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Kinetics and Mechanism of Hexachloroplatinate(IV) Reduction by Some Neutralized α-Hydroxy Acids in a Carbonate–Hydrogencarbonate Buffer Medium

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The kinetics of hexachloroplatinate(IV) reduction by some neutralized α-hydroxy acids such as glycolic, lactic, α-hydroxyisobutyric, mandelic, atrolactic, and benzilic acids in a carbonate-hydrogencarbonate buffer medium have been investigated. Platinum(IV) is reduced by the substrates to platinum(II) in a one-step two-electron process, whereas the substrates are oxidized to give formaldehyde, acetaldehyde, acetone, benzaldehyde, acetophenone, and benzophenone for the respective reactions. The pseudo-first-order rate constant is independent of the initial [platinum(IV)] as well as [OH$^-$]. The reaction rate increases with increasing [substrate], but decreases with increasing chloride concentration. The reactions obey the following rate expression:

$$-\mathrm{d}[\mathrm{Pt^{IV}}]_t/\mathrm{d}t = \frac{kK_e[\mathrm{A^-}][\mathrm{Pt^{IV}}]_t}{[\mathrm{Cl^-}]+K_e[\mathrm{A^-}]}. \tag{1}$$

The reactions proceed through an initial 1 : 1 complex formation between the reactants, followed by decomposition of the complex to give the respective reaction products via C–C bond cleavage. The reactivity of the α-hydroxycarboxylate towards Pt(IV) are as follows: atrolactic acid > mandelic acid > benzilic acid > α-hydroxyisobutyric acid > lactic acid > glycolic acid. Thermodynamic parameters for the decomposition step have been evaluated. The mechanism of the reactions is discussed.

The use of hydroxy acids in analytical chemistry is very common, their action as masking agents having been reviewed.[1] The pharmacological action of some hydroxy acids is associated with the coordination of these compounds to metal ion.[2] The kinetics of the oxidation of some α-hydroxy acids by a number of oxidants have been investigated[3] in an acid medium. The kinetics of the oxidation of α-hydroxy carboxylate by platinum(IV) has not been reported, although the kinetics of the oxidation of some organic[4] and inorganic compounds[5,6] by platinum(IV) have been studied. The reduction of the platinum(IV) complex can be carried out with outer-sphere as well as inner-sphere monoelectronic reductants. A possible first example of this outer-sphere pathway is in the reduction of platinum(IV) complex by $[\mathrm{Cr(bipy)_3}]^{2+}$.[7] Other examples are the reduction of $[\mathrm{PtCl_6}]^{2-}$ by $\mathrm{V^{II}}$,[8] of $[\mathrm{PtCl_2(pn)_2}]^{2+}$ by $\mathrm{Eu^{2+}}$,[9] of $[\mathrm{PtCl_6}]^{2-}$ by $\mathrm{Sn^{II}}$ and $\mathrm{Cu^{I}}$,[10] and of $[\mathrm{PtCl_4L_2}]$ [L = tertiary phosphine] by $\mathrm{Ir^{I}}$.[11] These reactions occur by a second-order rate law, first order in both the platinum(IV) complex and the reductant. However, very little work has been done on the oxidation of organic compounds by platinum(IV). The present report deals with the kinetics and mechanism of hexachloroplatinate(IV) reduction by some neutralized α-hydroxy acids in a carbonate–hydrogencarbonate buffer medium under different experimental conditions.

Experimental

Materials. Glycolic (E. Merck), lactic (E. Merck), α-hydroxyisobutyric (Fluka), mandelic (BDH), atrolactic (Aldrich Chem), and benzilic (E. Merck) acids were used without further purification, and their neutral salts were prepared by the addition of the requisite amount of NaOH. α-Deuteriomandelic acid was prepared following a procedure of Kemp and Waters[12] by equilibriating three times of sodium mandelate in a sealed tube at 150 °C for 7 d with sodium hydroxide (5%) in deuterium oxide (99.8%). Labile hydrogen was then removed by recrystallizing the free acid twice from water (mp 121°). Reagent-grade sodium hexachloroplatinate (Johnson–Matthey, London) was used as supplied. The platinum(IV) content of the salt was determined by an iodometric method.[13]

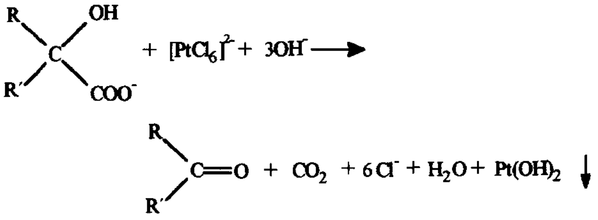
Inorganic materials were of the highest available purity. All solutions were made in doubly distilled water. Buffer solutions were prepared from a standard solution of sodium carbonate and sodium hydrogencarbonate. The pH of the solution was checked against the standard buffer solution with a pH meter.

Instrumentation. Spectral measurements were recorded in the UV-vis region using a Systronics (India) spectrphotometer. IR spectra were recorded on KBr discs using a Perkin–Elmer 783 ratio-recording infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz). A thermogravimetric analysis was performed in a Shimadzu Corporation (Japan) TG 50 instrument at a normal atmospheric environment by heating a sample (21.39 mg) at a rate of 15 °C min^{-1} up to 200 °C. The pH of the solution was measured at room temperature (ca. 25 °C) using an Elico, India (LI 120) pH meter calibrated against standard pH solutions. Mp determinations were carried out using a Gallen Kamp apparatus.

Kinetic Measurements. The reaction rate was determined spectrophotometrically using a carbonate–hydrogencarbonate buffer solution under the condition where [α-hydroxy carboxylate] $\gg$ [Pt^{IV}]. The absorption spectra of chloroplatinate solutions were recorded in the pH range 4—11.2. The compound has a maximum absorbance[14] at 261 nm in the pH range 4—6; when the solution is made slightly alkaline, the absorption maximum is shifted to 255 nm. It is already known[15] that $[PtCl_6]^{2-}$ is decomposed by light. It has been further recognised that the light from an unfiltered Hg lamp or UV light causes an aquation reaction as well as the hydrolysis of $[PtCl_6]^{2-}$. Consequently, in order to minimize the aquation and hydrolysis of $[PtCl_6]^{2-}$, rate measurements were carried out at a higher wavelength, namely 400 nm, in the concentration range $(1—10)\times10^{-3}$ mol dm^{-3}, where Beer's law is also valid. All of the kinetic investigations were carried out in a Systronics (India) UV-visible spectrophotometer using a thermostatted cell of 1 cm path length. The water was circulated from a bath maintained at the required temperature (±0.1 °C). At least 8—10 experimental readings were taken, depending upon the temperature of the experiment. The pseudo-first-order rate constants (k_{obsd}) were determined from the linear plots of $\log A$ (A = absorbance) against time, and the linearity was observed up to two half-lives. The k_{obsd} values were reproducible to within ±4%.

Stoichiometry. Reaction mixtures containing a known excess of [Pt^{IV}] over [α-hydroxy carboxylate] at fixed [OH^-] were made. After completion of the reactions the unreacted platinum(IV) was determined by the method mentioned above, showing that one mole of α-hydroxycarboxylate consumed one mole of Pt^{IV}. The reaction stoichiometry may be expressed as [α-hydroxy carboxylate] : [Pt^{IV}] = 1 : 1.

Product Analysis. A product analysis of the oxidations of α-hydroxy carboxylate by hexachloroplatinate(IV) was carried out with the reaction mixture: [α-hydroxy carboxylate] = 20×10^{-2} mol dm^{-3}, [Pt^{IV}] = 2×10^{-3} mol dm^{-3} and pH = 10. The reaction mixture (30 ml) for each substrate was kept at 30 °C for 120 min in a stoppered bottle, since the bp's of formaldehyde and acetaldehyde are low. It was then filtered to remove black ppt, which formed in the reaction mixture. In one part of the filtrate the oxidation products were tested by the formation of colors with different reagents, given in Table 1.[16—18] The other part of the filtrate was acidified with dilute H_2SO_4 and added to 2,4-dinitrophenylhydrazine hydrochloride solution, heated on a steam bath for 15 mins and left at room temperature for an hour when yellow crystals of 2,4-dinitrophenylhydrazone derivative of the product were obtained. The crystals were collected by filtration, washed with water and dried. The crude derivatives were chromatographed over neutral alumina (Brockman) and eluted with dry benzene. Thus obtained purified 2,4-DNP derivatives were crystallized from ethanol, filtered and dried to record the yield and mp of the samples. The melting points were checked against the literature values.[19] The results are furnished in Table 2. ^1H and ^{13}C NMR of the oxidation product of mandelic acid in $CDCl_3$ showed the –CHO proton peak at 10.05 and 192.4 ppm, respectively. These values are close to the literature values[20] of 9.98 and 192 ppm reported for the –CHO proton of benzaldehyde. The oxidations occur according to the equation.



(2)

where, R = R′ = –H for glycolic acid; R = –Me, R′ = –H for lactic acid; R = R′ = –Me for α-hydroxy isobutyric acid; R = –Ph, R′ = –H for mandelic acid; R = –Ph, R′ = –Me for atrolactic acid; R = R′ = –Ph for benzilic acid.

The black product obtained in the oxidations by platinum(IV) was hydrated PtO, as indicated by thermogravimetric and IR spectral analyses. There is also literature evidence[21] to indicate that platinum(II) oxide exists as $Pt(OH)_2$. This is supported by a thermogravimetric analysis of the solid product, which indicates that a loss of water takes place in one step. A weight-loss calculation based on $Pt(OH)_2$ confirmed the loss of only one water molecule. The IR spectrum of the thermogravimetric residue identified it as PtO by the presence of ν(Pt–O) at around 570 cm^{-1} and the absence of ν(O–H) in the 3600—3400 cm^{-1} region. The IR spectrum of an authentic sample of PtO was compared with that of the PtO obtained as a reaction product.

Table 1. Identification of Products of Reactions

Substrate	Product	Test	Color	% yield (2,4-DNP derivative)	Mp (°C) of 2,4-DNP derivative	Lit, mp (°C)[19] of 2,4-DNP derivative
Glycolic acid	CH_2O	Chromotropic acid and concd H_2SO_4	Pinkish violet[16]	87	164—165	166—167
Lactic acid	MeCHO	Equal volumes of 20% piperidine and 5% sodium nitroprusside	Blue[17]	88	146—147	148
α-Hydroxy-isobutyric acid	Me_2CO	Equal volumes of 5% sodium nitroprusside and 30% NaOH	Red[18]	82	125—126	126—128
Mandelic acid	PhCHO	—	—	95	236—237	235—237
Atrolactic acid	$PhCOCH_3$	—	—	83	238—239	238—240
Benzilic acid	Ph_2CO	—	—	88	237—238	238—239

Table 2. Variation of Pseudo-First-Order Rate Constants for the Oxidation of Substrates by Pt^{IV} at Different Temperatures $[Pt^{IV}] = 2\times10^{-3}$ mol dm^{-3}, pH = 10.0, $[Cl^-] = 2.8\times10^{-2}$ mol dm^{-3}

Temp/K	$[S]/10^{-1}$ mol dm^{-3}	$k_{obsd}{}^{a)}/10^{-3}$ s^{-1}	$k_{obsd}{}^{b)}/10^{-3}$ s^{-1}	$k_{obsd}{}^{c)}/10^{-3}$ s^{-1}	$k_{obsd}{}^{d)}/10^{-3}$ s^{-1}	$k_{obsd}{}^{e)}/10^{-3}$ s^{-1}	$k_{obsd}{}^{f)}/10^{-3}$ s^{-1}
298	1.5	0.149	0.167	0.183	0.234	0.258	0.203
	2.0	0.182	0.208	0.231	0.30	0.329	0.256
	3.0	0.25	0.288	0.316	0.422	0.468	0.357
	5.0	0.326	0.384	0.436	0.616	0.671	0.500
	6.0	0.371	0.441	0.483	0.682	0.769	0.568
	8.0	0.422	0.51	0.566	0.777	0.92	0.652
303	1.5	0.195	0.263	0.289	0.358	0.394	0.319
	2.0	0.241	0.326	0.366	0.454	0.508	0.405
	3.0	0.322	0.443	0.484	0.612	0.697	0.555
	5.0	0.448	0.62	0.667	0.857	1.06	0.789
	6.0	0.484	0.666	0.750	1.0	1.14	0.882
	8.0	0.555	0.75	0.858	1.15	1.30	1.040
308	1.5	0.288	0.349	0.405	0.538	0.577	0.493
	2.0	0.357	0.435	0.508	0.691	0.732	0.626
	3.0	0.469	0.577	0.671	0.968	1.03	0.833
	5.0	0.625	0.751	0.915	1.38	1.50	1.15
	6.0	0.697	0.882	1.04	1.50	1.66	1.30
	8.0	0.789	0.967	1.16	1.76	2.14	1.57
313	1.5	0.389	0.492	0.536	0.856	0.939	0.638
	2.0	0.485	0.60	0.684	1.07	1.20	0.812
	3.0	0.652	0.810	0.937	1.50	1.68	1.170
	5.0	0.857	1.12	1.24	1.88	2.32	1.530
	6.0	0.909	1.25	1.43	2.15	2.73	1.650
	8.0	1.03	1.36	1.59	2.50	3.33	2.020
318	1.5	0.526	0.682	0.75	1.52	1.64	1.06
	2.0	0.638	0.857	0.912	1.87	2.02	1.32
	3.0	0.833	1.15	1.26	2.52	2.72	1.76
	5.0	1.11	1.43	1.66	3.03	3.34	2.32
	6.0	1.20	1.58	1.87	3.75	4.28	2.72
	8.0	1.36	1.76	2.14	5.00	6.05	3.35

a) Glycolic acid, b) Lactic acid, c) α-Hydroxyisobutyric acid, d) Mandelic acid, e) Atrolactic acid, f) Benzilic acid.

Test for Free Radicals. Acrylonitrile [50% (v/v)] was added to the reaction mixture during the course of the reactions. No precipitation of white polyacrylonitrile in the absence or presence of methanol was formed (during the oxidation of α-hydroxy carboxylate by Pt^{IV}). The result is in conformity with a one-step, two-electron transfer process with no free radical intermediate.

Results and Discussion

Effect of Reactant Concentrations. The pseudo-first-order rate constants were determined at different concentrations of $[Pt^{IV}]$ in the range $(1—5)\times10^{-3}$ mol dm^{-3}, but at constant [α-hydroxy carboxylate], $[Cl^-]$, pH and temperature of 5×10^{-1}, 2.8×10^{-2} mol dm^{-3}, 10.0 and 298 K, respectively. The pseudo-first-order rate constant was found to be independent of the initial $[Pt^{IV}]$ in each case. The reactions were also studied at different [α-hydroxy carboxylate], but at constant $[Pt^{IV}]$, $[Cl^-]$, pH and temperature. The results indicate that the rate increases with increasing [α-hydroxy carboxylate] (Table 2). Plots of $1/k_{obsd}$ versus 1/[α-hydroxy carboxylate] gave straight lines with positive intercepts on the Y-axis at five different temperatures.

Effect of pH. The oxidations of [α-hydroxy carboxylate] were studied in an alkaline medium of pH ranging from 9.2—10.7, but at constant [α-hydroxy carboxylate], $[Pt^{IV}]$, $[Cl^-]$, ionic strength and temperature of 5×10^{-1}, 2×10^{-3}, 2.8×10^{-2}, 0.62 mol dm^{-3} and 298 K, respectively. The rate of the reaction remained unaffected at different hydroxide ion concentrations.

Effect of $[Cl^-]$. The reactions were carried out at 298 K, but at different $[Cl^-]$, $[(1—8)\times10^{-2}$ mol dm$^{-3}]$ varied by the addition of NaCl, but at constant $[Pt^{IV}]$, [α-hydroxy carboxylate], ionic strength and pH of 2×10^{-3}, 5×10^{-1}, 0.6 mol dm^{-3}, and 10.0. The value of k_{obsd} was found to decrease along with an increase of $[Cl^-]$. The plot of $1/k_{obsd}$ against $[Cl^-]$ is linear with a positive slope and positive intercept on the ordinate (Fig. 1). The observation that Cl^- inhibits the rate is in keeping with step (7) of the suggested mechanism.

Effect of Ionic Strength. The reactions were studied at different ionic strengths maintained by the addition of $NaClO_4$ $[(0.5—3)\times10^{-1}$ mol dm$^{-3}]$, but at constant $[Pt^{IV}]$, [α-hydroxy carboxylate], $[Cl^-]$, pH and temperature of 2×10^{-3}, 1.5×10^{-1}, 2.8×10^{-2} mol dm^{-3}, 10.0 and 298 K,

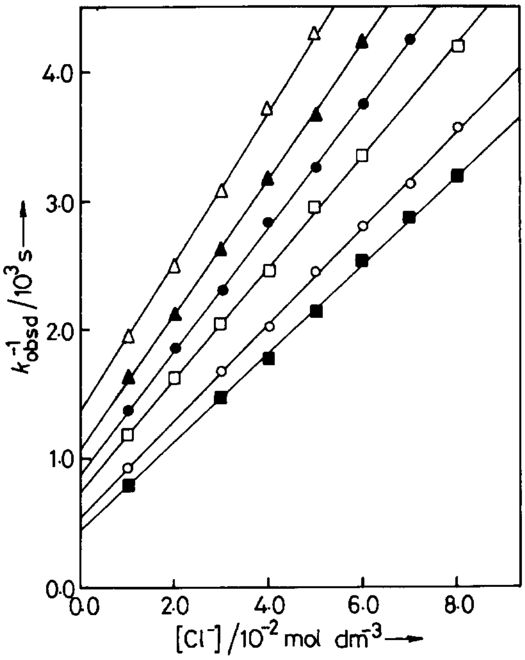


Fig. 1. Variation of pseudo-first-order rate constant with chloride ion concentration. Plots of k_{obsd}^{-1} versus $[Cl^-]$ for different substrates at 298 K. $[Pt^{IV}] = 2.\times10^{-3}$ mol dm^{-3}, [α-hydroxy carboxylate] $= 5\times10^{-1}$ mol dm^{-3} pH = 10.0, $\mu = 0.6$ mol dm^{-3}.
(△ = glycolic; ▲ = lactic; ● = α-hydroxyisobutyric; □ = benzilic; ○ = mandelic; ■ = atrolactic)

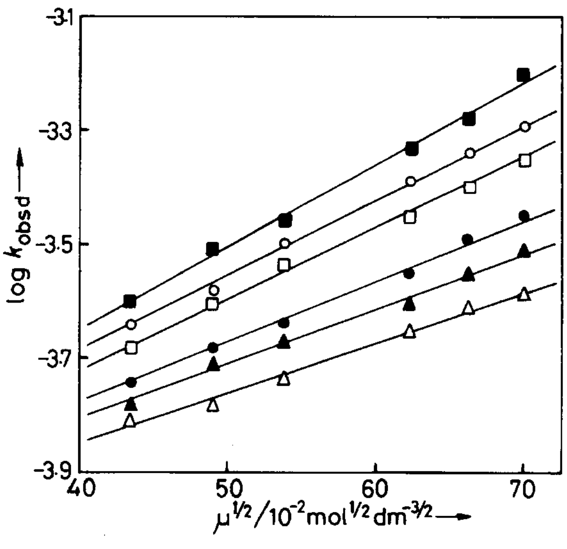


Fig. 2. Variation of pseudo-first-order rate constant with ionic strength. Plots of log k_{obsd} versus $\sqrt{\mu}$ for different substrates at $[Pt^{IV}] = 2\times10^{-3}$ mol dm^{-3}, [substrate] $= 1.5\times10^{-1}$ mol dm^{-3}, pH = 10.0, $[Cl^-] = 2.8\times10^{-2}$ mol dm^{-3}.
(△ = glycolic; ▲ = lactic; ● = α-hydroxyisobutyric; □ = benzilic; ○ = mandelic; ■ = atrolactic)

respectively. The pseudo-first-order rate constant increases along with an increase in salt concentrations (Fig. 2). This observation is to be expected if the reactions occur between ions of like charge.[22a]

Effect of Solvent. The influence of the solvent composition on the rate of oxidation of the mandelate ion was investigated at a constant temperature of 303 K. The concentrations of mandelate ion, chloride ion, ionic strength and pH are 3×10^{-1}, 2.8×10^{-2}, 0.4 mol dm^{-3} and 10.0, respectively. The solvent composition was varied by the addition of dioxane. The dielectric constant (ϵ) of the mixture was taken from the work of Akerlof and Short.[23] The values of k_{obsd} are 6.24×10^{-4}, 5.81×10^{-4}, 5.23×10^{-4}, 4.70×10^{-4}, and 3.85×10^{-4} s^{-1} at solvent composition of 0, 10, 20, 30, and 40% (V/V) corresponding to dielectric constant 76.7, 67.7, 58.5, 49.5, and 40.5, respectively. The results indicate that an increase in the dioxane concentration has a considerable retarding influence.

Activation Parameters. The empirical rate law is already shown in Eq. 1, where K_e and k denote the equilibrium constant for the formation of a 1 : 1 complex between the reactants and the disproportionation constant of this complex respectively. The values of K_e associated with step (7) and k associated with step (8) were then calculated from plots of the substrate effect. The results are given in Table 5. Plots of $\log K_e$ versus $1/T$ (Fig. 3) are linear and the enthalpy change (ΔH°) associated with the equilibrium step was calculated followed by the estimation of ΔS° from

$$\log K_e = [\Delta S^\circ - (\Delta H^\circ/T)]/2.303R. \tag{3}$$

Plots of $\log(k/T)$ versus $1/T$ (Fig. 4) are also linear. The values of $\Delta H^{\neq}$ were calculated from the respective slopes using the following relation, where R, N, and h have their usual significances:

$$k = \frac{RT}{Nh} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/R}. \tag{4}$$

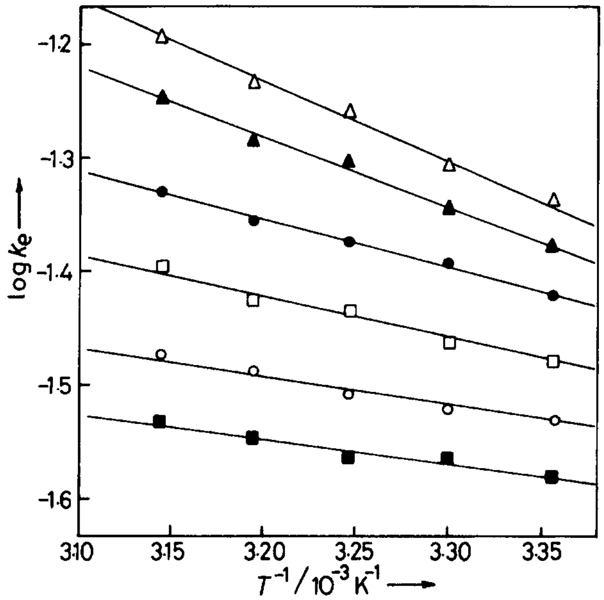


Fig. 3. Variation of equilibrium constant (K_e) with temperature. Plots of log K_e versus T^{-1}.
(△ = glycolic; ▲ = lactic; ● = α-hydroxyisobutyric; □ = benzilic; ○ = mandelic; ■ = atrolactic)

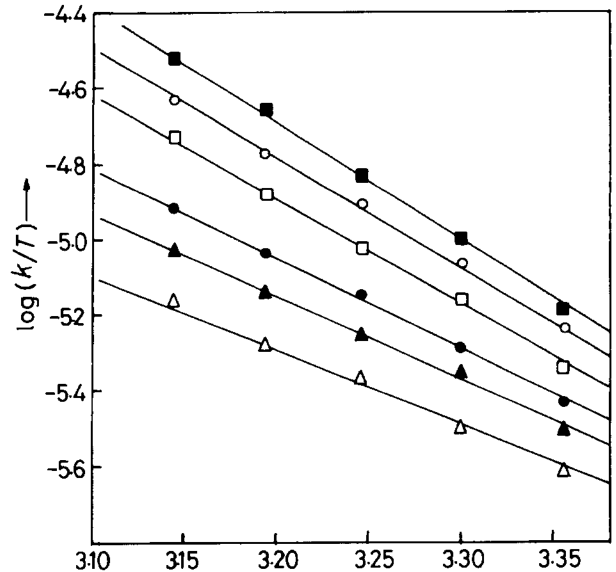


Fig. 4. Variation of disproportionation constant (k) with temperature. Plots of log (k/T) versus T^{-1}.
(△ = glycolic; ▲ = lactic; ● = α-hydroxyisobutyric; □ = benzilic; ○ = mandelic; ■ = atrolactic)

The thermodynamic parameters associated with the equilibrium step and the activation parameters associated with the rate determining step are recorded in Table 4. The fairly large and negative $\Delta S^{\neq}$ values may indicate a cyclic complex. However, for ions of the same sign the transition state will be a more highly charged ion, which would be expected to be strongly solvated so that more solvent molecules might be required than for the separate ions. This, would lead to a decrease in entropy in forming the transition state.[22b]

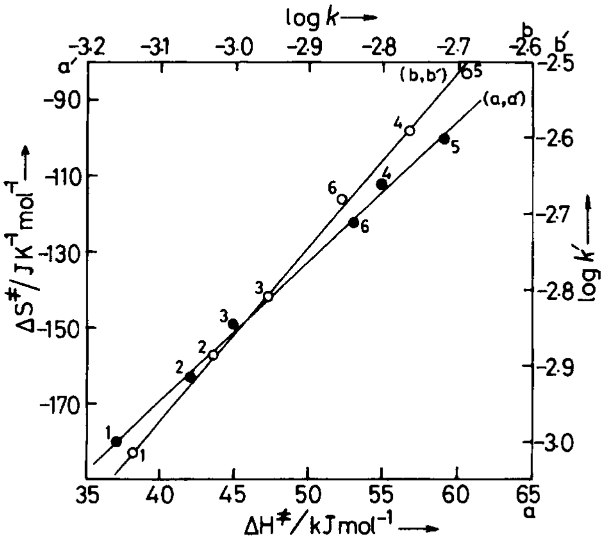


Fig. 5. Isokinetic plots for the oxidations of α-hydroxy carboxylates by platinum(IV) in buffer medium.
(a,a′): plot of $\Delta S^{\neq}$ vs. $\Delta H^{\neq}$,
(b,b′): plot of log k' vs. log k.
(1 = glycolic; 2 = lactic; 3 = α-hydroxyisobutyric; 4 = mandelic; 5 = atrolactic; 6 = benzilic)

The enthalpy of activation is linearly related to the entropy of activation ($r = 0.999$, Fig. 5) and the isokinetic temperature is 270 K. This indicates that a similar mechanism may be operative in all of the reactions. The isokinetic behavior is also supported by the linear plot of log k versus log k' ($r = 0.995$, Fig. 5) where k and k' are the disproportionation constants of the complex at temperature 298 K (T_1) and 303 K (T_2), respectively. The isokinetic temperature was calculated from the relation $\beta = T_1T_2(1-f)/(T_1-T_2f)$, where f is the slope of the Exner plot.[24] The value of β was found to be 271 K, which is lower than T, (mid point of the experimentally used range of temperatures). Although in most cases β is found to exceed T, there is literature evidence[25] for a large number of reactions for which β is lower than T. The rate of such reactions for which β–T is negative are believed to be entropy controlled.

The kinetic isotope effect using mandelic and α-deuteriomandelic acids was carried out at [substrate], [Pt^{IV}], [Cl$^-$], pH, and temperature of 3×10^{-1}, 2×10^{-3}, 2.8×10^{-2} mol dm^{-3}, 10.0 and 303 K, respectively. The k_H/k_D value has been found to be 1.11, which indicates that C–H bond cleavage does not occur.

The addition of OH$^-$ (pH 8—11.2) does not alter the absorbance, indicating that only one species of platinum(IV), possibly $[PtCl_5(OH)]^{2-}$, is formed in alkaline media. It has been reported[14] earlier that the photoaquation of $[PtCl_6]^{2-}$ takes place in 1.0 mol dm^{-3} $HClO_4$. Since the present reaction has been carried out in an alkaline medium, the presence of $[PtCl_5(OH_2)]^-$ seems to be unlikely. However, the reaction between $[PtCl_6]^{2-}$ and OH$^-$ to give $[PtCl_5(OH)]^{2-}$ and Cl$^-$ is not reversible, since the extinction coefficient and λ_{max} of $[PtCl_5(OH)]^{2-}$ remains unaltered, even in the presence of a vast excess of [Cl$^-$] in the alkaline medium.

There is literature evidence[13] to indicate that in alkaline medium (pH > 8) $[PtCl_6]^{2-}$ change to $[PtCl_5(OH)]^{2-}$ in a fast step.

$$[PtCl_6]^{2-} + OH^- \longrightarrow [PtCl_5(OH)]^{2-} + Cl^-. \qquad (5)$$

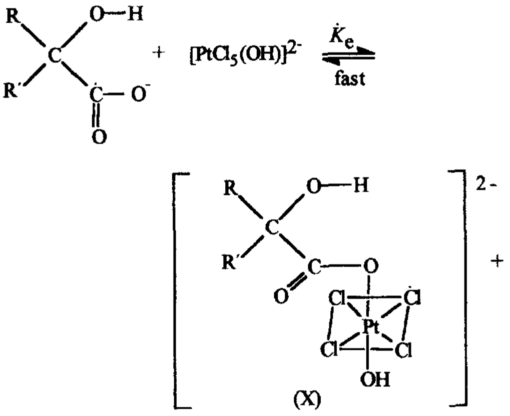
However, the above step is not reversible. A ligand replacement reaction between $[PtCl_5(OH)]^{2-}$ and OH$^-$ to give $[PtCl_4(OH)_2]^{2-}$ and Cl$^-$, followed by the oxidation of α-hydroxy carboxylate by $[PtCl_4(OH)_2]^{2-}$, can be ruled out since the dihydroxy platinum(IV) complex is unstable in aqueous solution and readily disproportionates according to the following equation:

$$2[PtCl_4(OH)_2]^{2-} \longrightarrow [PtCl_6]^{2-} + [PtCl_2(OH)_4]^{2-} \qquad (6)$$

Consequently, under the present experimental condition $[PtCl_5(OH)]^{2-}$ may only act as the oxidizing species.

The path by which platinum(IV) is reduced by different reductants has been the subject of much discussion,[26,27] which has been mainly concerned with the possibility of platinum(III) as an intermediate. The reductions of some platinum(IV) complex by different reductants have been shown to proceed via a free-radical mechanism.[28,29] However, the alternative mechanistic paths where by platinum(IV) undergoes a two-electron reduction have also been reported.[10,30,31]

The acid-dissociation constants[32] of some α-hydroxy acids except atrolactic acid at 298 K are known, the values are 1.47×10^{-4}, 1.38×10^{-4}, 2.2×10^{-4}, 3.89×10^{-4}, and 9.1×10^{-4} for glycolic, lactic, α-hydroxyisobutyric, mandelic and benzilic acids, respectively. Since the reactions were carried out in the pH range 9.2—10.7, the dissociation constant values[21] of the α-hydroxy acids suggest that they will remain dissociated to a large extent. The α-hydroxy carboxylate anion enter into the coordination sphere of octahedral platinum(IV) complex and replaces a chloride ligand to give an intermediate complex (X). This is further supported by the spectrophotometric evidence for the intermediate complex (X) formation. The absorbance of the reaction mixture initially increases and then gradually decreases. The initial increase in the absorbances indicates that an intermediate complex is formed between the reactants. The latter then decomposes to give products, as mentioned in steps (8) and (9). The observed kinetic isotopic effect suggests that oxidation occurs via the C–C bond cleavage, and not by C–H bond breaking. The fact that the carbenium ion is formed in step (8) is in conformity with the reactions between α-hydroxy acids and manganese(III).[12] Moreover platinum(II), which may also exist in alkaline medium as $[PtCl_3(OH)]^{2-}$ (Step 8), is also known in the literature.[33,34] The latter decomposes in excess alkali to give black ppt of hydrated platinum oxide, as mentioned in step (10). The oxidation of α-hydroxy carboxylate by Pt^{IV}, which have been studied in an alkaline medium, takes place by an inner-sphere mechanism.



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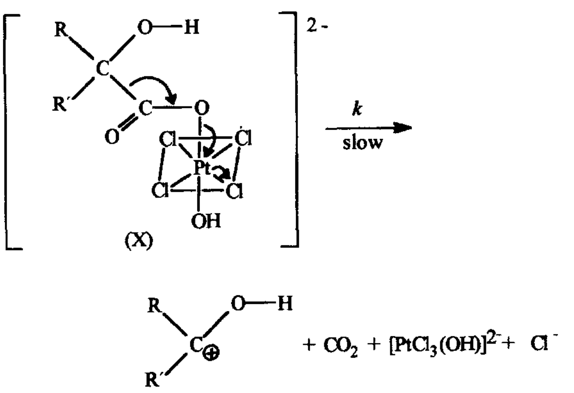

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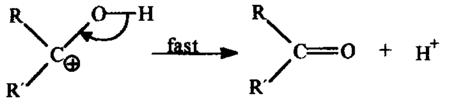

(9)

$$PtCl_3(OH)^{2-} + OH^- \xrightarrow{fast} Pt(OH)_2\downarrow + 3Cl^- \tag{10}$$

$$H^+ + OH^- \xrightarrow{fast} H_2O \tag{11}$$

The rate of disappearance of Pt^{IV} may be expressed as

$$-d[Pt^{IV}]_t/dt = k[X] \tag{12}$$

Now,
$$[X] = \frac{K_e[A^-][Pt^{IV}]_f}{[Cl^-]} \tag{13}$$

and
$$[Pt^{IV}]_t = [Pt^{IV}]_f + \frac{K_e[A^-][Pt^{IV}]_f}{[Cl^-]},$$

so that
$$[Pt^{IV}]_f = [Pt^{IV}]_t\Big/\left\{1+\frac{K_e[A^-]}{[Cl^-]}\right\}. \tag{14}$$

Equation 14 can be transformed into

$$-d[Pt^{IV}]_t/dt = \frac{kK_e[A^-]}{[Cl^-]}\frac{[Pt^{IV}]_t}{\left\{1+\frac{K_e[A^-]}{[Cl^-]}\right\}}, \tag{15}$$

So that the pseudo-first-order rate constant,

$$k_{obsd} = \frac{kK_e[A^-]}{[Cl^-]+K_e[A^-]},$$
$$\left(\text{where,}\quad k_{obsd} = \frac{1}{[Pt^{IV}]_t}\frac{d[Pt^{IV}]_t}{dt}\right). \tag{16}$$

Rearranging Eq. 16, we obtain

$$1/k_{obsd} = \frac{[Cl^-]}{kK_e[A^-]} + 1/k. \tag{17}$$

Thus, Eq. 17 can explain the linear plot of $1/k_{obsd}$ versus 1/[S]. From the intercept of the plot at each temperature the value of the disproportionation constant (k) at that temperature was evaluated; also the value of K_e at that temperature was calculated from the slope-intercept relationship (Table 3). Figure 1 shows an inverse dependence of the rate on $[Cl^-]$, which is in keeping with the rate law (17). The values of k and K_e at 298 K were evaluated from plot of $1/k_{obsd}$ against $[Cl^-]$ at that temperature, and are found (Fig. 1) to be in agreement with those obtained from the substrate effect at the same temperature (Table 3).

It is evident that in the slow step (8), the transition state will be much more polar than the intermediate complex (X) and the former will be more stabilized by the presence of ion atmosphere than the latter. Thus an increase in ionic strength will favor the transition state, thereby increasing the value of k (step 8). Consequently, an increase in k_{obsd} is expected, as observed in the present investigation (Fig. 2).

The reactions occur through the intermediate formation of complexes followed by the decomposition to give carbenium ion and platinum(II) in the rate determining step (8). The equilibrium constants (K_e) associated with the complex formation step and rate constants (k) associated with the rate-determining step are found to be in

Table 3. Equilibrium Constants for the Fast Step and Disproportionation Constants for the Slow Step for Different Effects at 298 K

Substrate	Effect of [S]		Effect of [Cl^-]	
	$K_e/10^{-2}$	$k/10^{-3}$ dm^3 mol^{-1} s^{-1}	$K_e/10^{-2}$	$k/10^{-3}$ dm^3 mol^{-1} s^{-1}
Glycolic acid	4.61	0.7315	4.766	0.7273
Lactic acid	4.20	0.921	4.096	0.930
α-Hydroxyisobutyric acid	3.80	1.11	3.676	1.143
Mandelic acid	2.95	1.715	2.934	1.818
Atrolactic acid	2.63	2.06	2.60	2.22
Benzilic acid	3.34	1.362	3.467	1.333

Table 4. Thermodynamic Data Associated with the Complex and the Activation Parameters Associated with the Slowest Steps

Substrate	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
Glycolic acid	13±4	19±13	37±4	−180±14
Lactic acid	12±2	12±7	42±2	−163±7
α-Hydroxyisobutyric acid	8±2	−0.4±7	45±4	−149±14
Mandelic acid	5±2	−13±7	55±4	−112±14
Atrolactic acid	4±2	−16±7	59±2	−100±7
Benzilic acid	7±2	−6±7	53±2	−122±7

the region $(2.63—4.61)\times10^{-2}$ and $(0.731—2.06)\times10^{-3}$ dm^3 mol^{-1} s^{-1}, respectively. The equilibrium constant is related to the rate constant, which is supported by the linear plot of $\log k$ vs. $\log K_e$ (Fig. 6). The values of k for all of the reactions are of the same order (10^{-3} dm^3 mol^{-1} s^{-1}), indicating that a similar mechanism is operative. There is a difference in the rate of oxidation of the α-hydroxycarboxylates, which seems to be due to the presence of methyl or phenyl group/groups on the α-carbon atom of glycolic acid. The introduction of a methyl group at the α-carbon of glycolic acid stabilizes the anion through stronger intramoleculer H-bonding; the value of K_e follows the order glycolic acid > lactic acid > α-hydroxyisobutyric acid. Again, the presence of a methyl group of α-carbon of glycolic acid increases the electron density on the α-carbon, thereby rendering the C–C bond breaking easier in the order glycolic acid < lactic acid < α-hydroxyisobutyric acid. On the other hand, the introduction of a phenyl group decreases the nucleophilicity of the anion, thereby diminishing the value of K_e. The value of k is higher in mandelic acid than other aliphatic α-hydroxy acids, which may be explained as being due to the formation of carbenium ion on the α-carbon (after removal of CO_2), which is stabilized through reasonance in the benzene ring. The value, however, slightly diminishes in benzilic acid.[35] The k values, which are in the order glycolic < lactic < α-hydroxyisobutyric < benzilic < mandelic < atrolactic acids, are in conformity with the results obtained earlier[35] in the oxidations of these compounds by bromate ion, which is also believed to be a two electron transfer oxidant.

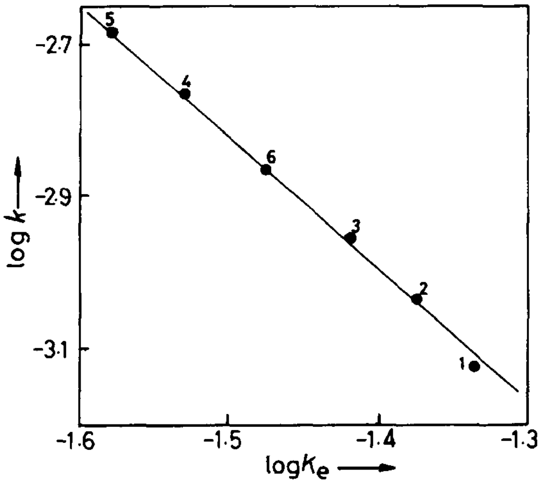

Fig. 6. Linear free energy relationship. The first Hammett plot of $\log k$ vs. $\log K_e$ for the oxidation of α-hydroxy carboxylates by Pt^{IV}.
(1 = glycolic; 2 = lactic; 3 = α-hydroxyisobutyric; 4 = mandelic; 5 = atrolactic; 6 = benzilic)

Recently, the oxidations of a number of inorganic and organic compounds by $[PtCl_6]^{2-}$ have been studied[36] in the acid region (0.1—1.0) mol dm^{-3} and also in the pH range 4—6, depending upon the substrates. The reactions have been shown to occur by a two-electron reduction process. Since the present reactions were carried out in a carbonate–hydrogencarbonate buffer medium, the rate constants cannot be compared with those obtained earlier with the oxidations of Fe(II), Sn(II), $S_2O_3{}^{2-}$, NH_2OH, and ascorbic acid by $[PtCl_6]^{2-}$. All of these reactions, except for ascorbic acid oxidation, are characterized by negative entropies of activation, like in the present studies involving α-hydroxy acids and platinum(IV).

Conclusion

The redox reaction involving hexachloroplatinate(IV) and α-hydroxy carboxylate ions proceeds through the intermediate formation of a 1 : 1 complex followed by a two-electron reduction to $[PtCl_3(OH)]^{2-}$ and the carbenium ion ( ). The latter then decomposes to give the respective carbonyl compounds. Pt^{II} complex, which is formed in the rate-determining step, further reacts in excess alkali to give black ppt of hydrated platinum oxide.

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