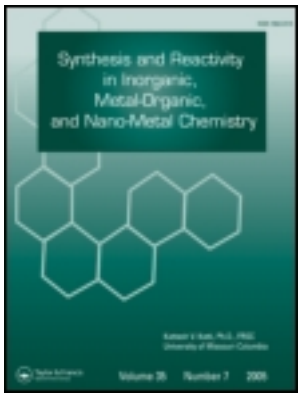

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STUDY OF THE SYNTHESES AND ANTIOXIDATIVE ACTIONS OF $(\eta\text{-}C_5H_5)_2Ti(IV)(Asp)_2$ AND $(\eta\text{-}C_5H_5)_2Ti(IV)(Sal)_2$

Zhengzhi Zeng [a]
[a] Department of Chemistry , Lanzhou University , Lanzhou, 730000, China
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STUDY OF THE SYNTHESES AND ANTIOXIDATIVE ACTIONS OF $(\eta\text{-}C_5H_5)_2Ti(IV)(Asp)_2$ AND $(\eta\text{-}C_5H_5)_2Ti(IV)(Sal)_2$

Zhengzhi Zeng

Department of Chemistry, Lanzhou University,
Lanzhou 730000, China
E-mail: fangjian@china.com

ABSTRACT

In this paper two metalorganic complexes of dicyclopentadienyltitanium(IV) with aspirin and dicyclopentadienyltitanium(IV) with salicylic acid have been synthesized. Their chemical compositions and structures have been studied by elemental analyses, XPS, IR, ^1H NMR. The formulas of the complexes were confirmed as $(Cp)_2Ti(Asp)_2$ and $(Cp)_2Ti(Sal)_2$ [Cp = cyclopentadienyl ion (η^5-C_5H_5), Asp = anion of aspirin (acetylsalicylate ion, $CH_3CO_2C_6H_4COO^-$), Sal = salicylate anion, $C_6H_4(OH)COO^-$], in which the carboxyl oxygen atoms of Asp and Sal are coordinated to Ti(IV) in a monodentate manner. It was found that the complexes of Sal or Asp and cyclopentadienyl ion have a "synergistic action" on the elimination of superoxide radicals ($O_2^{-\bullet}$) and hydroxyl radicals ($OH^\bullet$). The possible mechanism of these reactions has been discussed.

INTRODUCTION

In the 1990s, Qian[1] studied the elimination effect of salicylic acid on the lipid peroxidation in phosphatidylcholine liposomes. Experimental results show that salicylic acid can scavenge the hydroxyl free radicals ($OH^{\bullet}$) and superoxide free radicals ($O_2^{-\bullet}$). We[2] reported the antioxidative action of rare earth complexes with β-diketoisonicotinoyl hydrazone in 1998. It has been shown that complexes of rare earth(III) cations and ligands have an enhancement or synergistic effect, and that the antioxidative action of the ligand and complexes containing ferrocenyl groups far exceeds other ligands and complexes. It is not known whether the antioxidative action is caused by the iron(II) cation or cyclopentadienyl ion. This mechanism has not been resolved. In this paper two new complexes of dicyclopentadienyl-titanium-(IV) diaspirin and dicylcopentadienyltitanium(IV) disalicylate have been synthesized, and their composition and structure have been studied by elemental analyses, XPS, IR and ^{1}H NMR. The formulas of the complexes were comfirmed as $(Cp)_2Ti(Asp)_2$ and $(Cp)_2Ti(Sal)_2$ [in which Cp = cyclopentadienyl ion (η^5-C_5H_5), Asp = anion of aspirin (acetylsalicylate ion), Sal = salicylate anion]. The IR and XPS data show that the carboxy oxygen atoms of Asp and Sal are coordinated to Ti(IV) in a monodentate manner. We also have determined the inhibition rates (Ih and Ih*) of seven compounds [$(Cp)_2Ti(Asp)_2$, $(Cp)_2Ti(Sal)_2$, $(Cp)_2TiCl_2$, HAsp, HSal, $Ti(OH)_2$-$(Asp)_2$ and $Ti(OH)_2(Sal)_2$ to superoxide free radicals ($O_2^{-\bullet}$) and hydroxyl free radicals ($OH^{\bullet}$). The experimental data indicated that the complexes of Sal or Asp and cyclopentadienyl ion have an "synergistic action" for the elimination of the above radicals.

EXPERIMENTAL

Reagents and Apparatus

Reduced coenzyme I (NADH), phenazine metasulfate (PMS), nitroblue tetrazolium (NBT) and methional (3-methionpropionaldehyde) were purchased from Sigma. Tris-HCl (0.01 mol/L, pH = 8.0) and NaH_2PO_4-Na_2HPO_4(0.01 mol/L, pH = 7.4) buffers were prepared with twice distilled water. Ascorbic acid, aspirin (2-acetoxybenzoic acid, HAsp or H_3CCO_2-C_6H_4COOH), salicylic acid (*o*-hydroxybenzoic acid, HSal or HOC_6H_4-COOH), NaAsp, NaSal, $TiCl_4$, $Ti(OH)_2SO_4$, EDTA, $FeSO_4$ *etc*. were of analytical grade. Benzene and petroleum ether (60–90 °C) were dried over anhydrous calcium chloride for 30 h and THF was dried with potassium hydroxide for 24 h. Then these compounds were refluxed with sodium sand

and diphenyl ketone (benzophenone) until the color stabilized. Triethylamine was distilled after drying for 24 h with potassium hydroxide. Dicyclopentadienyltitanium dichloride was synthesized according to the literature[3]. $Ti(OH)_2(Asp)_2$ or $Ti(OH)_2(Sal)_2$ were prepared by the reactions of $Ti(OH)_2SO_4$ with NaAsp or NaSal.

A Bruker AM-400 NMR spectrometer (using $CDCl_3$ as solvent and TMS as internal reference), a Nicolet 170SX IR spectrometer, 4000-200 cm^{-1} (using KBr pellets), a DDS-11A electric conductivity apparatus and 721 UV-Vis spectrophotometer were used. The experiments of XPS were performed in an ESCALAB 2201-XL X-ray photoelectron spectrometer using Al K_α radiation, with the pressure of the residual gases better than 5×10^{-10} Torr. The working power (P) of the X-ray gun was 300 W using the C_{1s} spectrum (284.60 eV) as internal reference. A GC-9A gas chromatograph with a Paropark Q chromatographic column (3 m × 3 mm) was used.

Syntheses of Complexes

In an anhydrous alcohol solution (200 mL) 0.05 mol aspirin (9 g) or salicylic acid (6.9 g) was reacted with 0.05 mol sodium (1.2 g) to form white NaAsp (or NaSal) as precipitate. The precipitate was filtered and dried in a vacuum desiccator over phosphorus pentoxide. Then 8 mmol NaAsp (1.62 g) or NaSal (1.28 g) were refluxed with 2 mmol $(Cp)_2TiCl_2$ (0.5 g) in 60 mL benzene for 15 h. After cooling to room temperature, the insoluble residue was filtered. The filtrate was evaporated under vacuum to 1/6 of its original volume. On adding 20 mL dried petroleum ether and placing the mixture in a refrigerator overnight, orange crystals were obtained. After filtration, the precipitates of $(Cp)_2Ti(Asp)_2$ [or $(Cp)_2Ti(Sal)_2$] were dried in a vacuum desiccator over phosphorus pentoxide for 30 h. The carbon, hydrogen, nitrogen and chlorine contents of the above compounds were determined by an Elementar Vario EL elemental analyser. Titanium was determined by a gravimetric method.

Elimination Effect to Biological Free Radicals ($O_2^{-\bullet}$ and $OH^\bullet$)

The inhibition rates (or elimination rates) of different compounds toward superoxide anion free radical ($O_2^{-\bullet}$) and hydroxyl free radical ($OH^\bullet$) were determined according to the literature[2,4,5].

The compounds $(Cp)_2Ti(Asp)_2$, $(Cp)_2Ti(Sal)_2$, HAsp, HSal, $Ti(OH)_2(Asp)_2$, $Ti(OH)_2(Sal)_2$ and $(Cp)_2TiCl_2$ were dissolved in acetone-DMF

(1:2 V/V) to give a respective solution Z of 0.5 mg/mL for determination. Where Z is a solution one of the aforesaid seven compounds.

$O_2^{-\bullet}$ released from the reaction of NADH and PMS can react quantitatively with NBT to give a blue solution, and the absorbance of the solution has a linear relationship with the concentration of $O_2^{-\bullet}$ in the range of $0-1 \times 10^{-4}$ mol/L, which can be used to detect $O_2^{-\bullet}$. The capability of a biological free radical scavenger on $O_2^{-\bullet}$ can be expressed by the inhibition rate, Ih,

$$\mathrm{Ih} = \frac{\mathrm{A}_0 - \mathrm{A}}{\mathrm{A}_0} \times 100\%$$

where A_0 is the absorbance of a blank solution and A is the absorbance of a solution containing a free radical scavenger at different doses.

NADH, PMS and NBT were dissolved in tris-HCl buffer, respectively, to give a solution of 3.0×10^{-5} mol/L for use. The solutions of NADH (1.0 mL), PMS (1.0 mL) and NBT (1.0 mL) were added to the solution of 0.00, 0.25, 0.50, 0.75, 1.00 ml of Z, respectively (doses of 0.000, 0.125, 0.250, 0.375, 0.500 mg, respectively). After diluting them to 5.0 mL with tris-HCl buffer and keeping them below $37 \pm 1\,^{\circ}\mathrm{C}$ for 5 min the absorbance of the solutions was determined at the wave length of 560 nm with a reference solution of acetone-DMF (1:2 V/V).

The hydroxyl radical $OH^{\bullet}$ generated by the reaction of H_2O_2 with ascorbic acid using Fe^{2+}-EDTA as catalyst reacts with methional to release ethylene that can be detected by gas chromatography. The inhibition rate Ih^* of a free radical scavenger may be calculated as follows

$$\mathrm{Ih}^* = \frac{\mathrm{a}_0 - \mathrm{a}}{\mathrm{a}_0} \times 100\%$$

where a_0 is the yield of ethylene without free radical scavenger and a is the yield of ethylene with free radical scavenger.

8.4 mg $FeSO_4 \cdot 7H_2O$ (3 mmol) and an equimolar (11.1 mg) quantity of EDTA disodium ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$) were dissolved in 1000 mL NaH_2PO_4-Na_2HPO_4 buffer to give a solution of 3.0×10^{-5} mol/L. Methional and ascorbic acid were dissolved in this buffer solution, respectively, to give a 3.0×10^{-5} mol/L solution for use. The solutions of Fe^{2+}-EDTA (1.0 mL), methional (1.0 mL) and ascorbic acid (2.0 mL) were added to the solution of 0.00, 0.25, 0.50, 0.75, 1.00 mL of Z, respectively (doses of 0.000, 0.125, 0.250, 0.375, 0.500 mg, respectively). After diluting them to 5.0 mL with NaH_2PO_4-Na_2HPO_4 buffer, and keeping them below $37 \pm 1\,^{\circ}\mathrm{C}$ for 30 min the yields of ethylene were determined by gas chromatography.

RESULTS AND DISCUSSION

Properties and Composition of the Complexes

Elemental analyses, molar conductances (Λ_M, 1.0×10^{-4} mol/L in acetone, 10 °C), melting points *etc*. of the complexes are presented in Table I.

The chemical compositions of the complexes examined by elemental analyses correspond to the calculated values. The low conductance of the two complexes indicate that they are non-electrolytes. They are soluble in acetone, benzene, chloroform and THF, but insoluble in water, petroleum ether and diethyl ether. In acetone/benzene (1:1) the complexes were eluted on GF254 silica gel. The R_f (relative band speed) values are also presented in Table I. The Λ_M values of the two complexes are higher, and the R_f values are lower than those of $(Cp)_2TiCl_2$, which showed that their polarities are higher than that of $(Cp)_2TiCl_2$.

IR Spectra

The characteristic IR absorption peaks of the complexes and ligands are listed in Table II. In the complexes the stretching vibration band $\nu(C=O)$ (1700, 1670 cm^{-1}) ascribed to the carboxylic groups (COOH) of HAsp and HSal has disappeared, and the characteristic absorption band of the carboxylate group has appeared. The differences Δ of the unsymmetrical stretching vibration bands, ν_{as} (1636, 1600 cm^{-1}), and the symmetrical vibration bands, ν_s (1340, 1342 cm^{-1}), are 296 and 258 cm^{-1}, respectively, which indicate that the oxygen atoms of the carboxylate groups are coordinated to Ti(IV) in a monodentate manner[6]. The absorption bands of ν(O-H) of HSal and its complex are seen at 2500–3200 and 2600–3300 cm^{-1}, which show that the oxygen atom of the carboxy group forms an intramolecular hydrogen bond with the *o*-hydroxyl group. However, HAsp and its complex do not show the above absorption band. Compared to $(Cp)_2TiCl_2$, the characteristic absorption band of the cyclopentadienyl ion (η^5-C_5H_5) in the complexes shifts to higher wave numbers; the characteristic band of ν(Ti-O) appeared and the absorption band of ν(Ti-Cl) of $(Cp)_2TiCl_2$ disappeared which indicated still further that Asp or Sal take part in the coordination to the Ti(IV) ion.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligand and complex are listed in Table III. The integrated areas of the various protons correspond to the proton

Table I. Elemental Analyses and Physical Properties of the Complexes

Compound	M.W.	M.p. (°C)	Color	Found (Calcd) C	H	Ti	Λ_M $s \cdot cm^2 \cdot mol^{-1}$	R_f	Yield %
$(Cp)_2Ti(Asp)_2$	536.36	139–142	orange	62.86	4.57	9.06	3.61	0.31	78
$TiC_{28}H_{24}O_8$				(62.70)	(4.51)	(8.92)			
$(Cp)_2Ti(Sal)_2$	452.29	148–150	orange	63.56	4.41	10.60	5.24	0.51	80
$TiC_{24}H_{20}O_6$				(63.73)	(4.46)	(10.58)			
$(Cp)_2TiCl_2$	248.96	285	red	48.41	4.04	19.18	0.27	0.89	64
$TiC_{10}H_{10}Cl_2$				(48.24)	(4.05)	(19.23)			
$Ti(OH)_2(Asp)_2$	440.20	—	white	49.21	3.70	10.79	—	—	92
$TiC_{18}H_{16}O_{10}$				(49.11)	(3.66)	(10.87)			
$Ti(OH)_2(Sal)_2$	356.12	—	white	47.29	3.37	13.38	—	—	88
$TiC_{14}H_{12}O_8$				(47.22)	(3.40)	(13.44)			

Table II. Significant IR Bands of the Ligands and the Complexes (cm^{-1})[a]

Compound	-COO^-			η^5-C_5H_5			ν(O-H)	ν(COOH)	ν(Ti-Cl) ν(Ti-O)
	ν_{as}	ν_s	$\Delta\nu$	ν(C-H)	ν(C=C)	δ(C-H)			
$(Cp)_2Ti(Asp)_2$	1600 m	1342 m	258	3060 m	1457 m	1031 m 835 s	—	—	— 585 w
Hasp	—	—	—	—	—	—	—	1700 s	—
$(Cp)_2Ti(Sal)_2$	1636 m	1340 m	296	3090 m	1446 m	1018 m 829 s	2600–3300 b, s	—	— 596 w
Hsal	—	—	—	—	—	—	2500–3200 b, s	1670 s	—
$(Cp)_2TiCl_2$	—	—	—	3100 m	1440 m	1019 m 819 s	—	—	368 w
$Ti(OH)_2(Asp)_2$	1616 m	1326 m	290	—	—	—	3640–3540 b	—	−988, 940 w
$Ti(OH)_2(Sal)_2$	1621 m	1335 m	286	—	—	—	3640–3540 b	—	−1004, 942, 930 w

[a]s: strong, m: medium, w: weak, b: broad.

Table III. ^{1}H NMR Chemical Shifts (δ, ppm)

Compound	η^5-C_5H_5	C_6H_4	H_3CCO_2	OH
$(Cp)_2Ti(Asp)_2$	6.68 (s, 10H)	6.8–8.0 (m, 8H)	1.25 (s, 6H)	—
Hasp	—	7.0–8.5 (m, 4H)	2.35 (s, 3H)	—
$(Cp)_2Ti(Sal)_2$	6.67 (s, 10H)	6.8–8.0 (m, 8H)	—	11.92 (s, 2H)
Hsal	—	7.0–8.5 (m, 4H)	—	—
$(Cp)_2TiCl_2$	6.60 (s, 10H)	—	—	—

numbers in the structure of the complexes. The NMR signals of the substituted benzene ring (-C_6H_4) and acetyl group ($OCCH_3$) at 7.0–8.5 ppm and 2.35 ppm move to higher field at 6.8–8.0 ppm and 1.25 ppm, respectively. The NMR signals of the cyclopentadienyl protons (η^5-C_5H_5) move slightly to lower field and the NMR signals of the carboxy group disappear which verifies that the ligand coordinates to the metal cation in forming the complex. The structures of the complexes are shown in Fig. 1.

XPS Spectra[7]

To obtain further insight into the nature of bonding, the XPS spectra of the complexes were measured at room temperature. It was found that the data of atomic molar percent of the complexes are very close to those of the elemental analyses given above. The electron binding energy (BE) data of C_{1s} and O_{1s} for the complexes are listed in Table IV.

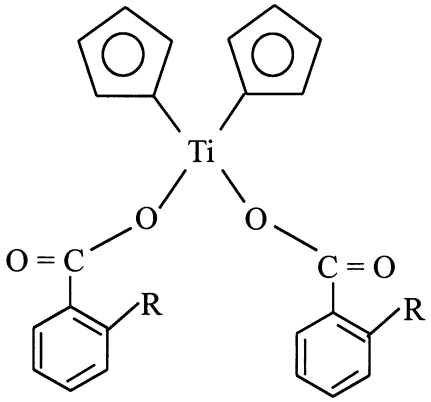

Figure 1. Suggested structure of the complexes (R = OH or $OOCCH_3$).

Table IV. XPS Spectra Data of the Complexes (eV)

Compound	A%[a]	Binding Energy (BE) (peak area)					
	C/O/Ti	C_{1s}^A	C_{1s}^B	C_{1s}^C	C_{1s}^D	O_{1s}^A	O_{1s}^B
$(Cp)_2Ti(Sal)_2$	24.2/5.8/1	283.02 (10.35)	287.97 (1.22)			531.24 (22.95)	533.50 (12.12)
$(Cp)_2Ti(Asp)_2$	28.4/8.1/1	283.12 (21.68)	289.22 (2.09)	287.24 (2.19)	286.30 (2.11)	531.33 (26.48)	527.66 (27.02)

[a]Atomic molar ratio in the complexes.

In $(Cp)_2Ti(Sal)_2$, the O_{1s} electron spectra are asymmetric and their deconvolution yields two components (O_{1s}^A and O_{1s}^B) which revealed the chemical shifts for oxygen. The weak intense component (O_{1s}^A) with the lower BE at 531.24 eV remains almost unchanged and belongs to the oxygen of the carbonyl (-COO^-) group. The strong intense component (O_{1s}^B) with the higher BE (533.50 eV) value belongs to the oxygen of the hydroxy group (-OH). The assignment is supported not only by IR spectra but also by their peak area ratio 22.95/12.12 (O_{1s}^A/O_{1s}^B), which is close to the atomic ratio (2/1) of two different types of oxygens in $(Cp)_2Ti(Sal)_2$ (Fig. 2). The same reason explains the different values for $(Cp)_2Ti(Asp)_2$. In $(Cp)_2Ti(Asp)_2$, the weak intensity component (O_{1s}^A) with the higher BE at 531.33 eV is assigned to the oxygen of the carbonyl (-COO^-) group and the strong intensity one ((O_{1s}^B) with the lower BE (527.66 eV) value is assigned to the oxygen of the acetyl group (-$OOCCH_3$). Their peak area ratio (O_{1s}^A/O_{1s}^B) is 26.48/27.02 which is also close to the atomic ratio (1/1) of two types of oxygens in $(Cp)_2Ti(Asp)_2$.

C_{1s} in $(Cp)_2Ti(Sal)_2$ is split into two peaks (C_{1s}^A and C_{1s}^B). C_{1s}^A belongs to the carbons of the cyclopentadieny radical (-C_5H_5) and benzene ring

$$(Cp)_2Ti(Sal)_2: \quad (C_5H_5)_2Ti(O_2\text{–}C\text{–}C_6H_4\text{–}OH)_2$$

$$C_{1s}^A \qquad O_{1s}^A\, C_{1s}^B\, C_{1s}^A \qquad O_{1s}^B$$

$$(Cp)_2Ti(Asp)_2: \quad (C_5H_5)_2Ti(O_2\text{–}C\text{–}\,C_6H_4\,\text{–}O_2\text{–}\,C\text{–}\,CH_3)_2$$

$$C_{1s}^A \qquad O_{1s}^A\, C_{1s}^B\, C_{1s}^A \qquad O_{1s}^B\;\; C_{1s}^C\, C_{1s}^D$$

Figure 2. Schematic representation of assignment of C_{1s} and O_{1s} for the complexes.

($-C_6H_4$), and C_{1s}^B is assigned to the carbons of carbonyl ($-COO^-$). The assignment is verified by their peak area ratio 10.35/1.22 (C_{1s}^A/C_{1s}^B) which is consistent with the atomic ratio (11/1) of two types of carbons in the complex. Unlike $(Cp)_2Ti(Sal)_2$, C_{1s} in $(Cp)_2Ti(Asp)_2$ is split into four peaks with the peak area ratios being 21.68/2.09/2.19/2.11 ($C_{1s}^A/C_{1s}^B/C_{1s}^C/C_{1s}^D$). The ratio is identical to the atomic ratio (11/1/1/1) of four types of carbons. C_{1s}^A, C_{1s}^B, C_{1s}^C and C_{1s}^D are assigned to the carbon of the cyclopentadieny radical ($-C_5H_5$) and benzene ring ($-C_6H_4$), carbonyl ($-COO^-$), acetyl group ($-OOCCH_3$) and methyl group ($-CH_3$), respectively[7].

Elimination of $O_2^{-\bullet}$ and $OH^\bullet$

The inhibition rates Ih (%) and Ih^* (%) of the ligand and the complex to superoxide free radicals ($O_2^{-\bullet}$) and hydroxyl free radicals ($OH^\bullet$) are presented in Table V. These data reveal that the inhibition rates of HAsp (or HSal) and $Ti(OH)_2(Asp)_2$ [or $Ti(OH)_2(Sal)_2$] to superoxide anion free radicals ($O_2^{-\bullet}$) and hydroxyl free radicals ($OH^\bullet$) are close, but the elimination actions of $(Cp)_2Ti(Asp)_2$ [or $(Cp)_2Ti(Sal)_2$] are greater than those of the corresponding ligands and compounds such as $(Cp)_2TiCl_2$, HAsp (or HSal), $Ti(OH)_2(Asp)_2$ [or $Ti(OH)_2(Sal)_2$] *etc*. It is shown that Ti(IV) does not produce an enhancement action to Asp or Sal, however, after formation of complexes with Sal (or Asp), larger inhibition rates are seen. It is possible that the ''synergistic action'' was produced by the mixed ligands (Cp and

Table V. Inhibition Rate of Seven Compounds to $O_2^{-\bullet}$ and $OH^\bullet$ Radicals (%)

	Ih (%)[a]					Ih^*(%)[b]				
	Dose/mg					Dose/mg				
Compounds	0.00	0.125	0.25	0.375	0.50	0.00	0.125	0.25	0.375	0.50
$(Cp)_2Ti(Asp)_2$	0	2.24	11.48	22.88	24.76	0	38.84	43.55	48.87	55.24
HAsp	0	2.12	10.60	18.05	21.45	0	38.26	41.11	45.45	52.20
$Ti(OH)_2(Asp)_2$	0	2.02	11.87	17.65	19.94	0	34.90	40.08	43.19	50.68
$(Cp)_2Ti(Sal)_2$	0	6.45	23.64	38.22	42.76	0	58.77	70.32	77.87	81.34
HSal	0	6.66	22.13	33.35	37.62	0	56.80	67.65	73.82	78.14
$Ti(OH)_2(Sal)_2$	0	6.21	21.53	31.78	33.23	0	54.11	63.55	67.60	71.08
$(Cp)_2TiCl_2$	0	7.13	17.88	24.67	29.81	0	31.32	34.65	41.76	50.58

[a]Ih (%): Inhibition rate of $O_2^{-\bullet}$ radical (%), $p < 0.05$, $p =$ probability of null hypothesis.

[b]Ih^* (%): Inhibition rate of $OH^\bullet$ radical (%), $p < 0.05$.

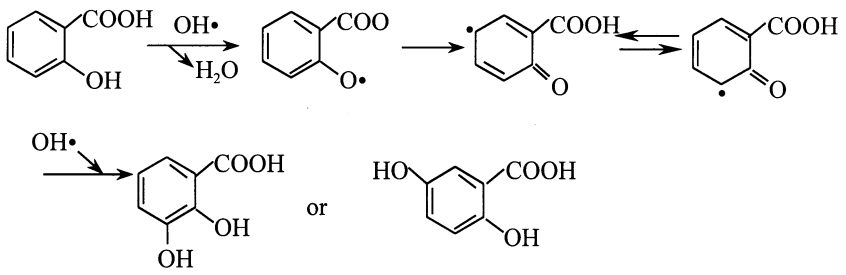

Figure 3. Reaction mechanism of elimination of hydroxyl free radical ($OH^{\bullet}$) by salicylic acid.

Asp or Sal). From the data in Table V it is indicated that the elimination capabilities of the compounds containing phenolic hydroxyl groups, such as $(Cp)_2Ti(Sal)_2$, $Ti(OH)_2(Sal)_2$, HSal *etc.* are all higher than those of compounds without phenolic hydroxyl groups such as $(Cp)_2Ti(Asp)_2$, $Ti(OH)_2(Asp)_2$ and HAsp. In fact, the reaction mechanism of the phenolic hydroxyl group to eliminate hydroxyl free radicals is probably that the hydrogen atom of the phenolic hydroxyl group of salicylic acid is substituted by a hydroxyl free radical to form a free radical at the benzene ring, which then forms dihydroxy benzoic acid with a hydroxyl free radical again[1]. The reactions are shown in Fig. 3.

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