

# Electro-catalytic Oxidation of 2-, 3- and 4-Picolines and of their Respective 1-Oxides Using a Polypyridine Complex of Ru(IV): Comparison with Toluene.

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2-, 3- e 4-picolinas, 2-, 3- e 4-picolinas-1-óxidos e cloretos de 1,2-, 1,3- e 1,4-dimetil-piridínio, junto com tolueno como composto de referência, foram submetidos a oxidações eletrocatalíticas pelo complexo de Ru(IV):  $[Ru^{IV}O(bpy)(trpy)](ClO_4)_2$  (bpy = bipyridina; trpy = tripiridina).

2-, 3- e 4-picolinas foram oxidadas aos correspondentes ácidos picolínico, nicotínico e isonicotínico com rendimentos de 52,5, 77,4 e 48,8% respectivamente. 2-, 3- e 4-picolinas-1-óxidos deram seus correspondentes 2-, 3- e 4-carboxi-piridinas-1-óxidos com rendimentos de 68,2, 49,2 e 63,4% respectivamente. Os cloretos de 1,2-, 1,3- e 1,4-dimetil-piridínio mostraram-se não reativos. Tolueno deu origem ao ácido benzóico com 40,3% de rendimento.

A determinação semi-quantitativa das velocidades foi feita com base nas curvas corrente *versus* tempo. As reatividades relativas e a inércia dos sais piridínicos estiveram de acordo com as previsões baseadas num mecanismo agora proposto "via" um intermediário radicalar inicialmente formado, com perda de um  $H^+$  e um elétron, seguido pela perda de um outro elétron dando um íon carbênio. Este reage com água originando os produtos de oxidação que foram obtidos.

Este mecanismo mostra um esquema geral de oxidação de compostos do tipo H-C-sistema  $\pi$ .

2-, 3- and 4-picolines, 2-, 3- and 4-picoline-1-oxides and 1,2-, 1,3- and 1,4-dimethylpyridinium chlorides, together with toluene as reference compound, were subjected to electro-catalytic oxidation conditions with the Ru(IV) complex:  $[Ru^{IV}O(bpy)(trpy)](ClO_4)_2$  (bpy = 2,2'-bipyridine; trpy = 2,2':6',2''-terpyridine).

2-, 3- and 4-picolines were oxidized to corresponding picolinic, nicotinic and isonicotinic acids in yields of 52.5, 77.4 and 48.8% respectively. 2-, 3- and 4-picoline-1-oxides gave correspondingly 2-, 3- and 4-carboxy-pyridine-1-oxides in yields of 68.2, 49.2 and 63.4% respectively. 1,2- 1,3- and 1,4-dimethyl-pyridinium chlorides were unreactive. Toluene gave benzoic acid in 40.3% yield.

Semi-quantitative determination of the velocities was made on the basis of the electric current versus time curves. The relative reactivities and the unreactivity of the pyridinium salts were in accordance with predictions based on a mechanism now proposed via an initially-formed radical intermediate, with loss of  $H^+$  and an electron; followed by loss of another electron giving a carbenium-ion intermediate. This reacts with water giving the observed oxidation products.

This mechanism indicates the generality of the oxidation of compounds containing the moiety H-C- $\pi$ -system.

**Key words:** polypyridyl complex of ruthenium; electro-catalytic oxidation.

## Introduction

The polypyridine complex of Ru(IV),  $[Ru^{IV}O(bpy)(trpy)](ClO_4)_2$  (I) (bpy = 2,2'-bipyridine; trpy = 2,2':6',2''-terpyridine) in aqueous medium promotes oxidation of C-H bonds in *inter alia* olefines,<sup>1,2</sup>arenes,<sup>3</sup> primary and second-

dary alcohols and diols<sup>4,5</sup>, allylic or vinylic ethers<sup>6</sup> giving aldehydes, ketones, carboxylic acids, esters and conjugated ketones.

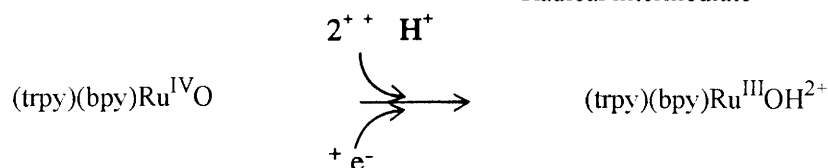
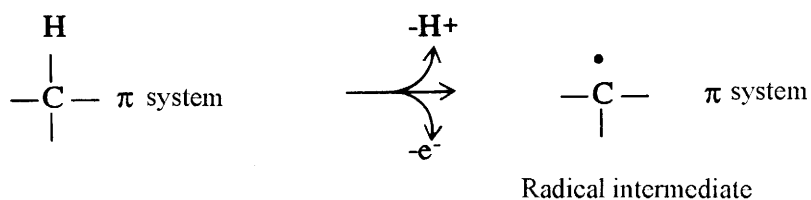
At pH 7, the formal potential for the Ru(IV) / Ru(II) couple is 0.56V (vs. SCE). In acting as an oxidant, the Ru(IV) complex (I) is reduced to a Ru(II) aqua complex *viz*,

$[\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{bpy})(\text{trpy})]^{2+}$  (II).<sup>7</sup> This can be re-oxidized to the Ru(IV) complex (I), in an electrolytic cell, by applying a potential of 0.8V through a platinum anode.

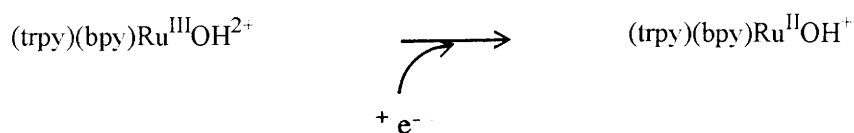
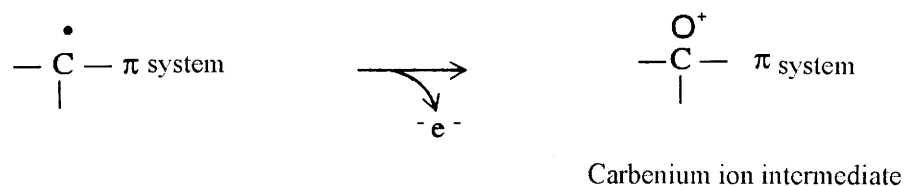
It is possible to isolate it and re-use it after large continuous use. The process is very economical because the stoichiometrically consumed reagent is water, while the reactions process at ambient temperature.

The oxidant has a high molecular weight and in some cases up to three equivalents of oxidant may be needed. Nevertheless in these conditions the process becomes electro-catalytic with use of only 1/30 to 1/40 of a molar equivalent of the Ru(IV) complex per molar equivalent of substrate: one equivalent corresponds to the transfer of two electrons.<sup>1,5</sup>

1<sup>st</sup> step redox reaction

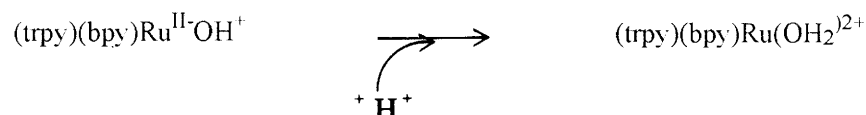
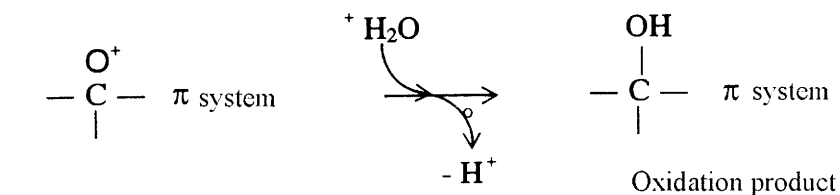


2<sup>nd</sup> step redox reaction



3<sup>rd</sup> step redox reaction

nucleophilic solvolysis



**Figure 1.** The subsequent oxidation to aldehyde and then to carboxylic acid follow pathways similar to that shown above.

From the redox potential data,<sup>7</sup> one can note that the potentials for the Ru(IV) / Ru(III) and Ru(III) / Ru(II) couples are so close (0.62V and 0.49V vs. SCE, respectively), and there is only a slight thermodynamic preference for the Ru(IV) as a one-electron oxidant. The proposed mechanism suggests that (I) is a two-electron oxidant toward organic substrates and the redox pathways involve the equivalent of hydride transfers<sup>8,9</sup>.

We associate this with stabilization of radical and/or carbenium ion intermediates. The carbenium ion formed by such oxidation is very readily attacked by water. In this way, primary, secondary and tertiary C-H functions give corresponding primary, secondary and tertiary alcohols. The primary and secondary alcohols suffer further oxidation<sup>4,5</sup>, without participation of water giving aldehydes and ketones respectively. The aldehyde then reacts with a third equivalent of oxidant with subsequent attack of water giving carboxylic acids. These posterior oxidation processes should occur more rapidly than the process forming alcohols. This is because both radicals and carbenium ion intermediates are expected to be additionally stabilised (see fig.1).

In electro-catalytic conditions, the observed current is proportional to the rate of the process<sup>10</sup>.

In controlled conditions, maintaining constant concentration of the Ru(IV) complex (I), substrate, buffer pH, temperature, electrode size, velocity of stirring, the *i* x *t* curves reflect the rate-limiting formation of electron-deficient carbon intermediate equivalent to hydride transfer,<sup>8,9</sup> and indicate the velocities of reaction of the various substrates, *i.e.* relative reactivities<sup>10,11</sup>.

Carrying out an exponential regression of the experimental data and carrying out a linear regression, when the correlations coefficients are close to unity, gives straight lines, the slopes of which or the half-lives indicate semi-quantitatively an order of reactivity for each class of substrates.

Such studies can be made directly while preparative oxidations are being carried out and are particularly useful. Reactions can be accompanied by knowledge of the numbers of Coulombs passed - either by integration of the *i* x *t* curve or reading the coulometer of the potentiostat.

This allows the process to be interrupted at any desired stage *e.g.*: to favour one of concurrent reactions. Again when there is more than one oxidation step, the reaction may be stopped at the desired stage<sup>1-5</sup>.

The present work constitutes a study of the oxidation of 2-, 3- and 4-picolines and of 2-, 3- and 4-picoline-1-oxides, referred to toluene as a standard substrate; while also confirming the unreactivities of 1,2-, 1,3- and 1,4-dimethyl pyridinium chlorides in the oxidation conditions used.

While there are several methods described for the oxidation of the picolines and their respective 1-oxides we know of none using indirect electrochemical methods such as with the mediation of Ru(IV) complexes. The present study shows that such an electro-catalytic process is possible and efficient, while there is biomedical interest in the carboxylic acids produced.

An important objective of the study was to support the general mechanism proposed by us that is based firstly on the inherent improbability of a simultaneous complete transfer of two electrons; recalling, in any case, that Ru(III) is a known oxidation state. The two steps electron--transfer

receives further support from the existence of close potentials for the couples Ru(IV) / Ru(III) and Ru(III) / Ru(II). Furthermore, the proposed radical and carbenium-ion intermediates gain stability by their linkage to a  $\pi$ -system. Clearly such general stabilization may be modified, favorably or otherwise, according to the specific nature and structure of the  $\pi$ -system.

The proposed mechanism predicts the formation of products which are experimentally observed. In addition, the reactivity order, predicted on the basis of this mechanism and of the known chemistry of pyridines and pyridine-1-oxides, corresponds well to experimentally observed reactivities.

For the compounds used in the present study the high reactivity of 4-picoline-1-oxide and to a lesser extent 2-picoline-1-oxide relative to the other substrates is of especial interest, bearing in mind that the hetero-aromatic N-oxide function has the ability to stabilize both electron-rich and electron-deficient reaction intermediates suitably placed in relation to it.

It is convenient to show the proposed mechanism in generic form, including the reduction of the Ru(IV) complex, to illustrate that it has much wider applicability than the present work.

Accompanying the overall organic reaction is the two electron reduction of  $[\text{Ru}^{\text{IV}}\text{O}(\text{bpy})(\text{trpy})]^{2+}$  to  $[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{bpy})(\text{trpy})]^{2+}$ . This gives the overall redox and stoichiometric balance.

Bearing in mind that substituent effects are greater in polar than in radical reactions the effects of substituents should be more marked in stabilization or destabilization of the carbenium ion intermediate.

## Results and Discussion

The choice of 2-, 3- and 4-picolines, their respective N-oxides, and 1,2-, 1,3- and 1,4-dimethyl-pyridinium chlorides, together with toluene as reference substrates, stemmed from synthetic and biomedical as well as mechanistic interest.

It is convenient to refer first to the unreactivity of the three dimethyl-pyridinium salts. This was forecast on the basis of the marked destabilization of the carbenium ion in-

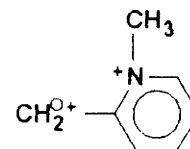


Figure 2.

termediates - greatest for the 1,2-dimethyl-pyridinium salt:

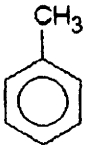
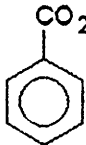
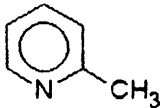
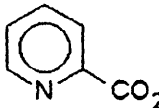
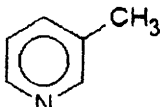
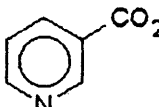
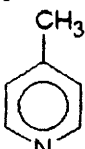
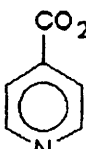
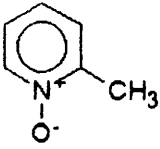
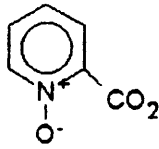
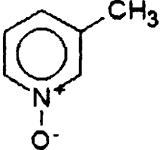
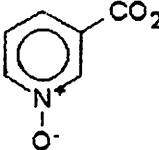

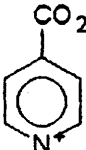
In testing for this, the *i* x *t* curves registered only residual currents.

The products and yields obtained by electro-catalytic oxidation of the other substrates are shown in Table 1.

The same experimental conditions were used for all the substrates and the yields of purified acids fell in the range 40 to 77%.

It is noteworthy but not surprising that in the oxidation of the picolines, the oxidation of the C-H bonds of the methyl group is preferred to electron-removal from the annular nitrogen atom.

**Table 1.** Catalytic Oxidation of picolines and picoline-1-oxides with  $[Ru^{IV}O(bpy)(trpy)]^{2+}$ <sup>a</sup>

Substrate <sup>b</sup>	Product	Yield <sup>c</sup>
 toluene <sup>d</sup>	 benzoic acid	40.3
 2-picoline <sup>e</sup>	 picolinic acid	52.2
 3-picoline <sup>e</sup>	 nicotinic acid	77.4
 4-picoline <sup>e</sup>	 isonicotinic acid	48.8
 2-picoline-1-oxide <sup>d</sup>	 2-carboxypyridine-1-oxide	68.2
 3-picoline-1-oxide <sup>d</sup>	 3-carboxypyridine-1-oxide	49.2
 4-picoline-1-oxide <sup>d</sup>	 4-carboxypyridine-1-oxide	63.4

<sup>a</sup> Catalyst concentration = 2.9mM.<sup>b</sup> Substrate concentration = 44.1 mM.<sup>c</sup> Based on the amount of oxidized substrate, calculated from the number of Coulombs passed, taking into account the number of equivalents necessary for total oxidation involving six electrons.<sup>d</sup> pH = 6.8<sup>e</sup> pH = 8.0

It needs to be recalled that the unshared electron-pair of such a nitrogen atom is in an  $sp^2$  hybridized orbital. Consequently, as is well known, such nitrogen atoms are substan-

tially less basic and nucleophilic than the nitrogen atoms of typical aliphatic amines, in which the unshared electron-pair is in an  $sp^3$  hybridized orbital. At the same time, the

first electron ionization energy is substantially greater for annular nitrogen. Furthermore, the intermediates which would form, viz.,  $\text{CH}_3\text{C}_5\text{H}_4\text{N}$  and  $\text{CH}_3\text{C}_5\text{H}_4\text{N}^+$  do not enjoy the stabilizing effect of the  $-\text{O}$ -system since the unshared electron orbital and vacant orbital respectively are orthogonal to the  $-\text{O}$ -system. An analogous difference is found in comparing  $\text{C}_6\text{H}_5\text{CH}_2^+$  with  $\text{C}_6\text{H}_5^+$ .

It is worth stressing that the high aqueous solubility of the hetero-aromatic oxidation products makes it difficult to isolate the full yields of the products. The recorded yields are thus not completely satisfactory.

The  $i \times t$  curves for each substrate were submitted to an exponential regression based on the equation  $f(x) = A \cdot e^{Bx}$ , which is related to the characteristic equation of a first order and homogeneous kinetics chemical reaction,  $i = i_0 \cdot e^{pt}$ .<sup>12</sup>

The correlation coefficients (R) obtained demonstrate the degree of concordance of experimental and theoretical  $i \times t$  curves. The nearer R is to unity the better the expression agrees with the experimental values. These can be compared among themselves when substrates of the same class are treated by the same process and using the same experimental conditions.

**Table 2.** Substrates, correlation coefficients R, initial current and  $t_{1/2}$  values.

Substrate	R	$i_{\text{initial}}$ (mA)	$t_{1/2}^a$ (hours)
2-picoline	.922	9.1	49.1
3-picoline	.883	10.3	40.8
4-picoline	.919	7.5	55.5
2-picoline-1-oxide	.967	4.8	41.5
3-picoline-1-oxide	.985	5.2	67.5
4-picoline-1-oxide	.992	22.6	9.0
toluene	.735	5.1	45.5

<sup>a</sup> from time range corresponding to three half-lives.

Table 2 shows  $i_{\text{initial}}$ , R and  $t_{1/2}$  values.

Only for 3-picoline and more particularly toluene were the R values less than 0.9. They were nevertheless included with the others in the calculation of half-lives ( $t_{1/2}$ ), based on theoretical data obtained from the exponential regression. The predication is the consistency between the mechanistic rationalization and comparison of the  $i \times t$  curves, experimental and theoretical, for all the substrates.

One notes first the order of reactivity 3-picoline toluene 2-picoline 4-picoline covering a modest range, from 40.8 to 55.5 hours.

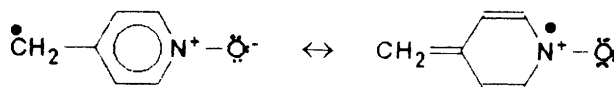
In clear contrast the picoline-1-oxides cover a much greater range - from 9.0 to 67.5 hours. Furthermore, 4-picoline-1-oxide is by far the *most* reactive of all the substrates measured while 3-picoline-1-oxide is clearly the *least* reactive. The values are conveniently positioned by the reactivity order: 4-picoline-1-oxide > 3-picoline 2-picoline-1-oxide > 3-picoline-1-oxide.

It is known that the ring nitrogen of pyridine is mildly activating for homolytic aromatic substitution ( $\text{S}_{\text{H}}\text{Ar}$ ) e.g. in radical phenylation; in the order ortho para meta. Analogously one can predict that in forming the radical intermediates in the electro-catalyzed oxidation of the three picolines and of toluene, the reactivity order should be: 2-picoline > 4-picoline > 3-picoline > toluene.

In forming the carbenium ion intermediate, however, the electron-deficient pyridine ring should result in some destabilization with the reactivity order: toluene > 3-picoline > 2- and 4-picolines.

Combining the effects on the two intermediates and giving more weight to the effects on the carbenium ion intermediate one expects the order: toluene > 3-picoline > 2-picoline > 4-picoline. A possible additional non-electronic effect is that of solvation which should favour the picoline reactions in comparison with that of toluene.

Combining these effects one has 3-picoline > toluene > 2-picoline > 4-picoline.



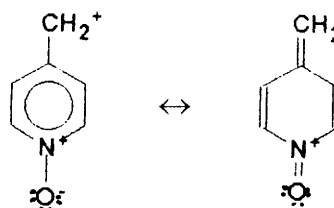
**Figura 3**

Turning next to the picoline-1-oxides one can forecast greater stabilization of the radical intermediates in the reactions of 2- and 4-picoline-1-oxides than for 3-picoline-1-oxide, toluene and the picolines. This is associated with the contiguity of the unpaired electron on ring nitrogen and the unshared pairs on the 1-oxide oxygen atom e.g.<sup>13</sup>

A notorious analogous effect is that of stabilization of radicals in ethers (followed by formation of alkylphenoxy radicals) on storage. Thus as regards the radical intermediate one has the order of stabilization 2- and 4-picoline-1-oxides > 3-picoline-1-oxide > toluene.

As regards stabilization of the carbenium ion intermediate the situation is quite special for 4-picoline-1-oxide and to a lesser extent 2-picoline-1-oxide due to the dual nature of the electronic effects of the hetero-aromatic-N-oxide function.

Whereas the positive charge on ring nitrogen destabilizes the carbenium ion intermediate electron donation by the negatively charged oxygen stabilizes it:



**Figura 4**

Clearly the compensation is more effective for 4-picoline-1-oxide which has the nitrogen atom more distant from the carbenium ion center and where conjugation is more extended.

No such stabilization occurs with the 3-picoline-1-oxide reaction which has marked destabilization by charged nitrogen. One thus has for the carbenium ion intermediate the reactivity order contribution: 4-picoline-1-oxide > 2-picoline-1-oxide > toluene > 3-picoline-1-oxide. This order is maintained when including also the contribution of effects on the radical intermediate.

Combining the analysis of the picolines and their respective N-oxides and toluene one has the predicted global reactivity order: 4-picoline-1-oxide > 2-picoline-1-oxide > 3-picoline > toluene > 2-picoline > 4-picoline > 3-picoline-1-oxide.

The experimental order is in accordance with the analysis, showing in fact a slight difference between 3-picoline and 2-picoline-1-oxide with  $t_{1/2}$  values of 40.8 and 41.5 hours respectively.

### Experimental

The electro-catalytic oxidations were carried out with a FAC-200 or PAR Model 273 potentiostat connected to a Varian Linear Recorder.

The cells used had 50ml capacity and contained a) a platinum gauze working electrode of 164 cm<sup>2</sup> in area (wire diameter 0.16mm) acting as anode. b) an auxiliary electrode in the form of a thin square platinum foil, 1 cm<sup>2</sup> in area, inside a tube of sintered glass, acting as cathode, c) a saturated calomel reference electrode and d) a Teflon-covered magnetic bar for stirring. The cell was closed with a Teflon cover with four holes - for the introduction of the electrodes and reagents.

Melting points (not corrected) were measured with a Thermolyne unit.

Infra-red spectra were registered on a Perkin-Elmer IR Spectrophotometer: both models 257 and 1430 were used. <sup>1</sup>H NMR spectra were registered on a Bruker AC-80 NMR Spectrometer using TMS as external reference. Spectra in the UV/visible range were registered on a Varian DMS 80 instrument. Mass Spectra were recorded on a Hewlett - Packard Model 5955 GC/MS instrument.

For chromatography in thin-layer or column modes silica-gel or alumina (Carlo Erba or Merck) were used.

2-, 3- and 4-picolines and their respective 1-oxides were all commercial products from Sigma and used without further purification. The 1,2-, 1,3- and 1,4-dimethyl-pyridinium chlorides were obtained as follows: a 50% excess of freshly prepared methyl iodide was added to the picoline dissolved in dry ether. The iodides were obtained as white precipitates. The anion was then exchanged because of the low potential of anodic oxidation of iodide ion. The dimethyl-pyridinium iodide in water was passed through a IR-120 AR column and eluted with water until the eluent was neutral to litmus. Then aqueous hydrochloride acid was passed through the column and the eluent evaporated. This gave the dimethyl-pyridinium chloride as a crystalline product with an average yield for the three salts of 33%.

The identities of the salts were confirmed by the usual methods.

*Electro-catalytic Oxidation Procedure:* each cell contained in a total volume of 34 ml of solution 0.25M phosphate buffer (pH 6.8 or 8.0) and  $1.0 \times 10^{-4}$  moles of Ru(II) salt (II) (whenever the substrates were poorly soluble in buffer solution, tert-butanol was used as co-solvent in an amount just enough to solubilize them). Then a potential of 0.8V versus SCE (saturated calomel electrode) was applied. That is sufficient to oxidize the Ru(II) complex to the Ru(IV) complex (I), with the deep red solution becoming pale-yellow. The substrates are unreactive under the experimental conditions in absence of the catalyst, i.e., under a potential of 0.8V vs. SCE the current were in the microampere range.  $1.5 \times 10^{-3}$  moles of substrate were added. This led to catalytic current in the milliamperage range.

The solution passed to deep red as oxidation occurred and the current was registered as a function of time.

The electrolyses were continued until the currents had fallen to values near 1mA or for a period long enough to obtain sufficient product for analysis.

During the electrolysis the maximum stirring rate of the magnetic unit was used. The temperature was maintained constant at 26°, in a temperature-controlled laboratory.

In the case of the three dimethyl-pyridinium salts only residual currents were observed, confirming their unreactivities.

In the case of the less reactive of the other substrates the solution develops a deep green color. This is due to a Ru(III) dimer:  $[(bpy)(trpy)Ru^{III}ORu^{III}(bpy)(trpy)]^{4+}$ . This results from disproportionation between the Ru(IV) and Ru(II) complexes which are both abundant because of the slowness of the oxidation process. In these cases a potential of 0.3V (versus SCE) was applied. The current reversed obtaining negative values then after a few minutes dropping to residual current value. The solution became deep red and the potential of 0.8V re-applied giving larger oxidation currents. It is well-known that Ru(III) - Ru(III) dimer is reduced to R(III) - Ru(II) at low potential, followed by a breakdown in the dimeric structure to give the associated Ru(II) monomers.<sup>14</sup>

After completion of the electro-chemical reactions, mixtures were treated as follows for oxidation of 2- and 4-picoline-1-oxides:

The picoline-1-oxide reaction mixtures were acidified and extracted in a liquid-liquid extractor (24 hours) using a mixture of diethyl ether and dichloromethane (9 : 1 V/V). This mixture does not extract the metal complex but does not extract all the hetero-aromatic carboxylic acids products due to their high aqueous solubility. The solvent was evaporated and the products purified by recrystallization from ethanol.

The reaction mixtures of the three picolines and of 3-picoline-1-oxide were evaporated to dryness at reduced pressure. The residue was extracted with hot methanol or hot benzene and filtered. The solution was poured into ether in order to precipitate the ruthenium complex, filtered and evaporated. The products were purified by recrystallization from ethanol.

For the toluene reaction, the benzoic acid produced was extracted with a mixture of diethyl ether-dichloromethane (9 : 1 V/V). The organic phase was washed with NaOH aq. (15%). The aqueous phase was carefully acidified with HCl. The benzoic acid which precipitated was filtered and dried.

The yields given in table 1 refer to purified products. They were identified and characterized by their m.ps. and the usual spectrophotometric and spectrometric techniques. The mass spectra were of particular value in characterizing the products.<sup>15</sup>

Except for 4-picoline-1-oxide with a  $t_{1/2}$  value of only 9.0 hours, the substrates had  $t_{1/2}$  values between 40.8 and 67.5 hours.

### Conclusions

In the electro-catalytic oxidations conditions used, with  $[Ru^{IV}O(bpy)(trpy)]^{2+}$  (I) a) 1,2-, 1,3- and 1,4-dimethyl-pyridinium chlorides are unreactive; b) 2-, 3- and 4-picolines form corresponding picolinic, nicotinic and isonicotinic

acids in yields of purified products 52.5, 77.4 and 48.8% respectively; c) 2-, 3- and 4-picoline-1-oxides form corresponding 2-, 3- and 4-carboxy-pyridine-1-oxides in yields of purified products 68.2, 49.2 and 63.4% respectively.

The observed reactivity order was 4-picoline-1-oxide > 3-picoline 2-picoline-1-oxide toluene 2-picoline 4-picoline 3-picoline-1-oxide. This order is not obvious, but is in fact predictable on the basis of the proposed mechanism. This envisages a pathway via an initially-formed radical, with loss of a hydrogen atom and a electron; followed by loss of another electron giving a carbenium ion intermediate. The latter reacts with water (nucleophilic solvolysis) giving the oxidation products isolated.

Accompanying this overall process the Ru(IV) complex (I) is reduced to  $[\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{bpy})(\text{trpy})]^{2+}$  (II) giving the complete stoichiometric balance.

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