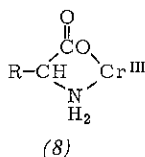
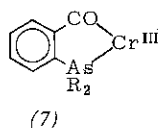


desired manner (7). The formation of a strained four membered chelate ring in preference to a more stable six membered ring may be justified in terms of the HSAB principle which favours coordination of two hard oxygens to the hard chromium(III) over those of one hard (oxygen) and one soft (arsenic) donors due to metal ions of higher charge and with a small number of d-electrons. On the other hand, the reported^(28–30) preferential stabilization of structure (8) over one similar to (3) in the α -amino acids [R-CH(NH₂)(CO₂H)] complexes (R = H, Et, PhCH₂, MeSCH₂CH₂, etc.) with chromium(III) is favoured by both the HSAB principle and the size of the chelate ring, since nitrogen and oxygen are both hard donors.



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(Received June 8th, 1981)

TMC 664

New Cationic and Anionic Tetracoordinate Nickel(I) Complexes

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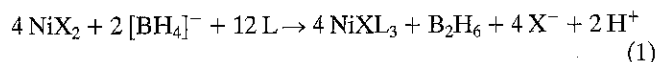
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Summary

The preparation, structural study and chemical behaviour of new cationic, monoanionic and dianionic tetracoordinate nickel(I) complexes of the types: [NiL₄][BPh₄] (L = PPh₃, AsPh₃ or SbPh₃), [PR₄][NiX₂L₂] (X = Cl, Br or I; L = PPh₃, AsPh₃ or SbPh₃) and [PR₄]⁺ = PPh₄, Ph₃PCH₂Ph or Ph₃PET) and [PR₄]₂[NiX₃L] (X = Cl, Br or I; L = PPh₃ and [PR₄]⁺ = PPh₄ or PPh₃CH₂Ph) are described.

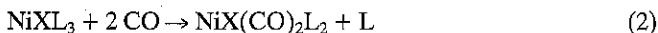
Introduction

The reduction of nickel(II) halides with NaBH₄ in ethanol in the presence of ligands, is a general method for preparing nickel(I) complexes as described in previous contributions⁽¹⁾. Nickel(I) complexes of NiXL₃ stoichiometry have been isolated in accordance with Equation (1) where X = Cl, Br or I and L = PPh₃ or AsPh₃:



The reaction of NiXL₃ with CO gas at room temperature produces pentacoordinate carbonyl complexes NiX(CO)₂L₂ (L = PPh₃)⁽¹⁾; Equation (2):

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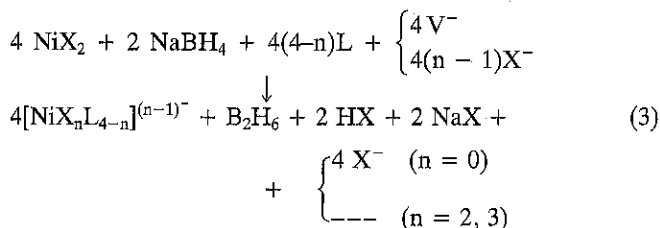


We have continued our study of the reduction of nickel(II) halides by NaBH_4 oriented towards the preparation of tetra-coordinate nickel(I) complexes with ligands containing group VB donor atoms. The following kinds of compounds have been isolated: a) Cationic complexes $[\text{NiL}_4][\text{BPh}_4]$; b) Monoanionic complexes $[\text{PR}_4][\text{NiX}_2\text{L}_2]$ and c) Dianionic complexes $[\text{PR}_4]_2[\text{NiX}_3\text{L}]$.

Results and Discussion

Preparations

The reduction of ethanolic solutions of nickel(II) halides with the strict stoichiometric quantity of NaBH_4 in the presence of the appropriate ligand permits isolation of different types of nickel(I) complexes, according to Equation (3):



In order to obtain cationic complexes ($n=0$) we operated in the presence of a bulky anion such as V^- , $[\text{BPh}_4]^-$, and isolated the salt of the above mentioned anion as a result of halide elimination. In order to obtain the anionic complexes ($n=2$ or 3) we add $[\text{PR}_4]\text{X}$. In this way X^- , in the required stoichiometry, together with $[\text{PR}_4]^+$, which acts as a counterion for the resulting anionic complex, are present in the reaction mixture. The elemental analyses of the complexes correspond to the stoichiometries given in Table 1.

All the complexes (1-16) are stable under nitrogen at room temperature in the solid state, but decompose in air and become green owing to traces of moisture. The stability of these species decreases as the donor atom size increases. We were unable to isolate dianionic complexes using AsPh_3 , whereas it proved possible to obtain complexes with SbPh_3 , as is evident by i.r. spectroscopy. Nevertheless, these complexes

are unstable and it was neither possible to obtain analytical data nor to carry out their structural study.

The complexes are insoluble in hydrocarbons, methanol, ethanol and water, but soluble in acetone, chloroform, tetrachloromethane, benzene and THF. Solution studies are impossible because the complexes decompose quickly to give green solutions and a white residue. Such decomposition corresponds to the disproportionation, Equation (4), behaviour which is general for nickel(I) complexes; the disproportionation products being also unstable or insoluble.



Therefore, spectroscopic or conductivity studies in solution were not possible.

I.r. spectra

The i.r. spectra of all the complexes show the characteristic vibrations for triphenylphosphine^(2,3), triphenylarsine^(3,4) or triphenylstibine^(4,5).

In the cationic complexes (1-3) the presence of the $[\text{BPh}_4]^-$ anion is not easily determined from the analysis of the i.r. spectra, because the phenyl group is common to both anion and ligands. However, the three spectra exhibit an absorption band at 800 cm^{-1} which is also present in the NaBPh_4 spectrum, thus confirming the presence of the $[\text{BPh}_4]^-$ anion. This absorption band can be assigned to the mode corresponding to the $\nu(\text{C}-\text{B})$ ^(6,7). The presence of the tetra-coordinate nickel(I) cationic species $[\text{NiL}_4]^+$ is consistent with these data.

In the monoanionic complexes of the $[\text{NiX}_2\text{L}_2]^-$ type where $\text{X} = \text{Br}$ or I and $\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3 , the vibrations corresponding to the $\nu(\text{Ni}-\text{X})$ stretching mode cannot be detected because the range of our apparatus does not cover the region below 200 cm^{-1} .

In the chloro complexes $[\text{NiCl}_2\text{L}_2]^-$ ($\text{L} = \text{AsPh}_3$ or SbPh_3) the absorption band, $\nu(\text{Ni}-\text{Cl})$, is not observed, probably because it is overlapped by a much more intense absorption due to an internal vibration of the ligand.

Accordingly, we have only studied the chlorophosphino complexes $[\text{NiCl}_2(\text{PPh}_3)_2]^-$. If we propose a tetrahedral geometry with C_{2v} symmetry, two absorption bands should be expected due to $\nu(\text{Ni}-\text{Cl})$. The i.r. spectra of these complexes

Table 1. Physical properties and analytical data for nickel(I) complexes

Complex	Colour	M.p. ^{a)} (°)	Found (Calcd.)%			
			C	H	Ni	X
(1) $[\text{Ni}(\text{PPh}_3)_4][\text{BPh}_4]$	yellow	105	80.8(80.8)	5.6(5.6)	4.0(4.1)	
(2) $[\text{Ni}(\text{AsPh}_3)_4][\text{BPh}_4]$	yellow-orange	65	71.8(71.9)	5.0(5.0)	3.6(3.7)	
(3) $[\text{Ni}(\text{SbPh}_3)_4][\text{BPh}_4]$	orange	115	64.3(64.4)	4.3(4.5)	3.1(3.3)	
(4) $[\text{PPh}_4][\text{NiCl}_2(\text{PPh}_3)_2]$	red	98	72.4(72.5)	5.0(5.1)	5.8(5.9)	7.4(7.1)
(5) $[\text{PPh}_4][\text{NiCl}_2(\text{AsPh}_3)_2]$	yellow-orange	71	66.1(66.6)	4.5(4.7)	5.6(5.4)	6.9(6.5)
(6) $[\text{PPh}_4][\text{NiBr}_2(\text{PPh}_3)_2]$	red	102	67.0(66.6)	5.3(4.6)	5.3(5.4)	14.1(14.8)
(7) $[\text{PPh}_4][\text{NiBr}_2(\text{AsPh}_3)_2]$	ocher	90	61.3(61.6)	4.4(4.3)	5.0(5.0)	13.2(13.6)
(8) $[\text{PPh}_4][\text{NiBr}_2(\text{SbPh}_3)_2]$	red	97	57.0(57.0)	4.0(4.0)	4.6(4.6)	12.6(12.6)
(9) $[\text{PPh}_4][\text{NiI}_2(\text{PPh}_3)_2]$	brown	57	61.2(61.2)	4.2(4.3)	5.0(5.0)	
(10) $[\text{PPh}_4][\text{NiI}_2(\text{AsPh}_3)_2]$	yellow	50	56.9(57.0)	3.6(3.7)	4.6(4.0)	
(11) $[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{NiCl}_2(\text{PPh}_3)_2]$	red	160	72.4(72.4)	5.5(5.5)	5.6(5.8)	6.9(7.0)
(12) $[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{NiCl}_2(\text{SbPh}_3)_2]$	brown	130	61.4(61.6)	4.2(4.4)	4.8(4.9)	5.9(6.0)
(13) $[\text{Ph}_3\text{PEt}][\text{NiI}_2(\text{PPh}_3)_2]$	brown	125	59.0(59.9)	4.3(4.6)	5.0(5.1)	
(14) $[\text{PPh}_4][\text{NiI}_3(\text{PPh}_3)]$	brown	120	58.7(57.4)	4.0(4.0)	4.0(4.2)	
(15) $[\text{PPh}_4]_2[\text{NiBr}_3(\text{PPh}_3)]$	red	100	63.2(63.9)	4.6(4.5)	4.5(4.7)	19.0(19.3)
(16) $[\text{Ph}_3\text{PCH}_2\text{Ph}]_2[\text{NiCl}_3(\text{PPh}_3)]$	brown	97	71.5(72.0)	5.2(5.2)	4.8(5.2)	8.9(9.4)

^{a)} With dec.

reveal a very weak absorption peak at 275 cm^{-1} and another much more intense one at 245 cm^{-1} , which can be assigned to the above mentioned vibrations. On the other hand, in the dianionic complexes no absorption band corresponding to $\nu(\text{Ni-X})$ ($X = \text{Br}$ or I) was observed. In the chloro complex, two absorption peaks are observed at 240 and 285 cm^{-1} . If we propose a tetrahedral geometry with a C_{3v} symmetry, we should expect two $\nu(\text{Ni-Cl})$ stretching vibrations to which these absorptions can be assigned.

Magnetic susceptibilities

The room temperature magnetic susceptibilities χ'_M of the complexes are shown in Table 2. Magnetic moments, μ_{eff} , are of the magnitude expected for mononuclear nickel(I) complexes containing an unpaired electron (d^9). All complexes exhibit normal paramagnetic behaviour which follows the Curie-Weiss law, between 200 and 300 K . The μ_{eff} variation with temperature is very low (ca. 0.1 B.M.) between 195 and 300 K , so that it has been ignored. Theoretically, for a ground term, T_2 , is possible to calculate a μ_{eff} of 2.20 B.M. which is temperature dependent.

The experimental values, μ_{eff} , for cationic complexes are in good agreement with the theoretical value for undistorted tetrahedral complexes⁽⁹⁾. We think that these complexes which possess four equivalent ligands must be minimally distorted since steric hindrance by the bulky ligands would make deformation towards a square-planar environment difficult.

Furthermore, we have studied the magnetic susceptibility, χ'_M , variation of the phosphino-complex between 195 and 300 K verifying that this behaviour follows the Curie-Weiss law, with $\theta = -22\text{ K}$.

The μ_{eff} values for monoanionic complexes, also correspond to paramagnetic nickel(I) species with an undistorted tetrahedral structure. The study of the temperature variable χ'_M for complex (7) revealed a behaviour pattern which follows the Curie-Weiss law, with $\theta = -106\text{ K}$.

As far as dianionic complexes are concerned, we could only study the magnetic behaviour of the chloro complex. The data are shown in Table 2 and are in good agreement with the values expected for a regular tetrahedral complex. We were unable to carry out a variable temperature magnetic study since decomposition prevents the measurement and the results are unreliable.

Table 2. Magnetic data and i.r. spectra for nickel(I) complexes

Complex	$10^6 \chi'_M$	μ_{eff} (B.M.) ^{a)}	$\nu(\text{C-B})$ (cm^{-1})	$\nu(\text{Ni-X})$ (cm^{-1})
(1) $[\text{Ni}(\text{PPh}_3)_4][\text{BPh}_4]$	2390	2.38	845	
(2) $[\text{Ni}(\text{AsPh}_3)_4][\text{BPh}_4]$			850	
(3) $[\text{Ni}(\text{SbPh}_3)_4][\text{BPh}_4]$	1839	2.10	852	
(4) $[\text{PPh}_4][\text{NiCl}_2(\text{PPh}_3)_2]$	2093	2.24		245w
(5) $[\text{PPh}_4][\text{NiCl}_2(\text{AsPh}_3)_2]$	2172	2.28		
(6) $[\text{PPh}_4][\text{NiBr}_2(\text{PPh}_3)_2]$	1947	2.16		
(7) $[\text{PPh}_4][\text{NiBr}_2(\text{AsPh}_3)_2]$	2170	2.28		
(9) $[\text{PPh}_4][\text{NiL}_2(\text{PPh}_3)_2]$	2240	2.31		
(11) $[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{NiCl}_2(\text{PPh}_3)_2]$	2050	2.20		275w, 245m
(12) $[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{NiCl}_2(\text{SbPh}_3)_2]$	2061	2.22		
(13) $[\text{Ph}_3\text{PEt}][\text{NiL}_2(\text{PPh}_3)_2]$	2162	2.27		
(16) $[\text{Ph}_3\text{PCH}_2\text{Ph}]_2[\text{NiCl}_3(\text{PPh}_3)]$	2670	2.25		285m, 240w

^{a)} At 297 K .

Table 3. Electronic spectra of nickel(I) complexes (diffuse reflectance).

Complex	$\nu(\text{cm}^{-1})$
(1) $[\text{Ni}(\text{PPh}_3)_4][\text{BPh}_4]$	19230sh, 15150sh, 10640
(3) $[\text{Ni}(\text{SbPh}_3)_4][\text{BPh}_4]$	13884sh, 10410
(4) $[\text{PPh}_4][\text{NiCl}_2(\text{PPh}_3)_2]$	21740sh, 15150sh, 11100
(16) $[\text{Ph}_3\text{PCH}_2\text{Ph}]_2[\text{NiCl}_3(\text{PPh}_3)]$	21745sh, 15870sh, 9260

Electronic spectra

The electronic absorption spectral studies of all the nickel(I) complexes described in this paper have been carried out in the solid state by means of diffuse reflectance, since all the complexes are unstable in solution.

The results obtained in the u.v.-vis near i.r. spectral region for cationic complexes $[\text{NiL}_4][\text{BPh}_4]$ are shown in Table 3. The arsino complex could not be studied because it is unstable in air.

In the $[\text{Ni}(\text{PPh}_3)_4]^+$ spectrum, an absorption band maximum is located at 10640 cm^{-1} which is asymmetric and exhibits two shoulders at 15150 and 19230 cm^{-1} . On the other hand, the SbPh_3 complex shows an absorption band at 10410 cm^{-1} , also asymmetric, with a shoulder at 13884 cm^{-1} .

This behaviour is consistent with a tetrahedral geometry and therefore the absorption band indicated must be undoubtedly assigned to the ${}^2T_2 \rightarrow {}^2E$ transition. The observed shoulders could be due to the splitting produced by spin-orbit coupling or to the presence of a distortion that in any case must be very small, in agreement with the μ_{eff} values which are very close to the theoretical values for a regular tetrahedral environment.

A comparative study of the spectra, reveals a shift of the absorption band corresponding to the ${}^2T_2 \rightarrow {}^2E$ transition from 10640 cm^{-1} ($L = \text{PPh}_3$) to 10410 cm^{-1} ($L = \text{SbPh}_3$), which confirms that SbPh_3 produces a field weaker than PPh_3 , as has been observed in other complexes. This assignment is in good agreement with results obtained in spectral and crystallographic studies of other nickel(I) complexes⁽⁹⁻¹¹⁾.

With respect to the monoanionic complexes, we note that the lack of stability of the majority of these species under conditions employed has made it impossible to obtain reliable results. Therefore we only discuss $[\text{PPh}_4][\text{NiCl}_2(\text{PPh}_3)_2]$. The electronic spectrum of this complex shows an asymmetric absorption band with a maximum at 11100 cm^{-1} and two shoulders at 15150 and 21740 cm^{-1} . This behaviour is similar to that observed for cationic complexes and it seems also reasonable in this case to assign the main absorption to the ${}^2T_2 \rightarrow {}^2E$ transition in a tetrahedral environment almost without distortion, in accord with the calculated μ_{eff} values.

However, it is not possible to explain the position of the band at a higher energy compared to that corresponding to $[\text{Ni}(\text{PPh}_3)_4][\text{BPh}_4]$, since replacement of PPh_3 by Cl should produce a decrease in splitting caused by the field. Possibly, as we have seen, the transition is not as simple as indicated and the position of the maximum could well depend on the way the bands overlap.

Since the neutral NiXL_3 complexes are distorted tetrahedral it seems unreasonable that the $[\text{NiX}_2\text{L}_2]^-$ species are not also distorted. However, we have to take into account the fact that the presence of two anionic ligands in the coordination sphere, and their mutual repulsion, must make distortion to square-planar difficult. This could well explain the spectral and magnetic behaviour observed for this monoanionic complexes.

The spectral data obtained from $[\text{Ph}_3\text{PCH}_2\text{Ph}]_2[\text{NiCl}_3(\text{PPh}_3)]$ is also in agreement with these proposals. The absorption band at 9260 cm^{-1} can be assigned to the ${}^2T_{2g} \rightarrow {}^2E_g$ transition which corresponds to a d^9 ion in a tetrahedral environment. This asymmetric band also contains shoulders at 15870 and 21745 cm^{-1} .

Experimental

Physical measurements

The i.r. spectra were recorded between $4000\text{--}200\text{ cm}^{-1}$ on a Perkin-Elmer 599 spectrophotometer using KBr pellets and Nujol dispersion with CsI cells.

The diffuse reflectance electronic spectra were recorded in the u.v.-vis-near i.r. region with a Perkin-Elmer 330 spectrophotometer, using BaSO_4 as calibrant.

Magnetic susceptibilities were measured by the Faraday method using a Bruker B-E.15 magnetic balance with a temperature control unit. $\text{HgCo}(\text{SCN})_4$ was used as calibrant and diamagnetism was corrected for using the appropriate Pascal's constants.

M.p. measurements have been made in a Thermovan Reichert microscope.

C and H analyses were made with a Perkin-Elmer 240 B microanalyzer. Nickel was determined with dimethylglyoxime⁽¹²⁾. Halogen was determined by White's method⁽¹³⁾.

All experiments were carried out in a nitrogen atmosphere.

Cationic complexes $[\text{NiL}_4][\text{BPh}_4]$

To $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.000 g, 4.210 mmol) in EtOH (15 cm^3) was added NaBPh_4 (2.280 g, 8.420 mmol). A white precipitate of NaCl immediately separated from the resulting green solution containing nickel(II) cationic species. To this solution the ligand L (L = PPh_3 , AsPh_3 or SbPh_3) (16.840 mmol) was added to give a white suspension which was stirred for 0.5 h at 20° . NaBH_4 (0.079 g, 2.105 mmol) in EtOH (15 cm^3) was then added dropwise to the white suspension. During the addition a colour change of the suspended solid was observed and when all the NaBH_4 had been added, a solid was separated by filtration, as yellow (1) (L = PPh_3), yellow-orange (2) (L = AsPh_3) or orange (3) (L = SbPh_3) crystals. The crystals were washed with EtOH ($3 \times 5\text{ cm}^3$) and dried *in vacuo*. Yield 50-60%.

Monoanionic complexes $[\text{PR}_4][\text{NiX}_2\text{L}_2]$

$[\text{PPh}_4][\text{NiCl}_2\text{L}_2]$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.500 g, 2.100 mmol) in EtOH (15 cm^3) was treated with the ligand L (L = PPh_3 or AsPh_3) (2.100 mmol) and $[\text{PPh}_4]\text{Cl}$ (1.039 g, 2.100 mmol). After 0.5 h stirring a green suspension was formed, which contained $[\text{PPh}_4][\text{NiCl}_3\text{L}]$ ⁽¹⁴⁾. When the ligand L (L = PPh_3 or AsPh_3) (2.100 mmol) was added to the green suspension followed by an EtOH solution (10 cm^3) of NaBH_4 (0.039 g, 1.050 mmol) the colour of the suspended solid changed. When the addition was completed, this solid was separated by filtration as red (4) (L = PPh_3) or orange (5) (L = AsPh_3) crystals which were washed with EtOH and dried *in vacuo*. Yield 50-60%.

$[\text{PPh}_4][\text{NiBr}_2\text{L}_2]$

NiBr_2 (1.000 g, 4.570 mmol) was suspended in EtOH (10 cm^3) and the ligand L (L = PPh_3 , AsPh_3 or SbPh_3) (4.570 mmol) and $[\text{PPh}_4]\text{Br}$ (3.480 g, 4.570 mmol) were

added. The suspension was stirred for 1 h and the green $[\text{PPh}_4][\text{NiBr}_3\text{L}]$ ⁽¹⁵⁾ formed. Ligand L (L = PPh_3 , AsPh_3 or SbPh_3) (4.570 mmol) was added to the green suspension followed afterwards by NaBH_4 (0.086 g, 2.285 mmol) in EtOH (12 cm^3) dropwise. When the addition was complete, crystalline red (6) and (8) (L = PPh_3 and SbPh_3) and ochre solids (7) (L = AsPh_3) were obtained which, were washed with EtOH ($2 \times 5\text{ cm}^3$) and dried *in vacuo*. Yield 70-50%.

$[\text{PPh}_4][\text{NiI}_2\text{L}_2]$

$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ (0.500 g, 1.180 mmol) was dissolved in EtOH (8 cm^3) and treated with ligand L (L = PPh_3 or AsPh_3) (1.180 mmol) and $[\text{PPh}_4]\text{I}$ (0.550 g, 1.180 mmol). After 0.5 h stirring, the second mole of ligand L (1.180 mmol) was added and an EtOH solution of NaBH_4 (0.024 g, 0.590 mmol) was added dropwise. When the NaBH_4 addition was completed the solid in suspension was separated by filtration as crystalline brown (9) (L = PPh_3) or yellow (10) (L = AsPh_3) solids which were washed with EtOH ($2 \times 4\text{ cm}^3$) and dried *in vacuo*. Yield 58-50%.

$[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{NiCl}_2\text{L}_2]$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.000 g, 4.210 mmol), ligand L (L = PPh_3 or SbPh_3) (8.410 mmol) and $[\text{Ph}_3\text{PCH}_2\text{Ph}]\text{Cl}$ (1.636 g, 4.210 mmol) were dissolved in EtOH (10 cm^3) and the solution was stirred for 0.5 h. An EtOH solution (10 cm^3) of NaBH_4 (0.079 g, 2.105 mmol) was then added dropwise and when the addition was complete, crystalline red (11) (L = PPh_3) or brown (12) (L = SbPh_3) solids were obtained. They were washed with EtOH ($2 \times 3\text{ cm}^3$) and dried *in vacuo*. Yield 75-40%.

$[\text{PPh}_3\text{Et}][\text{Ni}_2(\text{PPh}_3)_2]$

$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ (1.000 g, 2.490 mmol), PPh_3 (1.260 g, 4.980 mmol) and $[\text{PPh}_3\text{Et}]\text{I}$ (1.041 g, 2.490 mmol) were dissolved in EtOH (10 cm^3). The solution was stirred for 0.5 h. To the green solution an EtOH solution of NaBH_4 (0.044 g, 1.245 mmol) was added dropwise. When the addition was completed a crystalline red (13) solid was obtained. The solid was washed with EtOH ($2 \times 3\text{ cm}^3$) and dried *in vacuo*. Yield 40%.

Dianionic complexes $[\text{PR}_4]_2[\text{NiX}_3\text{L}]$

$[\text{PPh}_4]_2[\text{NiX}_3(\text{PPh}_3)]$

Nickel(II) halides (X = Br or I) (1.188 mmol), PPh_3 (1.188 mmol) and $[\text{PPh}_4]\text{X}$ (X = Br or I) (2.376 mmol) were dissolved in EtOH (10 cm^3) and the solution was stirred for a few minutes. An EtOH solution of NaBH_4 (0.024 g, 0.594 mmol) was added dropwise to the green suspension. When the addition was completed, crystalline red (15) (X = Br) or brown (14) (X = I) solids were formed which were washed with EtOH ($2 \times 3\text{ cm}^3$) and dried *in vacuo*. Yield 68-60%.

$[\text{Ph}_3\text{PCH}_2\text{Ph}]_2[\text{NiCl}_3(\text{PPh}_3)]$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.000 g, 4.200 mmol), PPh_3 (1.000 g, 4.200 mmol) and $[\text{Ph}_3\text{PCH}_2\text{Ph}]\text{Cl}$ (3.271 g, 8.400 mmol) were dissolved in EtOH (10 cm^3) and the solution was stirred for 0.5 h after which a blue precipitate was formed, and an EtOH solution (10 cm^3) of NaBH_4 (0.079 g, 2.100 mmol) was added

dropwise. When the addition was complete a crystalline brown (16) solid was obtained, which was washed with EtOH ($2 \times 4 \text{ cm}^3$) and dried *in vacuo*. Yield 50%.

Acknowledgements

We greatly appreciate financial support from Comisión Asesora de Investigación Científica Técnica, Spain.

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(Received June 29th, 1981)

TMC 672

Kinetics and Mechanism of the Oxidation of some Neutralized α -Hydroxy Acids by Hexachloroiridate(IV)

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Summary

The kinetics of oxidation of some neutralized α -hydroxy acids such as lactic (LA), mandelic (MA), α -hydroxyisobutyric (IB) and benzilic (BA) acid by hexachloroiridate(IV) have been studied. The oxidation products are acetaldehyde, benzaldehyde, acetone and benzophenone for the respective reactions, which are first order with respect to each substrate and to iridium(IV). The reaction rate increases with increase in pH and salt concentrations. The temperature influence is quite marked in all these reactions. A mechanism involving the formation of an unstable complex, which decomposes *via* a free radical pathway to give the respective reaction products, is proposed.

Introduction

The oxidation of some inorganic⁽¹⁻³⁾ and organic⁽⁴⁻⁶⁾ compounds by hexachloroiridate(IV) has been studied, but no attempt seems to have been made to investigate the mechanism of oxidation of α -hydroxy carboxylic acids by this oxidant. The reactions are too slow to be monitored in a highly acid medium ($> 10^{-3} \text{ M}$) and hence they have been carried out at lower acidities in the presence of a sodium acetate-acetic acid buffer. The present report deals with the kinetics and mechanism of oxidation of some α -hydroxy carboxylates by hexachloroiridate(IV) under different experimental conditions.

Experimental

Reagents

Na_2IrCl_6 (Johnson-Mathey) was used as supplied. Lactic (E. Merck), mandelic (BDH), α -hydroxyisobutyric (Fluka, AG) and benzilic (E. Merck, AG) acids were used without further purification and their Na salts were prepared by the addition of the requisite amount of NaOH. Inorganic materials were of the highest available purity. All solutions were made in doubly distilled H_2O . The oxidation studies were carried out in a NaOAc-HOAc buffer.

Kinetic measurements

A Perkin Elmer (digital) spectrophotometer was used to study the reaction kinetics. The $[\text{IrCl}_6]^{2-}$ absorption maximum lies at 488 nm and hence the disappearance of iridium(IV) was monitored at this wavelength using a cell of 1 cm path length. Neither $[\text{IrCl}_6]^{3-}$ nor its hydrolysed product $[\text{Ir}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ absorbs at this wavelength; the details have been reported in our earlier communication⁽¹⁾. Fresh reactant solutions were occasionally prepared for kinetic runs to ensure reproducibility of the data. The pseudo first order rate constants were calculated in the usual way. In most cases, duplicate rate measurements were reproducible to within $\pm 5\%$.

Results

Stoichiometry and products

Identification of aldehydes or ketones as the reaction products when hexachloroiridate(IV) is present in excess over substrates requires the stoichiometry, shown in Equation (1):

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