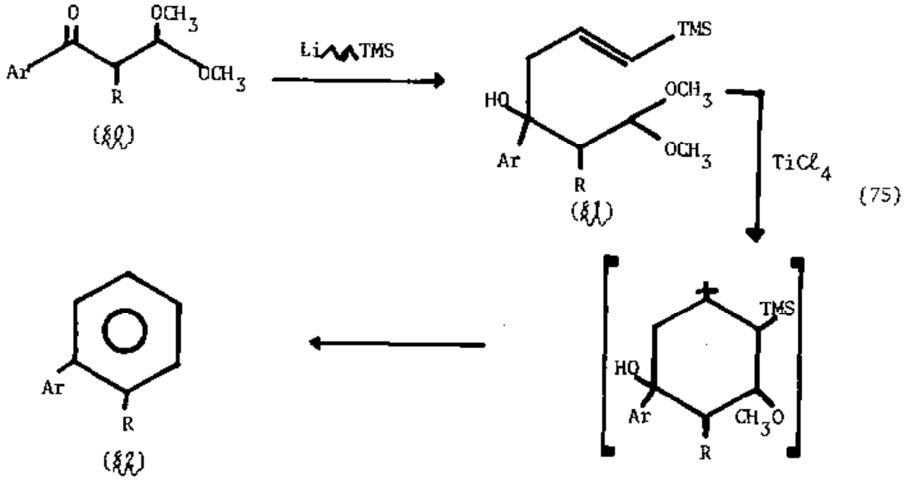
(73)

(75) (76) (77)

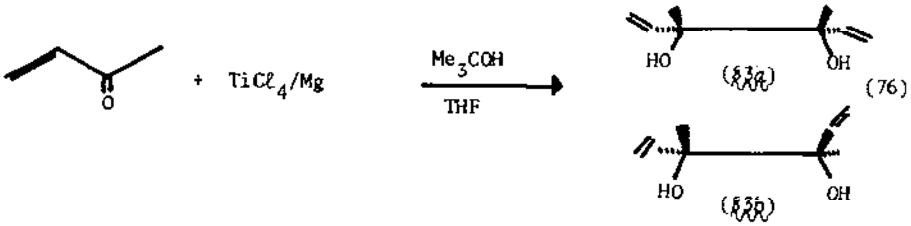
Condensation of propionylchloride and 4-acetoxy-2-methyl-1,3-pentadiene (78) in the presence of $TiCl_4$ gave the δ-diketone (79) (reaction 74) [326].



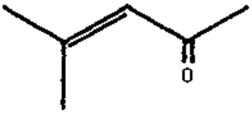
Addition of allyltrimethylsilyllithium at -78°C in THF to ketoacetals (80) produces vinylsilanes (81) in 67-91% yield after column chromatography on silica gel (reaction 75) [327]. Further treatment of (81) with $TiCl_4$ in dichloromethane solution containing ∿10% ether at -78°C, followed by gradual warming to 0°C, gave the biphenyl compounds (82). $Ti(^{i}PrO)_4$ and $Cl_2Ti(^{i}PrO)_2$ were less effective than $TiCl_4$ [327].



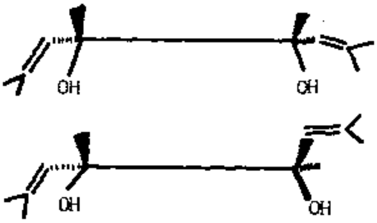
Reductive coupling of methyl-vinyl ketone with $TiCl_4$/Mg gave the pinacols (83a,b) [328]. Also, reduction of mesityl oxide (84) with low-valent forms of



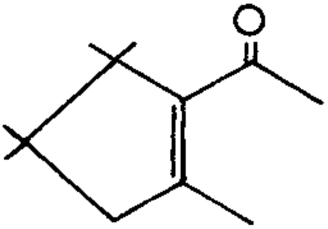
titanium and vanadium leads to pinacols (**85**) as the major product, whereas with low-valent forms of chromium, iron and zirconium, the ketone (**86**) is the major product. The nature of the low-valent titanium species has been investigated by electron paramagnetic resonance spectroscopy [329].



(**84**)



(**85**)



(**86**)

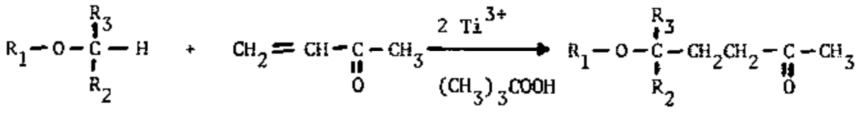
The effect of the electronic structure of substituted phenols on the kinetics of reactions in Ti(III)-H_2O_2-aliphatic alcohols-phenol systems has been reported [330]. Molecular orbital calculations suggest that a π,π complex forms in the reaction of $RC_6H_4^{\cdot}$ with $R'\dot{C}HOH$ in which the latter species is the electron donor; in the reaction of $RC_6H_4O^{\cdot}$ with $R'CH_2OH$, a σ,π complex forms in which $RC_6H_4O^{\cdot}$ is the electron donor. Treatment of the cluster compound $[TiMg_2Cl_2 \cdot THF]_{2x}$, prepared by treating $TiCl_4$ with Mg in THF with PhO_2CPh, produced PhOH (25.4%), PhMe (24.9%), PhCHO (19.2%), deoxybenzoin (16.7%), benzoin (5.5%) benzil (3.9%), $PhCH=CHPh$ (1.6%), $PhC\equiv CPh$ (1.0%), $PhCH_2CH_2Ph$ (1.0%), and hydrobenzoin (0.6%) [331].

A variety of fatty alcohols $Me(CH_2)_nOH$ (n = 7, 9, 11, 13, 15 and 17) have been prepared by hydration of $Me(CH_2)_{n-2}CH=CH_2$ over $TiCl_4/KBH_4$ [332]. Thus, addition of $Me(CH_2)_{15}CH=CH_2$ to a mixture of $TiCl_4$ and KBH_4 dissolved in $MeOCH_2CH_2OMe$ gives $Me(CH_2)_{17}OH$ in 94% yield. Also, a mixture of $TiCl_4/LiH$ (1:4) converts alcohols, glycols, amino alcohols, and glycol monoethers to complex hydrocarbon mixtures, the major components of which possess the same number of carbon atoms as the starting material [333]. For example, ROH (R = Me_2CH, Bu, Me_3C, n-C_6H_{13}) gave propylene, butane, $Me_3CH/Me_2C{=}CH_2$ and C_6H_{12}/C_6H_{14} as the major products; 1,3- and 1,4-butanediols gave 1- and 2-butenes and $CH_2{=}CHCH{=}CH_2$.

Deoxygenation of 7-oxabicyclo[2.2.1]hepta-2,5-diene systems occurs in the presence of $TiC\ell_4/LiA\ell H_4$ to give substituted benzenes [334]. Equimolar reaction of azoxybenzene with $TiC\ell_4$ gave azobenzene; in the presence of excess $TiC\ell_4$, 4-chloroazobenzene was obtained [335]. Use of $TiC\ell_4/Et_3N$ in the synthesis of chalcones from metallocenes and tetrathiafulvalene has been described by Besancon and co-workers [336]. Titanium tetrachloride forms a 1:2 adduct with $SN_2C_2C\ell_2$ (prepared from $(CN)_2$ and $S_2C\ell_2$) [337].

The initiation of the dimerization of 1,1-diphenylethylene by $A\ell Br_3$ and $TiC\ell_4$ in heptane at -30°C has been studied spectrophotometrically [338]. The possibility of co-catalysis by residual impurities was not precluded; $TiC\ell_4$ alone is not an initiator for the polymerization of isobutylene [338]. The factors affecting the molecular weight of alternatin copolymers of propylene with butadiene were investigated in the presence of $TiC\ell_4$/acetophenone/$A\ell(\underline{i}Bu)_3$[339]. Kakugo and co-workers [340] have tested the accuracy of ^{13}C nmr measurements to examine the monomer sequence distribution in ethylene-propylene copolymers prepared from delta $TiC\ell_3/Et_2A\ell C\ell$.

A new method of reductive homolytic alkylation of methyl vinyl ketone with ethers *via* a redox free-radical reaction 77 was recently described [341].

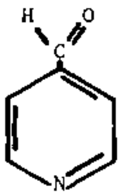


$$R_1-O-\overset{R_3}{\underset{R_2}{C}}-H \quad + \quad CH_2{=}CH-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3 \xrightarrow[(CH_3)_3COOH]{2\ Ti^{3+}} R_1-O-\overset{R_3}{\underset{R_2}{C}}-CH_2CH_2-\underset{O}{\underset{\|}{C}}-CH_3 \qquad (77)$$

The source of t-butoxy radicals was the redox couple $\underline{t}BuOOH/Ti^{3+}$. Rates of hydrogen abstraction were high (> 10^6 - 10^7 $\underline{M}^{-1}sec^{-1}$) and these reduce parasitic side reaction 78 involving reduction of the t-butoxy radical by Ti^{3+};

$$\underline{t}BuO^{\cdot} \quad + \quad Ti^{3+} \quad + \quad H^+ \longrightarrow \underline{t}BuOH \quad + \quad Ti^{4+} \qquad (78)$$

a high concentration of Ti^{3+} salt favours reduction of the α-ketoalkyl radical $R_1OC(R_2R_3)CH_2\dot{C}HCOCH_3$. Aqueous $TiC\ell_3$ reductively removes CN and halo groups from substituted pyridines by a two-electron transfer process and promotes reduction of pyridyl ketones and aldehydes to glycols by a one-electron transfer process [342]. For example, 2-cyanopyridine decyanates in the presence of aqueous $TiC\ell_3$ in acetic acid to give pyridine, and 4-CHOpyridine (87) gives the glycol (88). Electron withdrawing substituted carbonyl compounds, when allowed to react with two equivalents of aqueous $TiC\ell_3$ in the presence of acetone, acetaldehyde or benzaldehyde, afforded unsymmetrical 1,2-diols in high yield under simple experimental conditions (reaction 79) [343].



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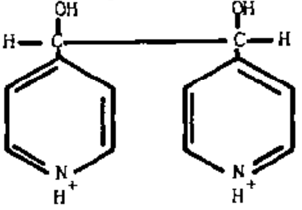

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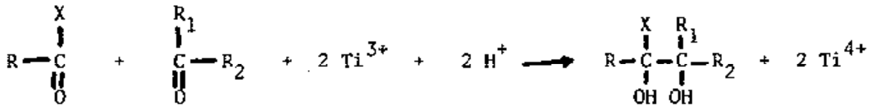


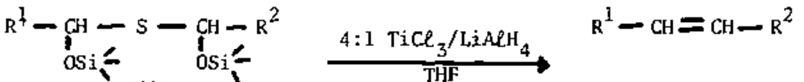
$$R-\overset{X}{\underset{O}{C}} + \overset{R_1}{\underset{O}{C}}-R_2 + 2\,Ti^{3+} + 2\,H^+ \longrightarrow R-\underset{OH}{\overset{X}{C}}-\underset{OH}{\overset{R_1}{C}}-R_2 + 2\,Ti^{4+} \qquad (79)$$

$X = CN, COOH, COOCH_3$, py

$R = CH_3, H$

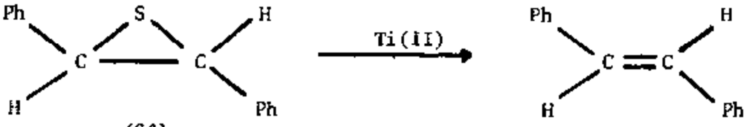
$R_1 = R_2 = CH_3$; $R_1 = H$, $R_2 = CH_3$; $R_1 = H$, $R_2 = Ph$.

Low-valent titanium compounds have been found to be effective deoxygenation reagents because of the high affinity of Ti for oxygen (reaction 80) [344]. Under identical conditions, benzaldehyde gave poorer yields of stilbene than the conversion of $R^1 = R^2 = Ph$- to stilbene. Thus, reaction of the α,α-bis(trimethylsiloxy)sulfide (89) with low-valent titanium does not proceed by reversion to aldehyde first, but rather probably proceeds *via* an episulfide intermediate. To test this, *trans*-1,2-diphenylepisulfide (90) reacted with Ti(II) to give *trans*-stilbene (reaction 81). Mixed olefins may



$$R^1-\underset{OSi\equiv}{CH}-S-\underset{OSi\equiv}{CH}-R^2 \xrightarrow[THF]{4:1\ TiC\ell_3/LiA\ell H_4} R^1-CH=CH-R^2 \qquad (80)$$

(89)



(90)

(81)

be obtained from unsymmetrical compounds of (**89**) [344].

Richardson [345] recently reported a method by which it is possible to prepare an olefin containing the *m*-trifluoromethylphenyl substituent, thus opening up McMurry's synthesis to a wider range of substituents than previously thought. The haloaromatic substituted olefins prepared by this method include (**91**) in 67% yield and (**92**) in 60% yield. The Ti(O) coupling

$$p\text{-}BrC_6H_4C(CH_3){=}C(CH_3)C_6H_4Br\text{-}p$$

(**91**)

$$m\text{-}CF_3C_6H_4C(CH_3){=}C(CH_3)C_6H_4CF_3\text{-}m$$

(**92**)

agent was prepared from the reduction of $TiC\ell_3$ with Li, the excess Li was filtered and the filtrate used to effect the ketone coupling. The above yields were in the range of that reported for hydrocarbon olefins, and this suggests that reduction of halogen substituents was not an important side reaction [345].

A semi-empirical analysis was reported for the kinetics of exchange reaction of Ti(III) binuclear carboxylates [346].

Molybdenum oxide, MoO_x ($2.9 > x > 2.3$), supported on β-TiO_2 is a unique catalyst on which olefins undergo metathesis without hydrogen scrambling at room temperature. A 1:1 mixture of *cis*-but-2-ene-d_o and *cis*-but-2-ene-d_8 gave mainly *trans*-but-2-ene-d_o, -d_4 and -d_8, and *cis*-but-2-ene-$d_4$347]. By contrast, the metathesis of *trans*-but-2-ene-$d_o$and *trans*-but-2-ene-d_8 gave only *trans*-but-2-ene-d_4 initially. Thus it appears that metathesis of *cis*-olefins preferentially yields *cis*-olefins with some *trans*-olefins, but metathesis of *trans*-olefins yields entirely *trans*-olefins. The stereoselective metathesis of propene, as well as the structure-retaining metathesis of *cis*- and *trans*-2-butene, was rationalized from structures of metallacyclobutane intermediates [347]. Earlier, Engelhardt [348] had studied the isomerization of *cis*-2-butene over reduced and unreduced molybdena-alumina catalysts. He reported that over unreduced catalyst, isomerization *via* a carbonium ion intermediate was the prevailing reaction in the early stages of the process but later suppressed; hence, *cis*-*trans* isomerization proceeded almost exclusively *via* metathesis. The assumption that metathesis of *cis*-2-butene over MoO_x/β-TiO_2 ($x = 2.3\text{-}2.9$) takes place without either intermolecular hydrogen transfer or isomerization *via* carbonium or alkyl intermediates was questioned [348]. In this regard, the mechanism of the isomerization of selectively deuterated *cis*-butenes over TiO_2

at 120° and 250°C has been investigated by Lemberton and co-workers [349]. On catalysts pretreated at 250°C and 350°C, *cis-trans* isomerization and double-bond shift proceed through a non-stereospecific carbonium ion pathway; whereas on the catalyst pretreated at 550°C, this reaction competes with reactions involving allylic species or σ-bonded carbonium ions.

The synthesis of light olefins using Ru/TiO_2 [350] and light hydrocarbons using Rh/TiO_2 [351] from hydrogenation of carbon monoxide has been reported.

EPR and nmr methods and quantum mechanics have been applied to study the reaction mechanism of the dehydration of formic acid on TiO_2 [352]. The specificity of TiO_2 to act almost exclusively as a dehydration catalyst appears to be due to the existence of surface electron donor centres [352] over which HCOOH loses its planar structure upon chemisorption [353]. The number of these electron donor centres was determined by adsorption of tetracyanoethylene or trinitrobenzene and ESR analysis of the paramagnetic anions formed [354]. These centres are Ti^{3+} ions and $O—Ti—OH$ groups for high and low pretreatment temperatures, respectively.

Titanium dioxide reversibly chemisorbs O_2 and weakly adsorbs MeOH, which is partially and completely oxidized [355].

Oxidative ammonolysis of p-tert-butyltoluene over TiO_2/V_2O_5 gave 83-87% of $p\text{-}(CH_3)_3CC_6H_4CN$, which under harsher conditions, converts to terephthalonitrile [356].

The electron Auger spectra of samples of TiI_4 heated at 20-1170°C indicated that the main surface contaminants are S, C, and Cℓ; at room temperature, carbon is present as graphite and is oxidized to CO with increasing temperature and at >600°C CO is desorbed [357]. In the presence of oxygen on the Ti surface, Cℓ is lost during heating whereas S forms surface compounds with Ti during heating to <800°C above which the Ti—S surface compounds decompose.

In contrast with nitrogenase, Ti(III)/pyrocatechol nitrogen-fixing systems reduce CN or acetonitrile to methylamine or ethylamine, respectively, by a four-electron reduction process [358]. In model systems containing $Ti(OH)_3$, some hydrocarbon products were also formed.

The selectivity of classical carbanions can be increased by first converting them to titanium reagents [359]. Varying the nature of the heteroatom at Ti leads to control over the chemo-, diastereo- and enantioselectivity. Four new developments were disclosed by Reetz and co-workers [359]: (a) organo-titanium reagents derived from stabilized and non-stabilized carbanions discriminate not only between aldehydes and ketones, but also between isomeric aldehydes; (b) enolizable ketones that react poorly with RLi or RMgX, owing to undesired protonation, undergo a smooth addition reaction; (c) unusually high diastereoselectivity in structurally different systems is observed, even in reactions involving amino derivatives, $RTi(NR_2)_3$; and (d) enantioselectivity using chirally-modified reagents is possible.

3.8 ADDENDA

Surface treatment of aluminum plates with organic titanium compounds to improve the quality of printed images and the durability of pre-sensitized plates have shown that the properties of the coating depend on the composition of the treating solution, heating and ultraviolet radiation [360]. A theoretical model, based on the extent of reaction as a function of time, has been applied [361] to reaction 82.

$$BaCO_3(s) + TiO_2(\text{rutile}) \longrightarrow BaTiO_3(s) + CO_2(g) \qquad (82)$$

A comparison of the powder products and films produced by the hydrolysis of ethanol and n-butanol solutions of $Ti(OEt)_4$, $Ti(OBu)_4$ and polybutoxytitanium showed the powders to be poorly crystalline [362]. A concentration dependence of boiling point change of $NbC\ell_5$ and $TaC\ell_5$ solutions in $TiC\ell_4$ has been observed. At concentrations of 0.0 to 0.2 mol of pentachloride per kg of $TiC\ell_4$, dimers are present with a degree of association of 1.16 to 1.18 [363].

Vapour phase growth of TiO_2 crystals formed by the hydrolysis of TiF_4 produced anatase below 1000°C and rutile above 900°C. A temperature of 1000°C is best for producing rutile. The formation of $TiOF_2$ is suggested as an intermediate gaseous-phase species [364]. The synthesis and properties of barium and calcium titanyl oxalates as inorganic ion-exchange materials has been reported in the Russian literature (not translated) [365]. The partition of Mn(II), Fe(III) and Ti(IV) in the bis(2-ethylhexyl)phosphoric acid/benzene system has been reported [366]. Distribution coefficients for tantalum, niobium and titanium between aqueous sulfate and kerosene containing tributylphosphate and thiuram have appeared [367]. A reactor filled with titanium can selectively remove the F_2 impurity which builds up in xenon fluoride lasers [368]. Alkylamine intercalation compounds have been prepared from $Na_2Ti_3O_7$ [369]; alcohol intercalation compounds were prepared from $TiOC\ell\text{-}BuNH_2$ intercalation compounds [370].

Several n-alkanols, n-alkylamines and n-alkyldiamines have been intercalated in the layered structure of $\gamma\text{-}Ti(HPO_4)_2$; the properties of these compounds were reported and discussed [371].

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REFERENCES

1. To whom correspondence should be addressed.
2. J.R. Ufford and N. Serpone, *Coord. Chem. Rev.*, 57 (1984) 301.
3. H. Wenzl, *Int. Met. Rev.*, 27 (1982) 140.
4. K.A. Davis, *J. Chem. Educ.*, 59 (1982) 158.
5. M. Krystek, *PTB-Mitt.*, 92 (1982) 6.
6. H. Koepf and U. Goeges, *Z. Naturforsch. B:Anorg. Chem.,Org. Chem.*, 36B (1981) 1205.
7. N. Klouras and Koepf, *Montash. Chem.*, 112 (1981) 887.
8. A.I. Sizov and B.M. Bulychev, *Zh. Neorg. Khim.*, 26 (1981) 2652.
9. D.W. Macomber, W.P. Hart, M.D. Rausch, R.D. Priester and C.U. Pittman Jr., *J. Am. Chem. Soc.*, 104 (1982) 884.
10. W Skupinski and A. Wasilewski, *J. Organomet. Chem.*, 220 (1981) 39.
11. J. Blenkers, H.J. De Liefde Meijer and J.H. Teuben, *J. Organomet. Chem.*, 218 (1981) 383.
12. C.M. Bolinger, J.E. Hoots and T.B. Rauchfuss, *Organomettalics Washington (D.C.)*, 1 (1982) 223.
13. S.C. Goel and R.C. Mehrotra, *Indian J. Chem., Sect. A*, 20A (1981) 1054.
14. K. Dey, A.K. Biswas and A.K.S. Roy, *Indian J. Chem., Sect. A*, 20A (1981) 848.
15. K.C. Malhotra, N. Sharma and S.C. Chaudry, *Transition Met. Chem.*, 6 (1981) 238.
16. N.K. Kaushik, A.K. Sharma and G.S. Sodhi, *Indian J. Chem., Sect. A*, 20A (1981) 847.
17. R.S. Arora, S.C. Hari, M.S. Bhalla and R.K. Multani, *Indian J. Chem., Sect. A*, 20A (1981) 184.
18. G.L. ampbell, G.D. Ellis and M.R. Chakrabarty, *J. Inorg. Nucl. Chem.*, 43 (1981) 2265.
19. S. Kumar and N.K. Kaushik, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 159.
20. B. Singh and V.D. Gupta, *Indian J. Chem., Sect. A*, 21A (1982) 433.
21. R. Chandra and R.N. Kapoor, *Ann. Chim. (Rome)*, 72 (1982) 309.
22. A Sousa, F. De La Fuente, M. Gayoso, R. Bastida and J. Romero, *An. Quim., Ser. B*, 78 (1982) 46.
23. C. Parrado, A. Sousa, M. Gayoso and J. Romero, *An. Quim., Ser. B*, 78 (1982) 32.
24. S. Saxena, Y.P. Singh and A.K. Rai, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 501.
25. V.V. Skopendo, A.I. Brusilovets and A.V. Sinkevich, *Dopov. Akad. Nauk. Ukr. RSR, Ser. B:Geol., Khim. Biol. Nauki*, (1982) 44.

26. Ts. B. Konunova, A. Yu. Tsivadze, A.N. Smirnov and S.A. Kudritskaya, *Zh. Neorg. Khim.*, 27 (1982) 1432.
27. K.S. Siddiqi, N.S. Neelam, F.R. Zaidi and S.A.A. Zaidi, *Croat. Chem. Acta*, 54 (1981) 421.
28. S.N. Rustamove and N. Yu. Ibragimov, *Prisadki Smas. Maslam*, 7 (1981) 63.
29. L.I. Ganago and L.V. Kovaleva, *Zh. Anal. Khim.*, 37 (1982) 1209.
30. V.S. Abakumova, G.D. Kholopova and M.L. Afanas'ev, *Zh. Neorg. Khim.*, 26 (1981) 2085.
31. K. Dehnicke and N. Krueger, *Chem.-ZTG.*, 106 (1982) 187.
32. G.A. Razuvaev, L.I. Vyshinskaya and S. Ya. Timoshenko, *Zh. Obshch. Khim.*, 51 (1981) 2004.
33. L.E. Manzer, *Inorg. Synth.*, 21 (1982) 135.
34. L.I. Kuznetsov, Yu.V. Kolodyazhnyi, O.A. Vlotskaya, N.L. Chikina, V.V. Kuz'menko and A.D. Garnovskii, *Koord. Khim.*, 8 (1982) 445.
35. I.E. Uflyand, V.P. Kurbatov, E.S. Kukharisheva and A.D. Pomogailo, *Izv. Sev.-Kauk. Nauchn. Tsentra Vyssh. Shk., Estestv. Nauki*, (1981) 54.
36. T.N. Lamova, B.D. Berezin, L.V. Oparin and V.V. Zvezdina, *Zh. Neorg. Khim.*, 27 (1982) 683.
37. V.I. Shapoval, L.I. Zarubitskaya and V.F. Grishchenko, *Ukr. Khim. Zh. (Russ. Ed.)*, 48 (1982) 608.
38. H. Schaefer and U. Floerke, *Z. Anorg. Allg. Chem.*, 479 (1981) 89.
39. E.N. Knyazeva and E.P. Klimenko, *Mashinostr. Tekhnol.*, 18 (1981) 64.
40. M. Saeki and M. Onoda, *Bull. Chem. Soc. Japan*, 55 (1982) 113.
41. H. Schaefer, *Z. Anorg. Allg. Chem.*, 486 (1982) 33.
42. T. Misono, Y. Abe, Y. Nagao and K. Nigorikawa, *Shikizai Kyokaishi*, 55 (1982) 76.
43. G. Plesch, E.A. Paukshtis and E.S. Sanko, *Chem. Zvesti*, 35 (1981) 613.
44. K.K. Narang and R.M. Dubey, *J. Sci. Res. Banaras Hindu University*, 30 (1980) 173.
45. V.V. Lukachina, *Zh. Neorg. Khim.*, 27 (1982) 1707.
46. R. Fischer and E. Tillmanns, *Z. Kristallogr.*, 157 (1981) 69.
47. A.M. Sych and Yu. A. Titov, *Zh. Neorg. Khim.*, 26 (1981) 1995.
48. A.A. Gurov and O.A. Sinegribova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 24 (1981) 1330.
49. N.V. Porotnikov, N.G. Chaban, K.I. Petrov and V.G. Savenko, *Zh. Neorg. Khim.*, 27 (1982) 1133.
50. V.V. Sakharov, V.G. Savenko, A.A. Nurgalieva and K.I. Petrov, *Zh. Neorg. Khim.*, 26 (1981) 2329.
51. M. Kiyama and T. Takada, *Bull. Chem. Soc. Japan*, 54 (1981) 2960.
52. R. Vatulescu, T. Budiu and G. Marcu, *Rev. Roum. Chim.*, 26 (1981) 851.
53. R. Vatulescu, T. Budiu and G. Marcu, *Rev. Roum. Chim.*, 26 (1981) 971.
54. G.P. Pez, P. Apgar and R.K. Crissey, *J. Am. Chem. Soc.*, 104 (1982) 482.
55. S.S. Wreford, M.B. Fischer, J.-S. Lee, J.E. Joyce and S.C. Nyburg, *J. Chem. Soc., Chem. Commun.*, (1981) 458.
56. L.P. Battaglia, A.B. Corradi and M. Nardelli, *Inorg. Chim. Acta*, 50 (1981) 125.
57. H. Koepf and J. Pickhardt, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 36B (1981) 1208.
58. A.K. Rappe and W.A. Goddard, *J. Am. Chem. Soc.*, 104 (1982) 297.
59. J.B. Lee, G.J. Gajda, W.P. Schaefer, T.R. Howeard, T. Ikariya, D.A. Straus and R.H. Grubbs, *J. Am. Chem. Soc.*, 103 (1981) 7358.
60. B.M. Bulychev, A.L. Kastenko, G.L. Soloveichik and V.B. Polyakova, *Trans. Met. Chem.*, 6 (1981) 240.
61. J.C..Bart, I.W. Bassi, M. Calcaterra, E. Albizzati, U. Giannini and S. Parodi, *Z. Anorg. Allg. Chem.*, 482 (1981) 121.
62. R. Sabatier, A.M. Vasson and A. Vasson, *Mater. Res. Bull.*, 17 (1982) 369.
63. M. Mori, K. Ohshima, S.C. Moss, R.F. Frindt, M. Plischke and J.C. Irwin, *Solid State Commun.*, 43 (1982) 781.
64. E. Tronc and R. Moret, *Synth. Met.*, 4 (1981) 113.
65. Y. LePage and P. Strobel, *J. Solid State Chem.*, 43 (1982) 314.

66. P.T. Dawson and S.A.J. Stazyk, *J. Vac. Sci. Technol.*, 21 (1982) 36.
67. I.L. Eremenko, Yu. Y. Skripkin, A.A. Pasynskii, V.T. Kalinnikov, Yu. T. Struchkov and G.G. Aleksandrov, *J. Organomet. Chem.*, 220 (1981) 159.
68. S. Cohen, H. Selig and R. Gut, *J. Fluorine Chem.*, 20 (1982) 349.
69. Z. Tun and I.D. Brown, *Acta Crystallogr., Sect. B*, B38 (1982) 1792.
70. H.D. Doerner and K. Dehicke, *Z. Anorg. Allg. Chem.*, 486 (1982) 136.
71. C.J. Dain, A.J. Downs and D.W.H. Rankin, *Angew. Chem.*, 94 (1982) 557.
72. G.V. Girichev, V.M. Petrov, N.I. Giricheva and K.S. Krasnov, *Zh. Strukt. Khim.*, 23 (1982) 56.
73. Y. Arnaud and M. Chevreton, *J. Solid State Chem.*, 39 (1981) 230.
74. V.V. Nemoshkalenko, M.M. Kindrat, V.P. Krivitskii, B.P. Mamko, V.M. Prokopenko and A.I. Kharlamov, *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, 18 (1982) 795.
75. M.C. Cadee and D.J.W. Ijdo, *Mater. Res. Bull.*, 17 (1982) 481.
76. Y. Piffard, R. Marchand and M. Tournoux, *Ann. Chim. (Paris)*, 6 (1981) 419
77. R. Nagarajan and C.R.K. Murty, *Bull. Mater. Sci.*, 3 (1981) 217.
78. D. Hanzel, M. Drofenik, V. Krasevec and A. Prodan, *Solid State Commun.*, 40 (1981) 899.
79. H. Lueken and L. Maqua, *Z. Anorg. Allg. Chem.*, 490 (1982) 64.
80. D. Sinram, C. Brendel and B. Krebs, *Inorg. Chim. Acta*, 64 (1982) L131.
81. W. Carrillo-Cabrera and T. Lundstroem, *Acta Chem. Scand., Ser. A*, A35 (1981) 545.
82. S.H. Sang, *Acta Chem. Scand., Ser. A*, A36 (1982) 207.
83. P. Strobel and Y. LePage, *J. Mater. Sci.*, 17 (1982) 2424.
84. G. Vlaic, J.C.J. Bart, W. Cavigiolo and S. Mobilio, *Chem. Phys.*, 64 (1982) 115.
85. L.M. Sheludchenko, Yu. N. Kucherenko and V.G. Aleshin, *J. Phys. Chem. Solids*, 42 (1981) 733.
86. A. Fujimori and N. Tsuda, *Solid State Commun.*, 41 (1982) 491.
87. P. Yang, L. Li and X Gao, *Fenzi Kexue Xuebao*, 2 (1982) 57.
88. S. Ahn, E.S. Park and K.H. Lee, *Taehan Hwahakhoe Chi*, 25 (1981) 61.
89. H. Kita, N. Henmi, K. Shimazu, H. Hattori and K. Tanabe, *J. Chem. Soc., Faraday Trans.* 1, 77 (1981) 2451.
90. A.S. Babenko and I.P. Danilov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 24 (1981) 1452.
91. A.I. Nikolaev, N.I. Kasikova and L.M. Zalkind, *Zh. Neorg. Khim.*, 27 (1982) 178.
92. A.I. Nikolaev, N.I. Kasikova, E.G. Il'in, A.G. Babkin and L.M. Zalkind, *Zh. Neorg. Khim.*, 27 (1982) 1267.
93. R. Nishimura and K. Kudo, *Corros. Sci.*, 22 (1982) 637.
94. E. Tonew, M. Tonew, B. Heyn and H.-P. Schroer, *Zentralbl. Bakteriol., Mikrobiol. Hyg., Abt. 1, Orig.*, A, 250 (1981) 425.
95. Yu. A. Lysenko, E.A. Troshino and L.I. Khokhlova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 25 (1982) 532.
96. N.S Enikolopyan, A.M. Bochkin, A.D. Pomogailo, A.I. Kuzaev, P.A. Ivanchenko, I.N. Ivleva and F.S. A'yachkovskii, *Dokl. Akad. Nauk. SSSR*, 265 (1982) 95.
97. Ya. I. Tursyan and L.M. Maluka, *Deposited Doc.*, (1980) SPSTL 218khp-D80.
98. H.V. Nguyen and V.M. Ivanov, *Deposited Doc.*, (1981) VINITI 3167-81, 171-3.
99. A.R. Dias, M.S. Salema and J.A. Martinho Simoes, *J. Organomet. Chem.*, 222 (1981) 69.
100. R.F. Childs, D.L. Mulholland and A. Nixon, *Can. J. Chem.*, 60 (1982) 809.
101. V.P. Vasil'ev and P.N. Vorob'ev, *Zh. Obshch. Khim.*, 51 (1981) 2165.
102. E. Takakura, *Asahikawa Kogyo Koto Semmon Gakko Kenkyu Hobun*, 19 (1982) 105.
103. A.K. Sharma and N.K. Kaushik, *Thermochim. Acta*, 49 (1981) 385.
104. E.A. Buketov, L.G. Gorokhova and M. Zh. Makhmetov, *Vestn. Akad. Nauk. Kaz. SSR*, 7 (1982) 49.
105. A.K. Sharma and S. Kumar, *J. Anal. Appl. Pyrolysis*, 3 (1982) 271.
106. M. Zikmund, M. Kohutova and G. Plesch, *Chem. Zvesti*, 36 (1982) 185.

107. A. Marais, G. Villers and R. Vautier, *IEEE Trans. Magn.*, Mag-17, 6 (1981) 2715.
108. A. Hartung and D. Babel, *J. Fluorine Chem.*, 19 (1982) 369.
109. A.V. Loshagin, A.P. Khaimenov and M.V. Smirnov, *Deposited Doc.*, (1981) VINITI 594-81.
110. S.K. Datta and D. Debabala, *Indian J. Cryog.*, 5 (1980) 96.
111. P.G. Pifferi, G. Lanzarini and M. Biancani, *Ann. Chim. (Rome)*, 71 (1981) 729.
112. S. Mohan and A. Mukunthan, *Indian J. Phys. (Part B)*, 56B (1982) 91.
113. Y. Hase, *An. Acad. Bras. Cienc.*, 53 (1981) 747.
114. I. Glavchev and V. Kabaivanov, *God. Vissh. Khim.-Tekhnol. Inst., Sofia*, 24 (1981) 221.
115. I.V. Ikonitskii, N.A. Buzina and L.S. Bresler, *Zh. Prikl. Spektrosk.*, 35 (1981) 1004.
116. H. Schaefer and U. Floerke, *Z. Anorg. Allg. Chem.*, 479 (1981) 89.
117. J. Goffart and L. Hocks, *Spectrochim. Acta, Part A*, 37A (1981) 609.
118. J. Lovy, R. Puffr, J. Stokr, D. Doskocilova and B. Schneider, *J. Mol. Struct.*, 77 (1981) 295.
119. H.O. Finklea and R. Vinthanage, *J. Phys. Chem.*, 86 (1982) 3621.
120. S. Banon, C. Chatillon and M. Allibert, *High Temp. Sci.*, 15 (1982) 17.
121. M.M. Mikhailov, V.P. Yanovskii and M. Dvaretskii, *Vzaimodeistvie Atom. Chastits S Tverd. Telom. Materialy 6-l vses. Konf., Minsk*, Ch. 1 (1981) 161.
122. M. Gupta, *Solid State Commun.*, 42 (1982) 501.
123. L.J. Swartzendruber, L.H. Bennett and R.E. Watson, *J. Phys. F. Metal Phys.*, 6 (1976) L331.
124. A.I. Kuz'min ans S.I. Kuznetsov, *Koord. Khim.*, 8 (1982) 159.
125. R.C.T. Slade, M.G. Cross and W.A. England, *Solid State Ionics* , 6 (1982) 225.
126. M.C.R. Symons and S.P. Mishra, *J. Chem. Soc., Dalton Trans.*, (1981) 2258.
127. M. Gabelica-Robert and Z. Gabelica, *Proc. Eur. Symp. Therm. Anal.*, 2nd (1981) 359.
128. R. Dams, M. Malinowski and H.J. Geise, *Trans. Met. Chem.*, 7 (1982) 37.
129. R.S. Rubins and T.D. Black, *J. Chem. Phys.*, 75 (1981) 128.
130. G.A. Kravets, T. Kh. Shokhireva, V.F. Anufrienko and T.M. Yurieva, *React. Kinet. Catal. Lett.*, 19 (1982) 85.
131. A.E. Foti and V.H. Smith Jr., *Mol. Phys.*, 45 (1982) 385.
132. D.E. Onopko and S.A. Titov, *Opt. Spektrosk.*, 51 (1981) 985.
133. A. Gupta and J.A. Tossell, *J. Electron Spectrosc. Relat. Phenom.*, 26 (1982) 223.
134. H. Hoechst, R.D. Bringans, P. Steiner and T. Wolf, *Phys. Rev. B: Condens. Matter*, 25 (1982) 7183.
135. A. Lebugle, R. Nyhokm and N. Maartensson, *J. Less-Common Met.*, 82 (1981) 269.
136. G. Vlaic, J.C.J. Bart, W. Cavigiolo and S. Mobilio, *Z. Naturforsch.* A, 36A (1981) 1192.
137. M.F. Lappert and B. Prolian, *Adv. Organomet. Chem.*, 5 (1967) 225.
138. C. Bloody and D. Gervais, *Inorg. Chim. Acta*, 52 (1981) 79.
139. E. Klei and J.H. Teuben, *J. Organomet. Chem.*, 222 (1981) 79.
140. S.R. Wade and G.R. Willey, *J. Chem. Soc., Dalton Trans.*, (1981) 1264.
141. B.H. Chang, H.S. Tung and C.H. Brubaker Jr., *Inorg. Chim. Acta*, 51 (1981) 143.
142. M. Pankowski and E. Samuel, *J. Organomet. Chem.*, 221 (1981) C21.
143. J.A. Smith and H.H. Brintzinger, *J. Organomet. Chem.*, 218 (1981) 159.
144. Yu. N. Kozlov, T.P. Vorob'eva and A.P. Purmal, *Zh. Fiz. Khim.*, 55 (1981) 2279.
145. T.S. Pritytskaya, A.M. Antipova, V.P. Mardykin and N.E. Strashevskaya, *Zh. Prikl. Khim. (Leningrad)*, 54 (1981) 2294.
146. V.M. Zadoshchenko, *Sb. Nauchn. Tr.- Vses. Nauchno-Issled. Inst. Lyuminoforov Osobo Chist. Veshchestv*, 19 (1980) 65.

147. R.C. Paul, R.K. Chadha and B.S. Bhandal, *Inorg. Chim. Acta*, 52 (1981) 125.
148. I. Cuadrado and M. Moran, *Trans. Met. Chem.*, 6 (1981) 329.
149. P. Sobota, *Probl. Metody Chem. Koord.*, (1981) 313.
150. G.I. Kadyrova and E.A. Ivanova, *Fiz.-Khim. Issled. Redk. Elem. Protessy Ikh Vydeleniya Redkomet. Syr'ya*, (1980) 3.
151. M.N. Godnera, O.L. Motov and R.F. Okhrimenko, *Deposited Doc .*, (1981) VINITI 2049-81.
152. M.A. Gornikova, Ya. G. Goroshchenko, V.N. Skomorokha and I.P. Vorob'eva, *Ukr. Khim. Zh. (Russ. Ed.)*, 48 (1982) 581.
153. N.E. Darienko, L.F. Galaktionova and I.N. Marenkova, *Issled. V. Obl. Tekhnol. Dvuokisi I Zhelezosoderzh. Pigmentov. M*, (1982) 27.
154. H. Einaga and Y. Komatsu, *J. Inorg. Nucl. Chem.*, 43 (1981) 2443.
155. H. Einaga and Y. Komatsu, *J. Inorg. Nucl. Chem.*, 43 (1981) 2449.
156. J. Slivnik, B. Druzina and B. Zemva, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, 36B (1981) 1457.
157. N. Serpone and D.G. Bickley, *Inorg. Chim. Acta*, 57 (1982) 211.
158. H.O. Finklea and R. Vithanage, *Sci. Tech. Aerosp. Rep.*, 20 (1982) Abstr. No. N82.
159. S. Okazako and K. Kuramochi, *Nippon Kagaku Kaishi*, (1982) 1141.
160. A.A. Dvernyakova, G.N. Novitskaya and L.L. Chmel, *Ukr. Khim. Zh. (Russ. Ed.)*, 47 (1981) 1205.
161. E.A. Avrutina, A.V. Gusev, S.I. Kol'tsov, G.N. Kuznetsova and A.A. Malygin, *Zh. Prikl. Khim. (Leningrad)*, 54 (1981) 2125.
162. M. Ashizuka, M. Miyoshi and M. Horikawa, *Kyushu Kogyo Daigaku Kenkyu Hokoku, Kogaku*, (1981) 71.
163. I.N. Marenkova, A.B. Lundin, N.K. Bulatov and I.I. Kalinichenko, *Zh. Prikl. Khim. (Leningrad)*, 55 (1982) 1252.
164. B. Yu, *Jinshu Xuebao*, 18 (1982) 164.
165. K. Kh. Razikov, T.A. Kirgizbaev, T.S. Ismailov and L.R. Ishanova, *Uzb. Khim. Zh.*, (1981) 25.
166. V.D. Lyubimov, S.I. Alyamovskii and G.P. Shveikin, *Zh. Neorg. Khim.*, 26 (1981) 2314.
167. N.T. Denisov, E.M. Burbo, S.I. Kobeleva, A.E. Shilov and N.I. Shualova, *Kinet. Katal.*, 23 (1982) 874.
168. A. Packter and S.A. Zaidi, *Z. Phys. Chem. (Leipzig)*, 263 (1982) 481.
169. M. Inoue, A. Kishioka and M. Kinoshita, *Nippon Kagaku Kaishi*, (1982) 743.
170. W.L. Ahlgren, *J. Electrochem. Soc.*, 128 (1981) 2123.
171. J.F. McAleer and L.M. Peter, *Faraday Discuss. Chem. Soc.*, 70 (1981) 67.
172. T. Suzuko and N. Kutsuwada, *Nippon Kogyo Daigaku Kenkyu Hokoku*, 11 (1981) 107.
173. V. Antonucci, P. Miceli, N. Giordano and J.C.J. Bart, *Ber. Bunsenges. Phys. Chem.*, 86 (1982) 681.
174. I.A. Krasil'nikova, Z.A. Iofa, E.V. Kasatkin and V.A. Safonov, *Deposited Doc.*, VINITI 2909-81 (1981).
175. Y. Matsumoto, T. Shimizu and A. Toyoda, *J. Phys. Chem.*, 86 (1982) 3581.
176. K.H. Houng, *Bull. Inst. Chem., Acad. Sin.*, 28 (1981) 27.
177. Y. Takahashi, A. Ogiso and R. Tomoda, *J. Chem. Soc., Faraday Trans. 1*, 78 (1982) 2563.
178. A.G. Sarkisyan, V.M. Arakelyan and Zh. R. Panosyan, *Izv. Akad. Nauk. Arm. SSR Fiz.*, 16 (1981) 206.
179. S.B. Deutscher, J.H. Richardson, S.P. Perone, J. Rosenthal and J. Ziemer, *Faraday Discuss. Chem. Soc.*, 70 (1981) 33.
180. L.J. Handley, J.F. McCann and D. Haneman, *J. Appl. Phys.*, 53 (1982) 4549.
181. J. Moser and M. Graetzel, *Helv. Chim. Acta*, 65 (1982) 1436.
182. Y.Nakato, A. Tsumura and H. Tsubomura, *Chem. Phys. Lett.*, 85 (1982) 387.
183. T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electroanal. Chem. Interfacial Electrochem.*, 138 (1982) 105.
184. P. Salvador and C. Gutierrez, *Chem. Phys. Lett.*, 86 (1982) 131.
185. H.R. Sprunken, R. Schumacher and R.N. Schindler, *Faraday Discuss. Chem. Soc.*, 70 (1981) 55.

186. J.R. Wilson and S.M. Park, *J. Electrochem. Soc.*, 128 (1981) 2369.
187. V.E. Kazarinov, V.N. Andreev and A.P. Mayorov, *J. Electroanal. Chem. Interfacial Electrochem.*, 130 (1981) 277.
188. M.S. Lin, N. Hung and M.S. Wrighton, *J. Electroanal. Chem. Interfacial Electrochem.*, 135 (1982) 121.
189. C. Yu, H. Lin, H. Liu and Y. Chan, *Cuihua Xuebao*, 3 (1982) 28.
190. M. Koudelka, J. Sanchez and J. Augustynski, *J. Phys. Chem.*, 86 (1982) 4277.
191. F.M. Tartakovskaya, S.P. Chernova, N.V. Makarinko, V.I. Ignat'ev and L.I. Derkachenko, *Zh. Prikl. Khim. (Leningrad)*, 55 (1982) 1578.
192. N. Ya. Bune, M. Yu. Portnova, V.V. Gorodetskii, M.M. Pecherskii, V.B. Yanke, V.P. Filatov, A.A. Garkusha and V.V. Losev, *Zh. Prikl. Khim.*, *(Leningrad)*, 54 (1981) 2027.
193. R.U. Bondar, N.V. Burym and E.A. Kalinovskii, *Vopr. Khim. Khim. Tekhnol.*, 65 (1981) 23.
194. D.A. Denton, J.A. Harrison and R.I. Knowles, *Electrochim. Acta*, 26 (1981) 1197.
195. C. Comninellis and E. Plattner, *J. Appl. Electrochem.*, 12 (1982) 399.
196. B.V. Rozentuller, K.N. Spiridonov and O.V. Krylov, *Dokl. Akad. Nauk. SSSR*, 259 (1981) 895.
197. P.H.M. DeKorte, R.U.E. 'Tlam and J. Schoonman, *J. Inorg. Nucl. Chem.*, 43 (1981) 2261.
198. V. Guruswamy, O.J. Murphy, V. Young, G. Hildreth and J. Bockris, *Solar Energy Mater.*, 6 (1981) 59.
199. P. Richardson, P. Ang and A. Sammells, *Adv. Hydrogen Energy; Hydrogen Energy Prog. 4*, 2 (1982) 805.
200. C. Gutierrez, P. Salvador and J.B. Goodenough, *J. Electroanal. Chem. Interfacial Electrochem.*, 134 (1982) 325.
201. F.T. Liou, C.Y. Yang and S.N. Levine, *J. Electrochem. Soc.*, 129 (1982) 342.
202. Y. Nakato and N. Takamore, *Nature*, 295 (1982) 312.
203. Yu. I Kiryukhin, Z.A. Sinitsyna, L.V. Romashov, V.A. Borovkova and Kh. S. Bagdasar'yan, *Dokl. Akad. Nauk. SSSR*, 261 (1981) 416.
204. A.H.A. Tinnemans and A. Mackor, *Recl.: J.R. Neth. Chem. Soc.*, 100 (1981) 295.
205. M.P. Dare-Edwards, J.B. Goodenough, A. Hammett, K.R. Seddon and R.D. Wright, *Faraday Discuss. Chem. Soc.*, 70 (1981) 285.
206. T. Li, C. Yu, H. Tang and Y. Chen, *Cuihua Xuebao*, 2 (1981) 156.
207. Y. Matsuda, M. Inoue, M. Morita, Y. Takasu, H. Mizuno and H. Miura, *Denki Kagaku oyobi Kogyo Butsuri Kagaku* 50 (1982) 258.
208. A. Armigliato, G. Celotti, A. Garulli, S. Guerri, P. Ostoja, R. Rosa and G. Martinelli, *Thin Solid Films*, 92 (1982) 341.
209. A.J. Vaccaro, T. Palanisamy and R.L. Kerr, *J. Electrochem. Soc.*, 129 (1982) 677.
210. A.J. Vaccaro, T. Palanisamy and R.L. Kerr, *J. Electrochem Soc*, 129 (1982) 682.
211. L.P. Klemann and G.H. Newman, *J. Electrochem. Soc.*, 129 (1982) 230.
212. M.S. Zanini and G.J. Tennenhouse, *J. Electrochem. Soc.*, 129 (1981) 1647.
213. A. Lisawska and S. Biallozar, *Electrochim. Acta*, 27 (1982) 105.
214. N.V. Petrova, V.N. Titova and V.A. Kazakov, *Elektrokhimiya*, 18 (1982) 489.
215. N.K. Merty and P.M.D. Murty, *Indian J. Chem.*, *Sect. A*, 21A (1982) 756.
216. M. Noel, P.N. Anantharaman and H.V.K. Udupa, *J. Appl. Electrochem.*, 12 (1982) 291.
217. A.I. Dikusar and O.A. Senina, *Elektron. Obrab. Mater.*, (1981) 64.
218. R. Bannehr, N. Jaeger, G. Meyer and D. Woehrle, *Makromol. Chem.*, 182 (1981) 2633.
219. J. Grobe, B.H. Schneider and H. Zimmermann, *Z. Anorg. Allg. Chem.*, 481 (1981) 107.

220. I. Taniguchi, K. Nakashima, H. Yamaguchi and K. Yasukouchi, *J. Electroanal. Chem. Interfacial Electrochem*, 134 (1982) 191.
221. F. Decker, M. Abramovich and J.F. Juliao, *An. Simp. Bras. Eletroquim. Eletroanal.*, 2nd (1980) 112.
222. V.I. Lushnikov, N.T. Presnova, L.S. Kanevskii, E.P. Kovsman and Yu. B. Vasil'ev, *Elektrokhimiya*, 18 (1982) 269.
223. A.H.A. Tinnemans and T.P.M. Koster, *Sol. Energy R and D Eur. Community, Ser. D*, (1982) 1.
224. M. Aldissi, F. Schue, L. Giral and M. Rolland, *Polymer*, 23 (1982) 246.
225. G. Fink and W. Zoller, *Makromol. Chem.*, 182 (1981) 3265.
226. K. Yankova, P. Nikolinski and F. Radenkov, *God. Vissh. Khim.-Tekhnol. Inst., Burgas, Bulg.*, 15, Pt. 2 (1981) 135.
227. K. Yankova, P. Nikolinski and F. Radenkov, *God. Vissh. Khim.-Tekhnol. Inst., Burgas, Bulg.*, 15, Pt. 2 (1981) 143.
228. L.K. Kurnosova, E.N. Kropacheva, I.G. Zhuchikhina, N.A. Konovalenko, V.I. Anosov and I.A. Ikonitskii, *Vysokomol. Soedin., Ser. A*, 23 (1981) 2225.
229. N.P. Shestak, E.P. Pronevich and E.V. Ivanenko, *Izv. Sev.-Kavk. Nauchn. Tsentra. Vyssh. Shk. Tekh. Nauki*, 2 (1981) 93.
230. W. Wieder, J. Witte and G. Marwede, *Ger. Offer.*, DE 3,004,420 (Cl. C08F210/12) (1981) 13.
231. L.F. Borisova, E.A. Fushman, A.N. Shupik, E.I. Vizen, L.N. Sosnovskaya and S.S. Lalayan, *Vysokomol. Soedin., Ser. A*, 23 (1981) 1984.
232. G. Bier, *Polym. Bull. (Berlin)*, 7 (1982) 177.
233. H. Tom Dieck and H. Mueller, *J. Organomet. Chem.*, 221 (1981) C7.
234. L. Verdet and J.K. Stille, *Organometallics (Washington D.C.)*, (1982) 1380.
235. R. Clement, *Eur. Polym. J.*, 17 (1981) 895.
236. O. Bortolini, C. Campello and F. DiFuria, *J. Mol. Catal.*, 14 (1982) 63.
237. O. Botolini, F. DiFuria and G. Modena, *J. Mol. Catal.*, 16 (1982) 69.
238. S.Y. Wang, S.H. Moon and M.A. Vannice, *J. Catal.*, 71 (1981) 167.
239. W.C. Wang, *Diss. Abstr. Int. B*, 43 (1982) 196.
240. T. Shimizu, *Hakodate Kogyo Koto Senmon Gakko Kiyo*, 16 (1982) 73.
241. L.G. Svintsova and G.P. Korneichuk, *Katal. Katal.*, 19 (1981) 57.
242. O.M. Il'inich and A.A. Ivanov, *Mattrialy 3-1 Vses. Konf. po. Kinet. Getorogen. Kahalitich. Reaktsii, 1980, Kalinin*, 1 (1980) 213.
243. L.S. Kravchuk, E.A. Makarova, I.A. Yursha, T.I. Larionova, N.I. Ivashchenko and S.V. Markevich, *Neftekhimiya*, 22 (1982) 42.
244. B.J. Tatarchuk and J.A. Dumesic, *J. Catal.*, 70 (1981) 308.
245. B.J. Tatarchuk and J.A. Dumesic, *J. Catal.*, 70 (1981) 323.
246. B.J. Tatarchuk and J.A. Dumesic, *J. Catal.*, 70 (1981) 335.
247. A.S. Lisitsyn, A.V. Golovin, V.I. Kuznetsov and Yu. I. Yermakov, *React. Kinet. Catal. Lett.*, 19 (1982) 187.
248. M.A. Vannice, *J. Catal.*, 74 (1982) 199.
249. C.U.I. Odenbrand and S.T. Lundin, *J. Chem. Technol. Biotechnol.*, 31 (1981) 660.
250. I. Mochida, H. Fujitsu, K. Takeshita and K. Tsuji, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1516.
251. E. Cesarotti, R. Ugo and R. Vitiello, *J. Mol. Catal.*, 12 (1981) 63.
252. O.I. Goncharova, A.A. Davydov and T.M. Yur'eva, *React. Kinet. Catal. Lett.*, 20 (1982) 119.
253. T. Kh. Shokhireva, T.M. Yurieva and G.K. Boreskov, *React. Kinet. Catal. Lett.*, 19 (1982) 151.
254. G.A. Kravets, T. Kh. Shokhireva, V.F. Anufrienko and T.M. Yurieva, *React. Kinet. Catal. Lett.*, 19 (1982) 85.
255. L.F. Weiserman and D.M. Hercules, *Appl. Spectrosc.*, 36 (1982) 361.
256. B.H. Chen and J. White, *J. Phys. Chem.*, 86 (1982) 3534.
257. S.D. Worley, C.A. Rice and G.A. Mattson, *J. Phys. Chem.*, 86 (1982) 2714.
258. P. Meriaudeau, O. Ellestad and M. Dufaux, *J. Catal.*, 75 (1982) 243.

259. P. Meriaudeau, H. Ellestad and C. Naccache, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1464.
260. R. Burch and A.R. Flambard, *React. Kinet. Catal. Lett.*, 17 (1981) 23.
261. K. Tanaka, K. Miyahara and K. Tanaka, *Bull. Chem. Soc. Japan*, 54 (1981) 3106.
262. E. Santacesaria, *React. Kinet. Catal. Lett.*, 19 (1982) 49.
263. G.A. Zenkovets, E. Paukstis, D.V. Tarasova and E.N. Yurchenko, *Kinet. Katal.*, 22 (1981) 1584.
264. Anonymous, (U.K.), *Res. Discl.*, 215 (1982) 64.
265. K. Mack, F. Turecek, V. Hanus, L. Petrusova, H. Antropiusova, A. Dodedlova and P. Sedmera, *Chem. Zvesti*, 36 (1982) 191.
266. D. Hoenicke and K. Griesbaum, *Appl. Catal.*, 2 (1982) 177.
267. T.M. Nakajima, H. Miyata and Y. Kubokawa, *Bull. Chem. Soc., Japan*, 55 (1982) 609.
268. G.P. Belov, T.S. Dzhabiev and I.M. Kolesnikov, *J. Mol. Catal.*, 14 (1982) 105.
269. R. Ruppert and J.-P. Sauvage, *Nouv. J. Chim.*, 6 (1982) 235.
270. E. Rodenas, T. Iizuka, H. Katsumata and K. Tanabe, *React. Kinet. Catal. Lett.*, 19 (1982) 341.
271. Y. Murakami, M. Inomata and A. Miyamoto, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1344.
272. S. Morikawa, K. Takahashi and S. Kurita, *Ryusan to Kogyo*, 34 (1981) 243.
273. S. Morikawa, K. Takahashi and J. Mogi, *Bull. Chem. Soc. Japan*, 55 (1982) 2254.
274. B.I. Pantukh, V.A. Rozentsvet and S.R. Rafikov, *Isv. Akad. Nauk SSSR , Ser. Khim.*, 5 (1982) 1189.
275. G.C. Vond and K. Bruckman, *Faraday Discuss. Chem. Soc.*, 72 (1981) 235.
276. P. Gajardo, E.F. Gleason and J.R. Katzer, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1462.
277. V.I. Varlamov, V.M. Komarov and A.A. Klimenkova, *Zh. Prikl. Khim. (Leningrad)*, 55 (1982) 1655.
278. A.I. Kharlamov, V.P. Krivitskii and M.M. Kindrat, *Kinet. Katal.*, 23 (1982) 654.
279. P.J. Pomonis and J.C. Vickerman, *Faraday Discuss. Chem. Soc.*, 72 (1981) 247.
280. Yu. A. Lysenko, E.A. Troshina and T.M. Pekhtereva, *Zh. Obshch. Khim.*, 51 (1981) 2058.
281. J.C. Conesa and J. Soria, *J. Phys. Chem.*, 86 (1982) 1392.
282. J.A. Schreifels, D.N. Belton and J.M. White, *Chem. Phys. Lett.*, 90 (1982) 261.
283. M.A. Enriquez and J.P. Fraissard, *J. Catal.*, 74 (1982) 89.
284. Y. Hu, D. He, and G. Xie, *Huaxue Tongbao*, 11 (1981) 652.
285. Y. Chen, Z. Wei, H. Liu and Y. Chen, *Cuihua Xuebao*, 2 (1981) 194.
286. E. Pelizzetti, M. Visca, E. Borgarello, E. Pramauro and A. Palmas, *Chem. Ind. (Milan)*, 63 (1981) 805.
287. Y. Oosawa, *Chem. Lett.*, 4 (1982) 423.
288. F.T. Wagner, *Diss. Abstr. Int., B*, 42 (1982) 4817.
289. K. Domen, S. Naito and T. Onishi, *J. Phys. Chem.*, 86 (1982) 3657.
290. D.H.W.M. Thewissen, M. Eeuwhorst-Reinten, K. Timmer, A.H.A. Tinnemanns and A. Mackor, *Sol. Energy R and D Eur. Community, Ser. D*, 1 (1982) 56.
291. S. Teratani, S. Choi, Y. Takagi, M. Kawai and K. Tanaka, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)*, 75 (1981) 244.
292. P. Pichat, J.M. Hermann and J. Disdier, *Nouv. J. Chim.*, 5 (1981) 627.
293. P. Pichat, H. Courbon, J. Disdier, M.N. Mozzanega and J.M. Hermann, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1498.
294. S. Teratani, J. Nakamichi, K. Taya and K. Tanaka, *Bull. Chem. Soc. Japan*, 55 (1982) 1688.
295. T. Sato, H. Koneko and T. Takahashi, *Chem. Lett.*, 10 (1981) 1469.
296. J. Cunningham and B.K. Hodnett, *J. Chem. Soc., Faraday Trans. 1*, 77 (1981) 2777.

297. Y. Kubokawa, M. Anpo and C. Yun, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1170.

298. M.S. Fujihira, Y. Satoh and T. Osa, *J. Electroanal. Chem. Interfacial Electrochem.*, 126 (1981) 277.

299. M. Fujihira, Y. Satoh and T. Osa, *Bull. Chem. Soc. Japan*, 55 (1982) 666.

300. M. Fujihira, Y. Satoh and T. Osa, *Nature*, 293 (1981) 206.

301. A.R. Gonzalez-Elipe and M. Che, *J. Chim. Phys. Phys.-Chim. Biol.*, 79 (1982) 355.

302. L.V. Lyashenko, V.M. Belousov and F.A. Yampol'skaya, *React. Kinet. Catal. Lett.*, 16 (1981) 237.

303. L.V. Lyasheñko, V.M. Belousov and F.A. Yampol'skaya, *Kinet. Katal.*, 23 (1982) 662.

304. V.I. Stepanenko, F.A. Yampol'skaya and L.V. Lyashenko, *Katal. Katal.*, 19 (1981) 49.

305. V. Augugliaro, A. Lauricella, L. Rizzuti, M. Schiavello and A. Sclafoni, *Adv. Hydrogen Energy, 198l, 2, Hydrogen Energy Prog.*, Vol. 2 (1981) 589.

306. A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 86 (1982) 241.

307. P. Pichat, J.M. Herrmann, H. Courbon and J. Disdier, *Can. J. Chem.*, 60 (1982) 27.

308. H. Hada, Y. Yonezawa and M. Saikawa, *Bull. Chem. Soc. Japan*, 55 (1982) 2010.

309. H. Hada, Y. Yonezawa, M. Ishino and H. Tanemura, *J. Chem. Soc., Faraday Trans. 1*, 78 (1982) 2677.

310. J. Cunningham, E.L. Goold and J.L.G. Fierro, *J. Chem. Soc., Faraday Trans. 1*, 78 (1982) 785.

311. H. Courbon, J.M. Herrmann and P. Pichat, *J. Catal.*, 72 (1981) 129.

312. S. Nagai, H. Arai and M. Hatada, *Radiat. Phys. Chem.*, 18 (1981) 807.

313. K. Saito, H. Yuki and S. Tomoyuko, *Can. J. Chem.*, 59 (1981) 1722.

314. L. Tang, D. Sallet and J. Lemaire, *Macromolecules*, 15 (1982) 1437.

315. G. Munuera, A. Navio and J. Soria, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1185.

316. T. Sakata, T. Kawai and K. Hashimoto, *Chem. Phys. Lett.*, 88 (1982) 50.

317. B. Klei, J.H. Teuben and H.J. de Liefde Meijer, *J. Chem. Soc., Chem. Commun.*, (1981) 342.

318. B. Demerseman and P.H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, (1981) 665.

319. J.H. Teuben, E.J.M. De Boer, A.H. Klazinga and E. Klei, *J. Mol. Catal.*, 13 (1981) 107.

320. F. Sato, T. Jinbo and M. Sato, *Synthesis*, (1981) 871.

321. K. Mach, F. Turecek, H. Antropiusova, L. Petrusova and V. Hanus, *Synthesis*, (1982) 53.

322. L.I. Zakharkin and N.F. Shemyakin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1981) 1856.

323. M.T. Reetz and R. Peter, *Tetrahedron Lett.*, 22 (1981) 4691.

324. V.S. Martin, S.S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda and K.B. Sharpless, *J. Am. Chem. Soc.*, 103 (1981) 6237.

325. M.T. Reetz and J. Westermann, *Synth. Commun.*, 11 (1981) 647.

326. R. Pardo and M. Santelli, *Tetrahedron Lett.*, 22 (1981) 3843.

327. M.A. Tius, *Tetrahedron Lett.*, 22 (1981) 3335.

328. J.M. Pons, J.P. Zahra and M. Santelli, *Tetrahedron Lett.*, 22 (1981) 3965.

329. R. Dams, M. Malinowski and H.J. Geise, *Bull. Soc. Chim. Belg.*, 90 (1981) 1141.

330. G.P. Aleeva, V.S. Kuts and N.A. Vysotkaya, *Ukr. Khim. Zh. (Russ. Ed.)*, 48 (1982) 724.

331. P. Sobota, J. Utko and J. Wroblewski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 28 (1980) 679.

332. S. Wu and Y. Zhou, *Lanzhou Daxue Xuebao, Ziran Kexueban*, 18 (1982) 166.

333. L. Yu. Gubaidullin and U.M. Dzhemilev, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1981) 2614.

334. Y.D. Xing and N.Z. Huang, *J. Org. Chem.*, 47 (1982) 140.

335. J. Yamamoto, Y. Ikeda, T. Inohara, H. Nakata and M. Umezu, *Nippon Kagaku Kaishi*, (1981) 1911.
336. J. Besancon, A. Radecki-Sudre, C. Degrand and J. Tirouflet, *C. R. Seances Acad. Sci., Ser. 2*, 293 (1981) 365.
337. H.W. Roesky and E. Wehner, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 36B (1981) 1247.
338. M. Masure, S.G. Nguyen-anh-Hung, G. Sauvet and P. Sigwalt, *Makromol. Chem.*, 182 (1981) 2695.
339. L.A. Kazaryan, E.N. Kropacheva and Yu. G. Kamenev, *Vysokomol. Soedin., Ser. A*, 23 (1981) 2232.
340. M. Kakugo, Y. Naito and K. Mizunuma, *Macromolecules*, 15 (1982) 1150.
341. A. Citterio, A. Arnoldi and A. Griffini, *Tetrahedron*, 38 (1982) 393.
342. A. Clerici and O. Porta, *Tetrahedron*, 38 (1982) 1293.
343. A. Clerici and O. Porta, *J. Org. Chem.*, 47 (1982) 2852.
344. T.H. Chan, J.S. Li, T. Aida and D.N. Harpp, *Tetrahedron Lett.*, 23 (1982) 837.
345. W.H. Richardson, *Synth. Commun.*, 11 (1981) 895.
346. Yu. V. Rakitin, V.V. Bolkov and V.T. Kalinnikov, *Koord. Khim.*, 7 (1981) 1824.
347. K. Tanaka, K. Miyahara and K. Tanaka, *J. Mol. Catal.*, 15 (1982) 133.
348. J. Engelhardt, *J. Catal.*, 72 (1982) 179.
349. J.L. Lemberton, G. Perot and M. Guisnet, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 993.
350. E.L. Kugler, *Prepr.-Am. Chem. Soc. Div. Pet. Chem.*, 25 (1980) 564.
351. F. Solymosi, I. Tombacz and M. Kocsis, *J. Catal.*, 75 (1982) 78.
352. M.A. Enriquez, J.P. Fraissard and B. Bigot, *Stud. Surf. Sci. Catal., Part B, New Horiz. Catal.*, 7 (1981) 1268.
353. B. Bigot, M.A. Enriquez and J.P. Fraissard, *J. Catal.*, 74 (1982) 84.
354. M.A. Enriquez and J.P. Fraissard, *J. Catal.*, 74 (1982) 77.
355. L.N. Kurina, V.N. Gerasimova, A.A. Davydov and N.N. Sudakova, *Teor. Eksp. Khim.*, 17 (1981) 713.
356. I.M. Chmyr, N.R. Bukeikhanov and B.V. Sukorov, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 3 (1982) 61.
357. V.K. Tskhakaya, R.S. Chilingarashvili and V.I. Yarygin, *Zh. Tekh. Fiz.*, 51 (1981) 1746.
358. K.I. Pershikova, L.A. Nikonova and A.N. Kitaigorodskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1258.
359. M.T. Reetz, R. Steinbach, B. Wenderoth and J. Westmann, *Chem. Ind. (London)*, (1981) 541.
360. T. Morishima, *Nippon Kagaku Kaishi*, (1982) 21.
361. M. Cournil and G. Thomas, *Ann. Chim. (Paris)*, 6 (1981) 367.
362. T.L. Luk, D.M. Ovchinnikov, K.N. Goroshko and V.G. Sokolov, *Deposited Doc.*, VINITI (1981) 2520-81.
363. S.N. Posevina and D.V. Drobot, *Zh. Neorg. Khim.*, 27 (1982) 797.
364. T. Oota, I. Yamai and M. Yokoyama, *Nagoya Kogyo Daigaku Kogakubu Fuzoko Yogyo Gijutse Kenyu Shisetsu Nenpo* , 8 (1981) 19.
365. O.M. Berezhkovskaya, F.A. Belinskaya and E.D. Makarova, *Ion. Obmen I. Ionometriya, Leningrad*, 3 (1982) 49.
366. M.F. Islam and R.K. Biswas, *J. Inorg. Nucl. Chem.*, 43 (1981) 1929.
367. G.I. Skabichevskaya, V.G. Maiorov, A.G. Babkin and M.N. Bogdanov, *Fiz.-Khim. Issled. Redk. Elem. Protessy Ikh . Vydeleniya Redkomet. Syr'ya*, (1980) 51.
368. A. Mandl, R. Slater and C.H. Appel, *Rev. Sci. Instrum.*, 53 (1982) 301.
369. H. Izawa, S. Kikkawa and M. Koizumi, *Nippon Kagaku Kaishi*, (1981) 1519.
370. J. Choy and A. Weiss, *Chayon Kwahak Taehak Nomunjip (Soul Taehakkyo)*, 7 (1982) 57.
371. U. Constantino, *J. Inorg. Nucl. Chem.*, 43 (1981) 1895.