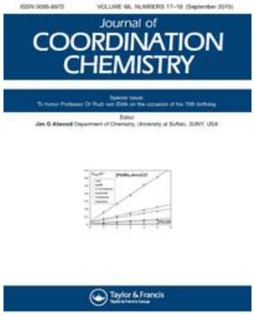

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Slow proton transfer to coordinated carboxylates: studies on $[Ni(O_2CR)\{PhP(CH_2CH_2PPh_2)_2\}]^+$ (R = Et or Ph)

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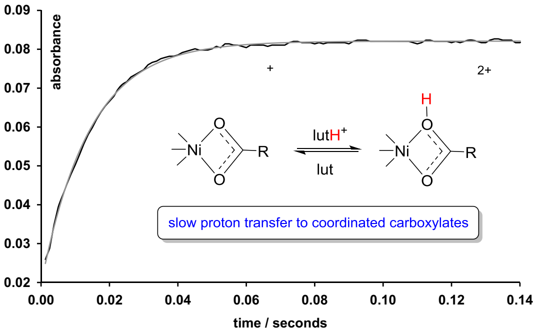

The reactions between $[Ni(O_2CR)(triphos)]^+$ (R = Et or Ph, triphos = $PhP(CH_2CH_2PPh_2)_2$) and mixtures of $lutH^+$ and lut (lut = 2,6-dimethylpyridine) have been studied in MeCN at 25.0 °C using stopped-flow spectrophotometry. The kinetics and spectroscopic changes indicate an equilibrium reaction, presumably involving protonation of an oxygen site (the only sites on the complex containing lone pairs of electrons). Proton transfer is slow and comparison of the kinetic data shows that the rates are insensitive to the R substituent. Using the kinetic data, the pK_as of $[Ni(HO_2CR)(triphos)]^{2+}$ ($pK_a = 14.5$) have been calculated showing that when coordinated to the $\{Ni(triphos)\}^{2+}$ site, RCO_2H is about 8 pK_a units more acidic than the free acid. Comparison of the kinetic results on the reactions of $[Ni(O_2CR)(triphos)]^+$ with mixtures of $lutH^+$ and lut and those of the analogous $[Ni(S_2CR)(triphos)]^+$ show that protonation at oxygen is at least 7.6×10^3 times faster than to sulfur, and the coordinated carboxylic acid is *ca.* 8 pK_a units less acidic than the corresponding coordinated carboxydithioic acid.

Keywords: Nickel; Protonation; Kinetics; Mechanism; Carboxylate

1. Introduction

The kinetics of the substitution reactions of carboxylates bound to cobalt(III) sites, such as $\{Co(NH_3)_5\}^{3+}$ and $\{Co(en)_2(amine)\}^{3+}$ (en = $H_2NCH_2CH_2NH_2$), have been studied

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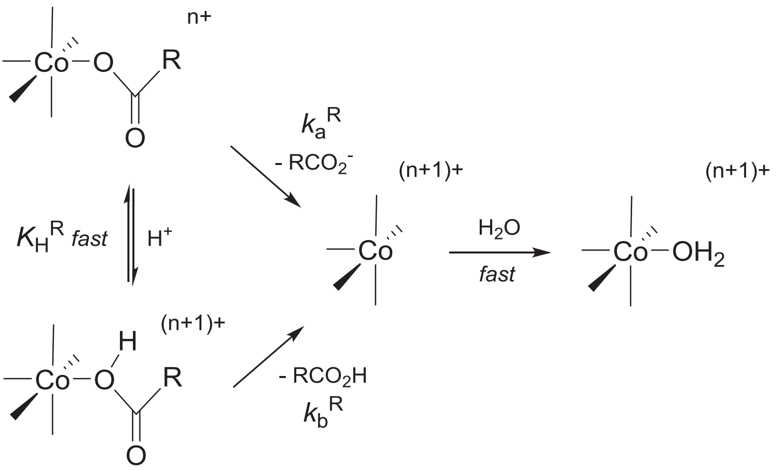
Dedicated to Professor Dr Rudi van Eldik on the occasion of his 70th birthday.



$$\boxed{\text{Rate} = \frac{\{k_a^R + K_H^R k_b^R[H^+]\}}{1 + K_H^R[H^+]}[Co] \sim \{k_a^R + K_H^R k_b^R[H^+]\}[Co]}$$

Figure 1. Substitution pathways for Co(III)-carboxylate complexes.

extensively and are invariably associated with the two term rate law shown on the right-hand side of figure 1 [1]. This simple rate law is a limiting form of the full rate law (shown on the left hand side) and applies when $K_H^R[H^+] < 1$. One term (k_a^R) is independent of the concentration of acid and corresponds to the dissociation of the carboxylato ligand followed by rapid binding of solvent (often water), and the other term ($K_H^R k_b^R$) depends on the concentration of acid, and has been proposed to involve initial protonation of the coordinated carboxylate prior to dissociation of the carboxylic acid and then rapid attack of solvent. For the systems studied to date, both pathways involve rate-limiting dissociation of the carboxylate or carboxylic acid and the protonation step is rapid. Studies on $[Co(O_2CMe)(NH_3)_5]^{2+}$ in water [1] show typical behavior of this type of complex, with $K_H^{Me} = 0.68$, $k_a^{Me} = 3.0 \times 10^{-7}\ s^{-1}$ and $k_b^{Me} = 1.2 \times 10^{-4}\ s^{-1}$. These results allow calculation of $pK_a^{Me} = -0.17$, showing that $MeCO_2H$ coordinated to the $\{Co(NH_3)_5\}^{3+}$ site is 5 pK_a units more acidic than the free acid. Direct measurement of the rates of protonation of the coordinated carboxylate in complexes such as $[Co(O_2CMe)(NH_3)_5]^{2+}$ has not been possible. The best limit for the rate constant for protonation of the coordinated carboxylate that can be estimated is $K_H^R \geq 3 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ (since the protonation is complete within the time of mixing acid with the complex, even at the lowest concentration of $[H^+] = 0.1\ mol\ dm^{-3}$).

Recent studies have shown that proton transfer reactions to ligands {PhY (Y = O, S or Se) [2, 3] or S_2CR [4]} bound to $\{Ni(triphos)\}^{2+}$ {triphos = $PhP(CH_2CH_2PPh_2)_2$} are often slow and, in some cases, the associated rate law is complicated because of the accumulation of hydrogen-bonded intermediates which precede proton transfer. In this article, we describe studies where we have extended our studies to $[Ni(O_2CR)(triphos)]BPh_4$ (R = Et or Ph) and the equilibrium protonation reactions of these complexes with mixtures of $lutH^+$ and lut (lut = 2,6-dimethylpyridine) in MeCN (equation (1)). We report the rates of proton transfer involving coordinated carboxylates and carboxylic acids and compare these results with the rates of proton transfer to the analogous sulfur sites [4].

$$[\mathrm{Ni(O_2CR)(triphos)}]^{+} + \mathrm{lutH}^{+} \rightleftharpoons [\mathrm{Ni(HO_2CR)(triphos)}]^{2+} + \mathrm{lut} \qquad (1)$$

2. Experimental

All manipulations were performed under an atmosphere of dinitrogen using Schlenk and vacuum line techniques or syring techniques as appropriate. The chemicals $NiCl_2 \cdot 6H_2O$, triphos, NaO_2CEt, NaO_2CPh, and $NaBPh_4$ were purchased from Sigma-Aldrich and used as received. [NiCl(triphos)]BPh_4 [5] and [lutH]BPh_4 [6] were prepared by the literature methods.

2.1. *Synthesis of [Ni(O_2CR)(triphos)]BPh_4 (R = Et or Ph)*

[NiCl(triphos)]BPh_4 (0.57 g, 0.6 mmol) was dissolved in *ca.* 20 mL of dry tetrahydrofuran, then a solution containing NaO_2CR {0.058 g (R = Et), 0.086 g (R = Ph), 0.6 mmol} in methanol was added. The solution changed rapidly from yellow to red and was stirred overnight. All volatiles were then removed *in vacuo* to produce a red microcrystalline solid. The dry solid was extracted into a minimum amount of CH_2Cl_2 leaving an insoluble white solid (NaCl). The mixture was filtered and the white residue washed with a small volume of CH_2Cl_2 (*ca.* 2 mL). Ethanol (*ca.* 3–4 times volume of CH_2Cl_2) was layered on the red solution. After several days of slow diffusion the red microcrystalline product was removed by filtration, washed with diethyl ether, and dried *in vacuo*. Although the complex appears to be stable in solution, when isolated as a solid it darkens in color over the course of several hours at room temperature. Consequently, we have been unable to obtain satisfactory elemental analyses and have only characterized the compounds by IR spectroscopy (table 1) and NMR spectroscopy (below).

[Ni(O_2CEt)(triphos)]BPh_4. ^1H NMR: 1.17 (t, J_{HH} = 6.4 Hz, 3H, CH_3); 3.73 (q, J_{HH} = 6.4 Hz, 2H, CH_2CH_3); 2.20–3.50 (br, 8H, CH_2); 6.60–8.45 (m, 45H, Ph). $^{31}P\{^1H\}$ NMR: 99.5 (t, J_{PP} = 55 Hz, PPh); 47.0 (d, J_{PP} = 55 Hz, PPh_2).

[Ni(O_2CPh)(triphos)]BPh_4. ^1H NMR: 1.07–2.85 (br, 8H, CH_2); 6.44–8.59 (m, 50H, Ph). $^{31}P\{^1H\}$ NMR: 100.1 (t, J_{PP} = 54 Hz, PPh); 46.9 (d, J_{PP} = 54 Hz, PPh_2).

2.2. *Kinetic studies*

All kinetic studies were performed using an Applied Photophysics SX.18 MV stopped-flow spectrophotometer, modified to handle air-sensitive solutions, connected to a RISC computer. The temperature was maintained using a Grant LTD 6G thermostat tank with

Table 1. Infrared spectra of NaO_2CR and [Ni(O_2CR)(triphos)]BPh_4 (R = Et or Ph).

	υ_{as}(COO) (cm^{-1})	υ_s(COO) (cm^{-1})	$\Delta\upsilon$ (cm^{-1})
NaO_2CEt	1554	1398	156
NaO_2CPh	1548	1405	143
[Ni(O_2CEt)(triphos)]BPh_4	1582	1480	102
[Ni(O_2CPh)(triphos)]BPh_4	1568	1483	85

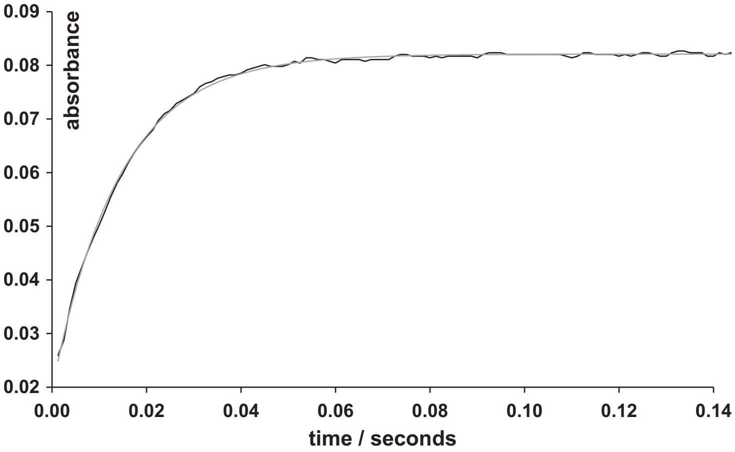


Figure 2. Stopped-flow absorbance-time curve for the reaction of $[Ni(O_2CEt)(triphos)]^+$ (0.25 mmol dm^{-3}) with $lutH^+$ (2.5 mmol dm^{-3}) and lut (0.2 mmol dm^{-3}) in MeCN at 25.0 °C ($\lambda = 350$ nm). The experimental trace is shown in black and the exponential curve fit is shown in gray. The curve fit is defined by $A_t = 0.0821 - 0.0625 \cdot \exp(-70.7t)$.

combined recirculating pump. The experiments were conducted at 25.0 °C. The wavelength used was $\lambda = 350$ nm. Acetonitrile was freshly distilled from CaH_2 (under an atmosphere of dinitrogen) immediately prior to use.

The solutions of complex and reactants ($lutH^+$ and lut) were prepared under an atmosphere of dinitrogen and transferred to the stopped-flow apparatus using gas-tight, all glass syringes. The kinetics were studied in dry MeCN under pseudo-first-order conditions, with $lutH^+$ and lut present in at least a 10-fold excess over the concentration of the complex. Mixtures of $lutH^+$ and lut were prepared from stock solutions of the two reagents. All solutions were used within 1 h of preparation. Under all conditions, the stopped-flow absorbance-time trace was an excellent fit to a single exponential, indicating a first-order dependence on the concentration of complex (figure 2). The dependences on the concentrations of $lutH^+$ and lut were determined from analysis of the appropriate graphs as explained in the results and discussion section.

3. Results and discussion

3.1. *Complexes*

The complexes, $[Ni(O_2CR)(triphos)]BPh_4$ (R = Et or Ph), have been prepared by reactions of $[NiCl(triphos)]BPh_4$ with the appropriate $Na(O_2CR)$. Although the compounds can be recrystallized from mixtures of dichloromethane and ethanol, we have been unable to grow crystals of suitable quality for X-ray crystallography. There are two likely possible structures for $[Ni(O_2CR)(triphos)]^+$: square planar containing a monodentate carboxylate or trigonal bipyramidal containing a bidentate carboxylate group (figure 3). We have previously prepared the analogous carboxydithioate complexes, $[Ni(S_2CR)(triphos)]BPh_4$ (R = Me, Et, Bu^n or Ph), and X-ray crystallography (for R = Et and Ph) shows the cation is best described

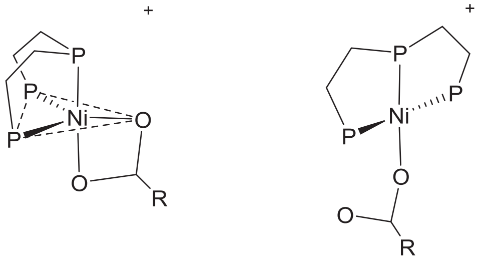


Figure 3. Possible structures of $[Ni(O_2CR)(triphos)]^+$. Phenyl substituents on triphos omitted for clarity.

as trigonal bipyramidal with the bidentate carboxydithioate ligand coordinated to one axial and one equatorial position [4]. It seems likely that the structure of $[Ni(O_2CR)(triphos)]^+$ is also five-coordinate as shown in figure 3. Consistent with this suggestion, the IR spectra of $[Ni(O_2CR)(triphos)]BPh_4$ indicate that the carboxylate ligand is bidentate. The data in table 1 summarizes the values of $\upsilon_{as}(COO)$, $\upsilon_s(COO)$, and $\Delta\upsilon$ $\{= \upsilon_{as}(COO) - \upsilon_s(COO)\}$ for the complexes and the corresponding sodium carboxylates. The value of $\Delta\upsilon$ when compared to that of the corresponding sodium carboxylate can be used as an indicator of the coordinating mode of the carboxylate group [7]. The $\Delta\upsilon$ for the complexes is smaller than that for the corresponding sodium carboxylates, indicating that the carboxylate is bidentate in $[Ni(O_2CR)(triphos)]^+$ [8].

3.2. *Kinetics*

When monitored on a stopped-flow apparatus, the reactions of $[Ni(O_2CR)(triphos)]^+$ with mixtures of $lutH^+$ and lut (solvent = MeCN) exhibit absorbance-time traces which are excellent fits to a single exponential curve, consistent with the reaction exhibiting a first-order dependence on the concentration of the complex (figure 2). The absorbance-time traces show characteristics of an equilibrium reaction. Thus, increasing the concentration of lut (at constant concentration of $lutH^+$) results in a decrease in the absorbance change and the final absorbance (see ESI).

The dependences on the concentrations of $lutH^+$ and lut were determined from plots of k_{obs}/[lut] *versus* $[lutH^+]$/[lut] as shown in figure 4. The kinetic data all fit on a single straight line and have a non-zero intercept. Consequently, the rate law for the reactions with $[Ni(O_2CR)(triphos)]^+$ is that shown in equation (2). When R = Et, $a = 2.64 \times 10^4$ dm^3 mol^{-1} s^{-1} and $b = 6 \times 10^4$ dm^3 mol^{-1} s^{-1}; when R = Ph, $a = 1.93 \times 10^4$ dm^3 mol^{-1} s^{-1} and $b = 5 \times 10^4$ dm^3 mol^{-1} s^{-1}. It should be noted that a common problem when working in aprotic solvents such as MeCN is the association of acids with their conjugate bases {i.e. the homoconjugation equilibrium} [9]. However, the homoconjugation equilibrium constant, involving formation of $\{lutH^+.lut\}$, is too small to measure. Consequently, no correction to the concentrations of $lutH^+$ or lut need to be made in analyzing the kinetic data for the reactions of $[Ni(O_2CR)(triphos)]^+$ with mixtures of $lutH^+$ and lut.

$$\text{Rate} = \{a[\text{lutH}^+] + b[\text{lut}]\}[\text{Ni}(\text{O}_2\text{CR})(\text{triphos})^+] \tag{2}$$

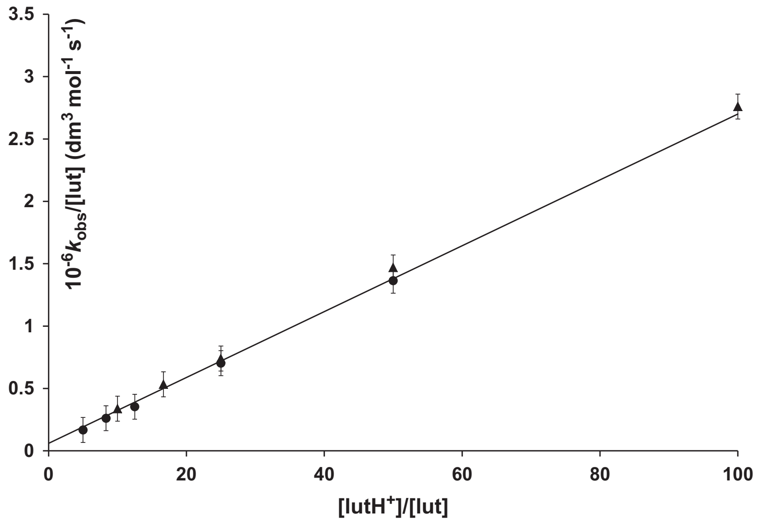


Figure 4. Graph of k_{obs}/[lut] *versus* [lutH$^+$]/[lut] for the reaction of [Ni(O$_2$CEt)(triphos)]$^+$ (0.25 mmol dm^{-3}) with lutH$^+$ in the presence of lut in MeCN at 25.0 °C. Data points correspond to: [lutH$^+$] = 2.5 mmol dm^{-3}, [lut] = 0.05 – 0.50 mmol dm^{-3} (●); [lutH$^+$] = 5.0 mmol dm^{-3}, [lut] = 0.05 − 0.50 mmol dm^{-3} (▲). The line is that defined by equation (2) and the parameters presented in the text. The error bars correspond to differences in k_{obs}/[lut] of ±0.1 × 10^6 dm^3 mol^{-1} s^{-1}.

3.3. *Mechanism*

The rate law presented in equation (2), together with the dependence of the spectroscopic changes on the concentrations of lutH$^+$ and lut, are consistent with an equilibrium reaction [10]. Similar behavior has been observed for the reactions of [NiX(triphos)]$^+$ (X = ArS, PhO, PhSe, and RCS$_2$) with acids [2–4]. The reactions of acids with [Ni(SAr)(triphos)]$^+$, [Ni(SePh)(triphos)]$^+$, or [Ni(S$_2$CR)(triphos)]$^+$ exhibit a complicated rate law (equation (3)), which reveals the complexity of the mechanism of proton transfer in these systems, as shown in figure 5. It seems likely that the reaction of [Ni(O$_2$CR)(triphos)]$^+$ with lutH$^+$ follows this mechanism. The mechanism involves initial rapid hydrogen bond formation between [Ni(O$_2$CR)(triphos)]$^+$ and lutH$^+$ (K_1^R), followed by intramolecular proton transfer (k_2^R). If K_1^R[lutH$^+$] < 1, equation (3) simplifies to equation (4). Equation (4) is of the same form as the experimental rate law and comparison of equations (2) and (4) allow the elementary rate constants shown in table 2 to be determined. Furthermore, a limiting value for K_1^R can be estimated. Since the observed rate law for the reactions of [Ni(O$_2$CR)(triphos)]$^+$

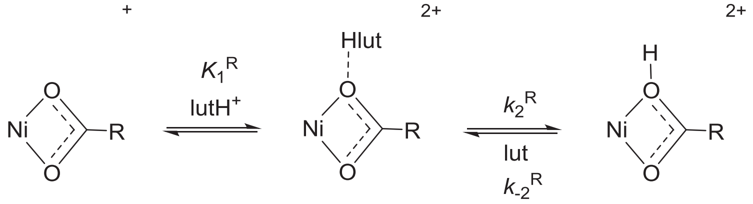


Figure 5. Mechanism of protonation of [Ni(O$_2$CR)(triphos)]$^+$.

Table 2. Elementary rate and equilibrium constants for reaction of $[Ni(O_2CR)(triphos)]^+$ with mixtures of $lutH^+$ and lut in MeCN at 25.0 °C.

R	$K_1^Rk_2^R$ ($dm^3\ mol^{-1}\ s^{-1}$)	k_{-2}^R ($dm^3\ mol^{-1}\ s^{-1}$)	$K_1^RK_2^R$	pK_a^R
Et	2.64×10^4	6.0×10^4	0.44	14.5
Ph	1.90×10^4	5.0×10^4	0.38	14.5

with mixtures of $lutH^+$ and lut corresponds to equation (4), the $K_1^R[lutH^+]$ term in equation (3) must make a negligible contribution to the denominator, even at the highest concentration of $lutH^+$ used, and hence $K_1^R \le 0.1/[lutH^+]_{max}$ and $K_1^{Et} \le 20$, and $K_1^{Ph} \le 10\ dm^3\ mol^{-1}$.

$$\mathrm{Rate} = \frac{\{K_1^Rk_2^R[\mathrm{lutH}^+]}{1 + K_1^R[\mathrm{lutH}^+]} + k_{-2}^R[\mathrm{lut}]\}[\mathrm{Ni(O_2CR)(triphos)}^+] \tag{3}$$

$$\mathrm{Rate} = \{K_1^Rk_2^R[\mathrm{lutH}^+] + k_{-2}^R[\mathrm{lut}]\}[\mathrm{Ni(O_2CR)(triphos)}^+] \tag{4}$$

The kinetics observed for the reaction between $[Ni(O_2CR)(triphos)]^+$ and $lutH^+$ in the presence of lut are consistent with simple protonation of the complex. However, the kinetics of the similar protonation reactions of $[Ni(S_2CMe)(triphos)]^+$ with mixtures of HCl and Cl^- indicate that, upon protonation, chelate ring-opening of the coordinated carboxydithionic acid occurs. This proposal is supported by DFT calculations, which indicate that protonation of the sulfur site in the equatorial position (but interestingly, not the axial sulfur) results in chelate ring-opening for all $[Ni(S_2CR)(triphos)]^+$. However, with the R = Et, Bu^n or Ph derivatives, proton transfer is rate-limiting. It is only for the R = Me complex that the protonation step is sufficiently fast that chelate ring-opening becomes rate-limiting [4]. It is entirely possible that $[Ni(O_2CR)(triphos)]^+$ also undergoes chelate ring-opening if the carboxylate is bidentate. However, there is no evidence for chelate ring-opening from the kinetics and so figure 5 shows only the simple protonation of $[Ni(O_2CR)(triphos)]^+$ and the coordination of the complex maintains its integrity throughout the reaction. Clearly, if chelate ring-opening does occur in $[Ni(HO_2CR)(triphos)]^{2+}$, then chelate ring-opening must also be an equilibrium reaction.

3.4. ***Rates of proton transfer***

The results of the protonation reactions of $[Ni(O_2CR)(triphos)]^+$, together with earlier results on $[Ni(S_2CR)(triphos)]^+$, allow us to compare: (i) the effect that the R substituent has on the rates of proton transfer to $[Ni(O_2CR)(triphos)]^+$ and (ii) the rates of proton transfer to analogous coordinated oxygen and sulfur sites in $[Ni(Y_2CR)(triphos)]^+$ (Y = O or S; R = Et or Ph).

The data in table 2 shows that the rates of proton transfer from $lutH^+$ to $[Ni(O_2CR)(triphos)]^+$, and from $[Ni(HO_2CR)(triphos)]^{2+}$ to lut, are affected little by the R substituent $\{(K_1^{Et}k_2^{Et}/K_1^{Ph}k_2^{Ph})^O = 1.4$ and $(k_{-2}^{Et}/k_{-2}^{Ph})^O = 1.2\}$. Studies on the reactions of $[Ni(S_2CR)(triphos)]^+$ with mixtures of HCl and Cl^- show that the rates of proton transfer in these systems are also rather insensitive to the nature of R $\{(K_1^{Et}k_2^{Et}/K_1^{Ph}k_2^{Ph})^S = 18$ and $(k_{-2}^{Et}/k_{-2}^{Ph})^S = 1.9\}$ [4].

It is not possible to make a direct comparison of the rates of proton transfer to [Ni(S_2CR)(triphos)]$^+$ and [Ni(O_2CR)(triphos)]$^+$ (R = Et or Ph) because the large differences in rates necessitates the use of different acids for the two different types of complexes. However, qualitative experiments allow an estimate of the differences in the rates of proton transfer to the analogous oxygen and sulfur sites. The reactions between anhydrous HCl (pK_a = 8.9 in MeCN) [9] and [Ni(O_2CR)(triphos)]$^+$ are complete within the dead time of the stopped-flow apparatus (2 ms), even when [HCl] = 1.0 mmol dm^{-3}, from which we can estimate $(K_1^R k_2^R)^O \geq 3 \times 10^5$ dm^3 mol^{-1} s^{-1}. For reactions of the analogous [Ni(S_2CR)(triphos)]$^+$ with HCl, the rates have been measured $\{(K_1^{Et} k_2^{Et})^S = 39.5$ and $(K_1^{Ph} k_2^{Ph})^S = 2.18$ dm^3 mol^{-1} s$^{-1}\}$ [4]. Consequently, protonation of oxygen in [Ni(O_2CR)(triphos)]$^+$ is at least 7.6×10^3 times faster than to the sulfur site in [Ni(S_2CR)(triphos)]$^+$. Comparison of the protonation of [Ni(O_2CR)(triphos)]$^+$ and [Ni(S_2CR)(triphos)]$^+$ by lutH$^+$ indicates that the difference in rates of protonation is even larger. The rates of the reactions between [Ni(O_2CR)(triphos)]$^+$ and lutH$^+$ (pK_a = 14.1 in MeCN) [11] have been measured (table 2), but there is no discernable reaction between lutH$^+$ (10 mmol dm^{-3}) and [Ni(S_2CR)(triphos)]$^+$ over at least 500 s, indicating $(K_1^R k_2^R)^S \leq 0.14$ dm^3 mol^{-1} s^{-1}. Consequently, in [Ni(Y_2CR)(triphos)]$^+$, protonation at Y = O is at least 1.4×10^5 times faster than to Y = S. This large difference in the rates of protonation of [Ni(Y_2CR)(triphos)]$^+$ is very different from the behavior observed with [Ni(YPh)(triphos)]$^+$ (Y = O, S or Se), where proton transfer by lutH$^+$ occurs at very similar rates ($k^O : k^S : k^{Se} = 1 : 12 : 9$) [3]. DFT calculations on the structure of the hydrogen-bonded precursor intermediate {[Ni(YPh)(triphos)]$\cdots$Hlut}$^{2+}$ reveal that although the acid can hydrogen bond with a geometry (bond lengths and angles) optimal for proton transfer, the structure of the square planar complex and in particular the bulky phenyl substituents on triphos do not allow much space for the lutH$^+$ to bind. Consequently, the acid may find it difficult to penetrate the array of phenyl substituents to achieve an optimal configuration, thus slowing the reaction. Consequently, the rates of proton transfer involving [Ni(YPh)(triphos)]$^+$ principally reflect the steric issues of lutH$^+$ accessing the Y site. Whereas in square planar [Ni(YPh)(triphos)]$^+$ there are two PPh$_2$ groups 90° from the Y site, in the five-coordinate [Ni(Y_2CR)(triphos)]$^+$ there is not so much congestion surrounding the Y donor because each PPh$_2$ group is subtended 120° away from the equatorial Y site. Consequently, the lutH$^+$ can access the Y sites in [Ni(Y_2CR)(triphos)]$^+$ more easily than in [Ni(YPh)(triphos)]$^+$ and thus the rates of proton transfer to [Ni(Y_2CR)(triphos)]$^+$ more reflect the nature of Y.

3.5. *The acidities of [Ni(HO$_2$CR)(triphos)]$^{2+}$*

The rate constants shown in table 2 allow us to calculate the equilibrium constant, $(K_1^R K_2^R)^O = (K_1^R k_2^R)^O/(k_{-2}^R)^O$, for the reaction shown in equation (1). These values together with the literature value of pK_a = 14.1 [11] for lutH$^+$ in MeCN allow calculation of $(pK_a^R)^O = 14.5$ for [Ni(HO$_2$CR)(triphos)]$^{2+}$ for both R = Et and Ph (table 2). The pK_as of free RCO$_2$H in MeCN are also essentially independent of the R substituent {EtCO$_2$H, pK_a = 22.6[†]; PhCO$_2$H, pK_a = 21.5 [12]}. These results indicate that RCO$_2$H coordinated to the {Ni(triphos)}$^{2+}$ site is about 8 pK_a units more acidic than the free acid.

A similar analysis of the kinetics of the reactions between [Ni(S_2CR)(triphos)]$^+$ and mixtures of HCl and Cl$^-$ shows that the $(pK_a^R)^S$ are also rather insensitive to the R substituent

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[†] Calculated pK_a (in water) using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2014 ACD/Labs), then correcting to the pK_a in MeCN using equations in reference 12.

$\{(pK_a^{Et})^S = 7.9$ and $(pK_a^{Ph})^S = 6.9\}$ [4]. The corresponding free RCS_2H also have similar pK_as (R = Et, pK_a = 13.4; R = Ph, pK_a = 13.2) (see footnote †), and these data indicate that, upon coordination, these acids increase their acidity by about six pK_a units. Comparison of the results for $[Ni(S_2CR)(triphos)]^+$ with those of the analogous $[Ni(O_2CR)(triphos)]^+$ indicates that the differences in acidities of RCS_2H and RCO_2H are similar irrespective of whether they are coordinated or free. Free RCS_2H are about nine pK_a units more acidic than free RCO_2H, while the coordinated RCS_2H are about eight pK_a units more acidic than coordinated RCO_2H.

4. Conclusion

This article reports kinetic studies on the protonation reactions of coordinated carboxylates in $[Ni(O_2CR)(triphos)]^+$ with mixtures of $lutH^+$ and lut. The proton transfer to these complexes from $lutH^+$, and corresponding deprotonation of $[Ni(HO_2CR)(triphos)]^{2+}$ by lut, are significantly slower ($k \sim 10^4$ dm^3 mol^{-1} s^{-1}) than the diffusion-controlled limit in MeCN ($k = 3.7 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) [13]. Using the kinetic data, the $(pK_a^R)^O = 14.5$ of the $[Ni(HO_2CR)(triphos)]^{2+}$ have been calculated.

Considering the results described herein, together with those of the analogous reactions of $[Ni(S_2CR)(triphos)]^+$, allow comparison of the protonation chemistry of analogous coordinated oxygen and sulfur sites. One significant difference between $[Ni(O_2CR)(triphos)]^+$ and $[Ni(S_2CR)(triphos)]^+$ is that the rates of protonation of the carboxylate are significantly (at least 1.4×10^5 times) faster than to the analogous carboxydithioate. In addition, comparison of the pK_as of $[Ni(HY_2CR)(triphos)]^+$ (Y = O or S) shows that the carboxydithioate is a much stronger acid than the corresponding carboxylic acids ($\Delta pK_a \sim 7.6$).

The results with $[Ni(Y_2CR)(triphos)]^+$ (Y = O or S) are quite different to those reported earlier for the analogous protonation chemistry of $[Ni(YPh)(triphos)]^+$ (Y = O, S or Se) [3], where the rates of proton transfer and pK_a^Y are insensitive to the nature of Y. We suggest that the proton transfer involving $[Ni(YPh)(triphos)]^+$ is principally affected by the bulky phenyl substituents on the triphos ligand interfering with the approach of the sterically demanding $lutH^+$ toward the Y site and attaining an optimal geometry within the hydrogen bonded precursor intermediate, $\{[NiYPh)(triphos)]\cdots Hlut\}^{2+}$. Consequently, the pK_a^Y for $[Ni(HYPh)(triphos)]^+$ (calculated from the rate constants for proton transfer) do not reflect the true acidities of the coordinated acids. Although we have been unable to determine the structure of $[Ni(O_2CR)(triphos)]^+$, X-ray crystallography of $[Ni(S_2CR)(triphos)]BPh_4$ shows the Ni coordination geometry is a trigonal bipyramid (figure 3). Accordingly, the Y sites in $[Ni(Y_2CR)(triphos)]^+$ are less congested, allowing $lutH^+$ easier access and so the rates of proton transfer more reflect the nature of Y. Consequently, the pK_as (calculated from the rate constants) are more likely to reflect the true difference in acidities of the coordinated acids.

It is interesting to note that although the rate constants for protonation of coordinated carboxylates (reported herein) are slower than the diffusion-controlled limit, they are still relatively fast, and certainly faster than the dissociation of the carboxylic acid in the Co(III) complexes reported earlier (figure 1) [1]. Consequently, relatively slow proton transfer to coordinated carboxylates could be a more widespread characteristic than has so far been appreciated.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

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References

[1] (a) T.J. Przystas, J.R. Ward, A. Haim. *Inorg. Chem.*, **12**, 743 (1973); (b) A.C. Dash, R.K. Nanda. *J. Inorg. Nucl. Chem.*, **38**, 119 (1976); (c) D. Smith, M.F. Amira, P.B. Abdullah, C.B. Monk. *J. Chem. Soc., Dalton Trans.*, 337 (1983); (d) Y. Kitamura, K. Yoshitani, T. Itoh. *Inorg. Chem.*, **27**, 996 (1988); (e) G. Pradhan, R.K. Nanda, A.C. Dash. *Transition Met. Chem.*, **14**, 309 (1989).

[2] (a) V. Autissier, W. Clegg, R.W. Harrington, R.A. Henderson. *Inorg. Chem.*, **43**, 3098 (2004); (b) V. Autissier, P.M. Zarza, A. Petrou, R.A. Henderson, R.W. Harrington, W. Clegg. *Inorg. Chem.*, **43**, 3106 (2004).

[3] A. Alwaaly, R.A. Henderson. *Chem. Commun.*, **50**, 9669 (2014).

[4] A. Alwaaly, W. Clegg, R.A. Henderson, M.R. Probert, P. Waddell. *Dalton Trans.*, **44**, 3307 (2015).

[5] W. Clegg, R.A. Henderson. *Inorg. Chem.*, **41**, 1128 (2002).

[6] K.L.C. Grönberg, R.A. Henderson, K.E. Oglieve. *J. Chem. Soc., Dalton Trans.*, 3093 (1998).

[7] (a) J. Catterick, P. Thornton. *Adv. Inorg. Chem. Radiochem.*, **20**, 291 (1977); (b) H. Wu, Y. Gao, K. Yu. *Transition Met. Chem.*, **29**, 175 (2004).

[8] K. Chandra, R.K. Sharma, B.S. Garg, R.P. Singh. *J. Inorg. Nucl. Chem.*, **42**, 187 (1980).

[9] (a) J.F. Coetzee. *Prog. Phys. Org. Chem.*, **4**, 45 (1967); (b) K. Izutsu. *Acid–Base Dissociation Constants in Dipolar Aprotic Solvents*, Blackwell Scientific, Oxford (1990).

[10] J.H. Espenson. *Chemical Kinetics and Reaction Mechanisms*, Vol. 45, McGraw-Hill, New York (1981).

[11] G. Cauquis, A. Deronzier, D. Serve, E. Vieil. *J. Electroanal. Chem. Interfacial Electrochem.*, **60**, 205 (1975).

[12] B.G. Cox. *Acids and Bases: Solvent Effects on Acid–Base Strength*, Oxford University Press, UK (2013).

[13] F. Wilkinson, A.F. Olea, D.J. McGarvey, D.R. Worrall. *J. Braz. Chem. Soc.*, **6**, 211 (1995).