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In Situ Vibrational Study of the Initial Steps during Urea Electrochemical Oxidation

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The electrochemical oxidation of urea has been studied by *in situ* Fourier transform infrared spectroscopy in supporting electrolytes of different pH. It has been found that the adsorbates and reaction products are strongly pH-dependent. In acidic solutions, the urea is adsorbed through the nitrogen atoms. A two-proton loss is proposed for the adsorption process, related to an excess reversible charge at the end of the hydrogen adsorption/desorption. Adsorbed CO is formed as a result of the hydrolysis of the urea molecule close to the platinum electrode. The main product detected has been CO_2. For neutral solutions, the urea molecule leads to the formation of CNO^- and $[N_2O_2]^{2-}$ ions at potentials in the double-layer region of the platinum electrode. At higher potentials, formation of NO_2 and NO_3^- have been detected. In alkaline media the coordination of adsorbed urea depends on the potential. At lower potentials urea is coordinated through a single NH_2 group, and at more anodic potentials the adsorbed urea changes to an adsorption through the oxygen atom.

1. Introduction

The electrochemical oxidation of urea has been the subject of some interest in the past due to the possibility of developing portable dialysis devices.[1] The effect of urea on glucose sensor devices or biofuel cells has been also the reason for some investigation of the urea oxidation.[2] The results found for the oxidation of urea on platinum electrodes in phosphate-buffered solutions (pH 7.4) have discouraged further development of such devices. The main reason is the formation of the byproducts together with CO_2 and N_2. The mass spectra (differential electrochemical mass spectrometry, DEMS) showed the formation of toxic products such as NO_2 and N_2O,[3] which have anesthetic effects. These products have been detected in a large range of potentials, thus making it difficult to use platinum electrodes for this purpose.

The electrochemistry of urea, however, presents some intriguing features, mainly in acidic media, which have attracted the interest of some researchers in recent years.

In acidic media, it has been observed that the contact of urea with polycrystalline platinum electrodes at low potentials produces an adsorbed residue whose oxidation proceeds at the same potential range as that of adsorbed carbon monoxide.[4] Interestingly this process takes place only after flushing the solutions containing urea for one containing only the supporting electrolyte. In the presence of dissolved urea no voltammetric oxidation peak at this potential range (∼600−900 mV) is observed.

On the other hand, when urea is present in solution, two additional voltammetric peaks of a reversible reaction with the centers at −0.2 and 0.1 V *vs* Ag/AgCl for polycrystalline platinum and one unusually sharp, very reversible volammetric peak at −0.05 V *vs* Ag/AgCl for the Pt(100) single crystal are observed.[5]

This behavior has been interpreted, mainly in the case of urea/Pt(100), as a first-order phase transition between a monolayer of urea in the more anodic potential range to a monolayer of adsorbed hydrogen in the more cathodic potential range.[5,6] A more detailed investigation using low-energy electron diffraction (LEED) shows a c(2×4) structure on the positive side of the sharp voltammetric peak, while on the cathodic side a (1×1) unreconstructed structure could be deduced.[6]

Auger spectra of the emersed electrode with a c(2×4) LEED pattern show that the urea molecule is preserved with the C═O and C−N bonding, but the N−H bond cleavage could not be excluded.[6]

In the case of polycrystalline platinum, the anomalous voltammetric peak observed at −0.2 V could have its origin on some kind of phase transition, although the polycrystalline nature of the electrode makes it difficult to describe this phase transition or even to detect an ordered layer as in the case of Pt(100). On the other hand, it seems to us that a faradic charge transfer, as already proposed for the voltammetric reversible peak,[5] does not rule out phase transition effects. In alkaline media, the urea seems to be more stable than in acidic media at low potentials. To our knowledge, no spectroscopic identification of the products of urea oxidation in alkaline media has been reported so far. It is expected that the main products are N_2 and CO_3^{2-}, but side reactions can produce some other byproducts, as in the case of neutral media.

In the investigation of adsorbed urea and of the initial stages of urea oxidation, no vibrational data have been reported so far. Specular reflectance IR spectra can give some idea about the type of coordination of the adsorbed urea molecule, albeit nitrogen coordination has been anticipated by other authors.[5,6]

It is the objective of this work to explore the possible products and adsorbates formed during the initial steps of the urea oxidation on platinum electrodes in acidic, neutral, and alkaline media by using *in situ* Fourier transform infrared spectroscopy (FTIR) measurements to identify reaction products and intermediates.

2. Experimental Section

The *in situ* FTIR experiments were carried out using a BOMEM DA8 infrared spectrometer, equipped with a nitrogen-cooled mercury cadmium telluride detector. The electrochemical cell used for both cyclic voltammetry and *in situ* IR spectroscopy was made of polytetrafluoroethylene and equipped with a CaF_2 prismatic window with 60° beveled faces.

A polycrystalline platinum electrode with a diameter of 10 mm was used for the spectroscopic experiments. A platinum wire with a small sphere at the extremity was used for the

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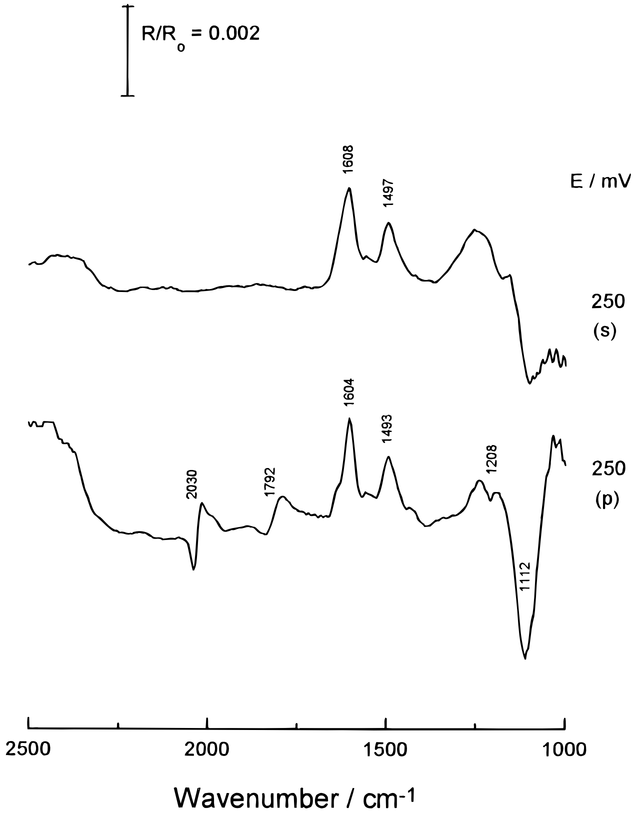

Figure 1. *In situ* reflection−absorption spectra of the platinum electrode in a solution containing 0.1 M urea in 0.1 M $DClO_4$ in D_2O obtained with s-polarization (upper spectrum) and p-polarization (lower spectrum): reference potential, −0.16 V; sample potential, 0.25 V; spectral resolution, 8 cm^{-1}.

electrochemical experiments. A platinum flat ring was used as the counter electrode; Ag/AgCl was used as the reference electrode. All potentials are referred to this electrode if not otherwise indicated.

Solutions were prepared from Merck Suprapur or P. A. chemicals and Millipore Milli Q water. Solutions of 0.1 M $HClO_4$ + 0.1 M H_4N_2CO, 0.1 M KF + 0.1 M H_4N_2CO, and 0.1 M KOH + 0.1 M H_4N_2CO were used for acidic, neutral, and alkaline media investigations, respectively. For the spectroscopic experiments, deuterated reagents have been used.

The *in situ* FTIR spectra were obtained by stepping the potential between the reference and sample potential progressively, *i.e.* after each measured potential the electrode was stepped to the reference potential. Each spectrum corresponds to 512 scans. The reference potential was set at −0.16 V for the acidic and neutral solutions and −0.75 V for alkaline solutions. Spectra were computed as the reflectance ratio R/R_0 (sample/reference). This procedure results in positive bands due to the loss of solution species and negative bands due to formation of new species.

3. Results and Discussions

3.1. Oxidation of Urea in Acidic Solutions. Figure 1 shows the *in situ* reflection−absorption spectra of the platinum electrode in the presence of 0.1 M urea solution in 0.1 M $DClO_4$ in D_2O using s- and p-polarized radiation. The use of s- and p-polarized radiation allows the distinction between bands due to adsorbed species and those of species dissolved in solution, since s-polarized radiation does not interact with molecules adsorbed at the electrode.

The spectra obtained with s-polarized light shows the typical bands of urea in the D_2O solution pointing upward, namely the bands centered at 1610 and 1490 cm^{-1}. These bands have been assigned to the C=O and asymmetric $C-N_2$ stretching vibrations.[7] The fact that the bands are pointing upward in the case of the R/R_0 spectra implies that urea is consumed when the electrode potential is changed from −0.16 V to the sample potential at 0.25 V *vs* Ag/AgCl.

The p-polarized light spectrum shows the same bands pointing upward due to the urea loss from solution together with two bipolar bands located at 2030 and 1792 cm^{-1}. These two bands are located at the position of adsorbed CO in the a-top and multicoordinated form at polycrystalline platinum electrodes. The bipolar nature of the bands means that the urea molecule decomposes in acid solution close to the electrode. Adsorbed CO is then formed as an intermediate species due to the urea hydrolysis. It is well known that urea hydrolyzes more easily in acidic media than in neutral media. However, CO_2 and ND_4^+, due to purely chemical hydrolysis, in solution have not been detected during the time scale of the experiments. Thus, it is very likely that the platinum surface catalyzes the urea decomposition, with CO as an adsorbed reaction intermediate. CO_2 has been detected only for potentials above 0.45 V originating from the electrochemical decomposition of urea. Another possibility is that at low potentials the CO_2 produced by hydrolysis is reduced to adsorbed CO at the platinum surface.

A close comparison of the two spectra shows a shoulder located at 1632 cm^{-1} for the case of the p-polarized light only, indicating that this shoulder can be assigned to some adsorbed species. To separate this band from the band of dissolved urea depletion in the thin electrolyte layer, we can carry out a difference spectrum between the s- and p-polarized light. To do so, we need to scale the s-polarized spectrum to the same intensity as that of the p-polarized spectrum. Since the band located 1490 cm^{-1} has the same shape in both spectra, we can use it to normalize the intensity of both spectra. The two spectra are then ratioed to eliminate the upward pointing bands at 1610 and 1495 cm^{-1} in order to reveal the shoulder more in detail. As can be seen in the spectra of Figure 2, a very well-defined potential-dependent band between 1617 and 1629 cm^{-1} can be identified.

It has been observed that this adsorbate presents a reversible behavior, since the spectral band disappears when the electrode potential is made more negative. The presence of this band can be related with the suggestion based on voltammetric experiments that some reversibly adsorbed species at the platinum electrode in acidic media is present when urea is present in solution. We reproduce in Figure 3 the cyclic voltammogram of the platinum electrode in a 0.1 M $HClO_4$ solution without and with urea in solution. The result is basically the same as that reported by Wiekowski et al.,[5] showing an excess of adsorption/desorption charge in the presence of urea. At higher urea concentrations the same qualitative behavior is observed, but an overall decrease in the adsorption/desorption of hydrogen can be observed in Figure 3b for 0.2 M H_2NCONH_2 in solution. This overall decrease is related to the formation of adsorbed CO, as demonstrated by the spectrum with p-polarized light in Figure 1. The adsorbed CO blocks the sites for hydrogen adsorption. However, the reversible peak located at 0.07 V *vs* Ag/AgCl is observed as well, indicating the presence of the reversibly adsorbed species.

The potential-dependent band centered between 1619−1629 cm^{-1} is located in the typical range for C=O stretching vibrations. Platinum−urea complexes coordinated *via* nitrogen present a C=O band at 1715 cm^{-1},[8] a wavenumber *ca.* 30 cm^{-1} higher than that of the C=O stretching vibration of free urea (1683 cm^{-1}). For deuterated urea, the mode with the predomi-

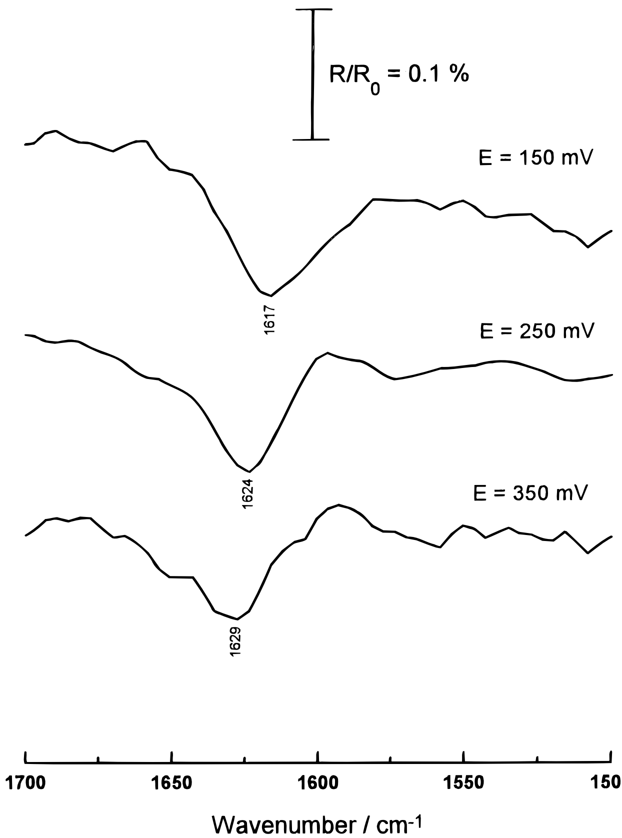

Figure 2. Spectra obtained from the ratio between s- and p-polarized radiation for different electrode potentials. The s-polarized radiation spectra were scaled to the same intensity as that of the p-polarized light spectra.

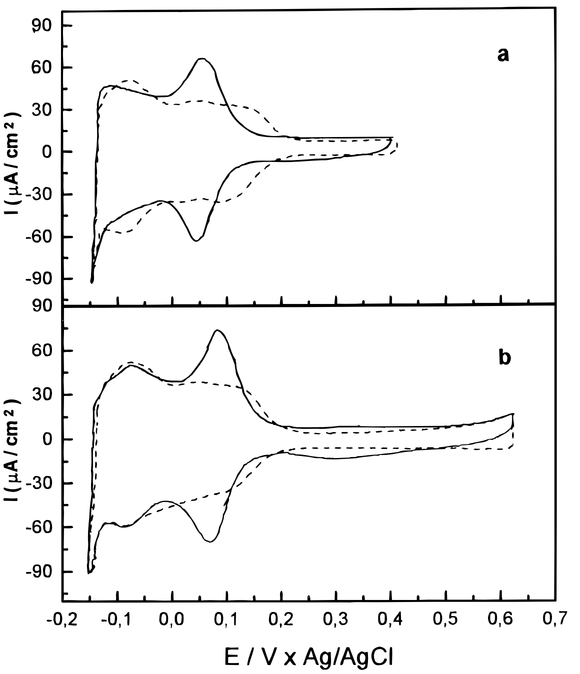

Figure 3. Cyclic voltammograms of the polycrystalline platinum electrode in 0.1 M $HClO_4$ (dashed lines) and containing 0.2 M H_2NCONH_2 (full line) (charge increase upon urea introduction, 25 μC cm^{-2}) (a) and 5 × 10^{-4} M H_2NCONH_2 (charge increase upon urea introduction, 53.6 μC cm^{-2}) (b) at 50 mV s^{-1}.

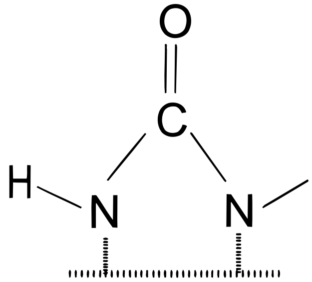

Figure 4. Schematic representation of the most probable structure for adsorbed urea on a polycrystalline platinum electrode in acidic solutions.

nance of C=O stretching vibration is located at 1610 cm^{-1}. The strong shift of the 1683 cm^{-1} band upon deuteration is due to the coupling of this vibration with NH_2 deformation, as stated by Yamaguchi et al.[7] The surface-coordinated urea has the band center for the C=O vibration at *ca*. 10−20 cm^{-1} higher than that for the same mode of free deuterated urea. Thus, the difference in band shifts between adsorbed urea and urea complexes are not very different.

Although the band shift upon coordination observed in the spectrum of Figure 2 is lower than that of the platinum complexes, there is no *a priori* reason to believe that for adsorbed urea the same band shift should be expected, as discussed below.

The excess charge for the hydrogen desorption from polycrystalline surfaces when urea is present in solution gives a value of 53.6 μC cm^{-2}. Radiotracer determination of the urea adsorption coverage for the same solution concentration up to 0.35 V *vs* reversible hydrogen electrode (RHE)[9] gives 2.5 × 10^{-10} mol cm^{-2}. If we consider that adsorbed urea occupies two adsorption sites, the excess charge obtained above gives 2.8 × 10^{-10} mol cm^{-2} if two electrons are transferred per molecule upon urea adsorption. If two electrons are transferred for each adsorbed molecule, it is sound to suppose that two protons are released per urea molecule, giving an adsorbed molecule with the formula HNCONH. In this case, the most likely geometry for the adsorbed molecule is as shown in Figure 4, where the urea molecule loses two protons and is adsorbed *via* two nitrogen atoms, in agreement with the spectroscopic data.

The partial oxidation of the adsorbed urea (accompanied by the two-proton loss) could rationalize this lower band shift compared to that of the Pt/urea complexes. *Ab initio* calculation of the vibrational spectrum of H_2NCONH_2 and HNCONH gives a strong decrease of the vibrational mode where the C=O displacement dominates. Namely, for the calculated spectrum the neutral urea has this mode at *ca*. 1900 cm^{-1}, while for the urea without two protons this mode lies at *ca*. 1250 cm^{-1}. The theoretical value for this mode lies too high as compared to the experimental result, but the relevant result here is that the proton loss leads to a strong decrease in band frequency for the free urea. It could be expected that such effect also occurs for adsorbed urea. It is worthwhile to say that the overall intensity decreases upon proton loss, according to the calculations. Attempting to explain such a low band shift for the adsorbed urea, we need to consider the electronic charge density over the atoms in the molecule. The *ab initio* calculation gives a decrease in the electronic density on the oxygen atoms from −0.61 to −0.49 for the free urea molecule. The partial oxidation of the adsorbed urea thus decreases the overall charge density of the molecule, even after the proton loss to maintain the neutrality of molecule. The lower electronic density over the oxygen atoms should cause a decrease in bond order, thus producing a lower band shift as compared to the platinum complexes.

The observed band position corresponds to a mean coverage of *ca*. 0.2, considering two adsorption sites per adsorbed molecule. Since both lateral interactions and the electric field

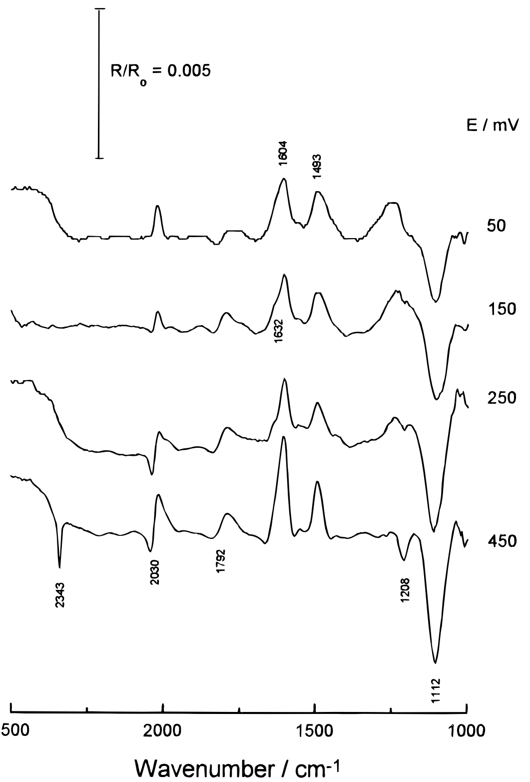

Figure 5. *In situ* reflection−absorption spectra of the platinum electrode in a solution containing 0.1 M urea in 0.1 M $DClO_4$ in D_2O obtained with p-polarization at the different electrode potentials indicated: reference potential, −0.16 V; spectral resolution, 8 cm^{-1}.

at the interface shift the band to higher wavenumbers, it would be expected that the singleton frequency at zero field is even smaller than the observed value.

The set of spectra at different potentials is presented in Figure 5. At all potentials a-top and multicoodinated adsorbed CO are present, and the shoulder assigned to the adsorbed urea is shifted to higher wavenumbers at more anodic potentials. At 0.45 V it is possible to observe the production of CO_2, originating from the electrochemical oxidation of the urea molecule in solution. N_2 is also produced, as can be seen by the DEMS experiment in Figure 6, where the production of N_2 follows the production of CO_2.

3.2. Oxidation of Urea in Neutral Media. The spectra of Figure 7 show the oxidation of urea at different potentials. The reference potential in this case has been taken in the double-layer region, since the desorption into the thin solution layer causes drastic changes in the pH for neutral solutions.

The main feature at low potentials (below 250 mV) is located at 2161 cm^{-1} and can be assigned to the CNO^- ion, resulting from the oxidation of the urea molecule. For the spectra at 50, 150, and 250 mV another feature at about 1608 cm^{-1} due to the consumption of urea from the solution can be detected. At 250 mV the CNO^- band decreases in intensity, and another positive band located at 1418 cm^{-1} can be detected. This positive band grows at 350 mV.

For more clarity the spectrum obtained at 350 mV has been reproduced in Figure 8, together with a spectrum obtained with s-polarized light at the same potential.

Practically all observed bands are present in both spectra. The band at 2161 cm^{-1} in the p-polarized light spectrum is much weaker in the s-polarized spectrum, but the band position allows the assignment of this band to dissolved OCN^- (see discussion below).

The band at 1418 cm^{-1} is an upward pointing band, meaning that this species is consumed at 0.35 V. This band cannot be

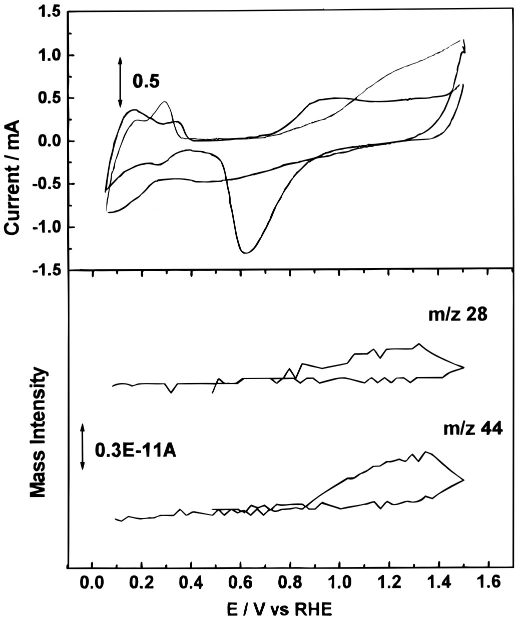

Figure 6. Cyclic voltammograms obtained during a voltammetric cycle of an electrodeposited platinum electrode in 0.1 M $HClO_4$ and for the oxidation of 0.1 M urea in $HClO_4$ aqueous solution (upper panel). On line simultaneous detection of *m*/*z* 44 (for CO_2) and 32 (for N_2) during the electrochemical oxidation of 0.1 M urea in 0.1 M $HClO_4$.

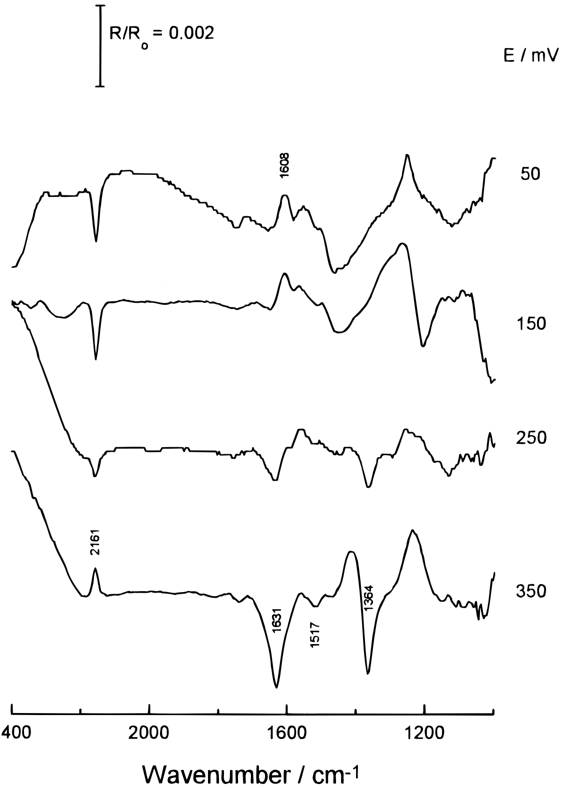

Figure 7. *In situ* reflection−absorption spectra of the platinum electrode in a solution containing 0.1 M urea in 0.1 M KF in D_2O obtained with p-polarization at the different electrode potentials indicated: reference potential, −0.16 V; spectral resolution, 8 cm^{-1}. The reference potential was taken in the “double-layer” region to avoid large pH changes in the thin layer.

assigned to the urea molecule, which means that at the reference potential (−0.16 V) the urea decomposes generating some dissolved product, which is consumed at more positive potentials. s-Polarized light indicates that they are due to dissolved species.

It is important to remark that the 1631 cm^{-1} band occurs at

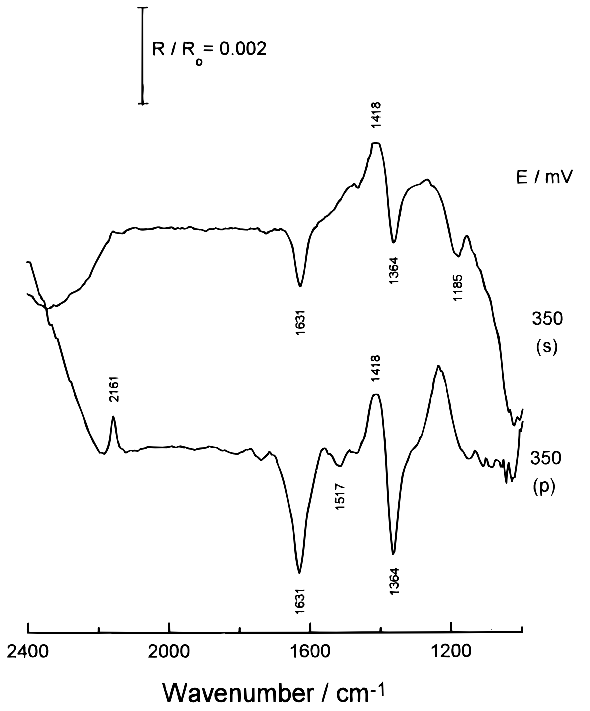

Figure 8. *In situ* reflection−absorption spectra of the platinum electrode in a solution containing 0.1 M urea in 0.1 M KF in D_2O obtained with s- and p-polarization at 0.35 V: reference potential, −0.16 V; spectral resolution, 8 cm^{-1}.

the same band position as the C═O stretching vibration wavenumber of the adsorbed urea in acidic media. To distinguish both products, we make use of the surface selection rule. The surface selection rule asserts that s-polarized light does not interact with adsorbed species. Because in neutral media the 1631 cm^{-1} band is also observed with s-polarized light, this feature is assignable to dissolved products, in contrast with acidic media, where this band is not observed with s-polarized light. Using the surface selection rule, the 1418 and 1364 cm^{-1} bands are equally due to dissolved products.

The band centered at 1418 cm^{-1} can be assigned to the trans $[N_2O_2]^{2-}$ ion, which presents the symmetric N−O stretching at 1419 cm^{-1} in the solid state.[8] Another band in the spectral window, above 1050 cm^{-1} (the cutoff of the CaF_2 prismatic window), due to the N−N stretching at 1121 cm^{-1} is expected to be very weak and difficult to observe.

The products formed present basically two bands, one at 1631 cm^{-1}, which can be assigned to the dissolved nitrogen-containing species by taking into account the spectral range in which they appear.

At this potential range, it is reasonable to expect N_2O, NO, NO_2, and NO_3^- as oxidation products, moreover if we take into account that $[N_2O_2]^{2-}$ is the intermediate product. Using DEMS, Bolzan and Iwasita[3] detected N_2O and NO_2. Detection of nitrate ions is not possible by DEMS.

N_2O presents bands at 2224 and 1285 cm^{-1} which are not observed in the spectra of Figure 7. On the other hand, the antisymmetric stretching mode of NO_2 presents one band at 1610 cm^{-1} . The symmetric stretching, which is expected at 1318 cm^{-1}, is hardly observed even in the gas phase.[8] The closeness between the expected band for NO_2 and the observed spectral feature at 1631 cm^{-1} allows a tentative assignment of this band to dissolved NO_2. Finally the band observed at 1364 cm^{-1} lies very close to the expected degenerate stretching vibration of the nitrate ion. Therefore, the products which better fit the bands observed in the spectra of Figure 7 are NO_2 and NO_3^-.

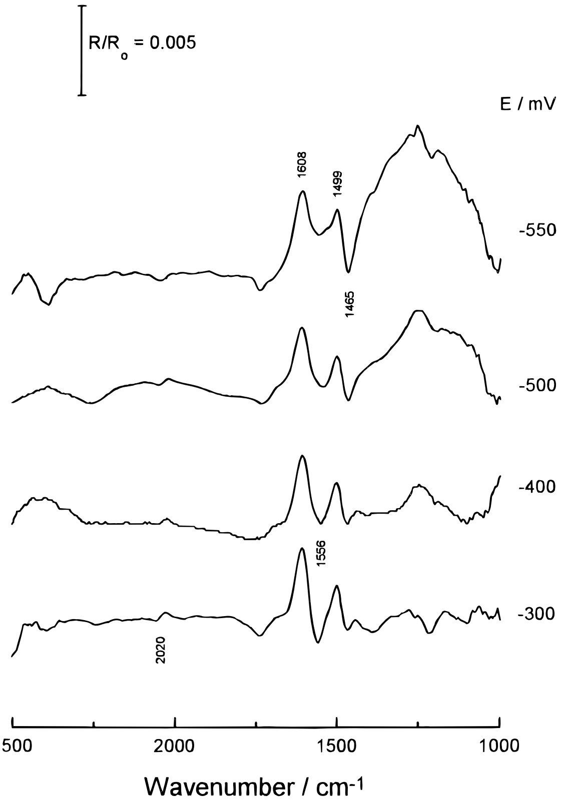

Figure 9. *In situ* reflection−absorption spectra of the platinum electrode in a solution containing 0.1 M urea in 0.1 M KOD in D_2O obtained at the different electrode potentials indicated in the figure: reference potential, −0.75 V; spectral resolution, 8 cm^{-1}.

It is very likely that the $[N_2O_2]^{2-}$ ion disproportionates to give NO_2 and NO_3^-, according to the overall electrochemical oxidation:

$$[N_2O_2]^{2-} + 3H_2O \rightarrow NO_2 + NO_3^- + 6H^+ + 7e \qquad (1)$$

3.3. Adsorption of Urea in Alkaline Media. In alkaline solution the contact of urea with the electrode produces a very small amount of adsorbed CO, as can be observed in the spectra of Figure 9. On the other hand the consumption of urea from solution during the step from −0.75 to −0.55 V can be clearly detected in all spectra.

Parallel to the consumption of urea, it is possible to observe another interesting spectral feature, which changes with the applied potential. A strong band located at 1456 cm^{-1} at potentials below 0.5 V can be observed. This band decreases in intensity and practically vanishes for potentials higher than −0.4 V. Simultaneously another feature located between the two bands of urea in solution can be observed for potentials higher than −0.4 V.

The band located at 1556 cm^{-1} is present only with p-polarization, as in Figure 10, at −0.3 V. It can be concluded that the band at 1556 cm^{-1} is due to some adsorbed species. The band at 1465 cm^{-1} has not been observed with s-polarized light as well, thus it should also be an adsorbed species.

The evolution of the spectra of Figure 9 indicates that the adsorbed species changes the allowed spectral feature, which indicates either a change in the chemical identity of the adsorbate or a change in symmetry without changing the chemical nature of the adsorbed species.

The assignment of spectral features of adsorbed species can be done by analyzing similar coordination compounds. A good

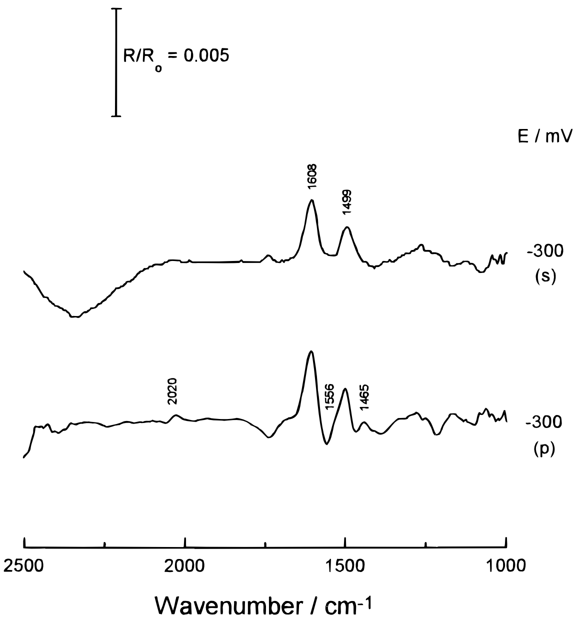

Figure 10. *In situ* reflection−absorption spectra of the platinum electrode in a solution containing 0.1 M urea in 0.1 M KOD in D_2O obtained with s- and p-polarization at −0.3 V: reference potential, −0.75 V; spectral resolution, 8 cm^{-1}.

correlation between adsorbed ions and molecules and ligands in inorganic complexes has been found.[11,12]

In inorganic complexes both NH_2 (or nitrogen) and oxygen coordination of urea to the metallic center are known. It is likely that these two kinds of coordination are also possible on surface.

Urea/platinum complexes present nitrogen coordination with the symmetric CN stretching located at 1020 cm^{-1}, the unsymmetric CN stretching at 1395 cm^{-1}, and C═O stretching at 1715 cm^{-1}. On the other hand urea/chromium complexes present the oxygen-bonded urea coordinated to the metallic center with the symmetric CN stretching at 1020 cm^{-1} and the unsymmetric and the C═O stretching at *ca.* 1505 cm^{-1}.

The feature observed at lower potentials at 1465 cm^{-1} fits relatively well with that of the unsymmetric CN stretching of nitrogen-bonded complexes, while the 1556 cm^{-1} feature is closer to that of the C═O stretching of oxygen-bonded complexes.

The unsymmetric CN stretching mode of a C_{2v} molecule displays the dipole moment displacement (the dynamic dipole moment) perpendicular to the molecular axis. Therefore, it would be forbidden in the case of a molecule coordinated by two nitrogen (or NH_2) groups. One possibility would be that the urea molecule is adsorbed through only one NH_2 group and is tilted on the surface. In this case the molecule loses the C_{2v} symmetry. In the case of the CN vibration, the number of spectral features remains the same, since no degenerate modes are present for the C_{2v} symmetry.

The important result is that the axis through the C═O bonding for a tilted molecule is almost parallel to the surface and the dynamic dipole moment is almost perpendicular to the surface. In this case the mode, which was the unsymmetric stretching vibration in the C_{2v} symmetry, is allowed by the surface selection rule and can be detected. On the other hand, the C═O stretching vibration should present a very small component perpendicular to the surface and should be hardly observable.

On the other hand, the oxygen-end-down molecule presents again the C_{2v} symmetry, where the C═O stretching is allowed while the unsymmetric CN stretching is forbidden by the surface selection rule. The symmetric CN stretching is a very weak band for urea in solution and it should be difficult to be observed. In the present case, the D_2O solvent probably encloses this band, making its detection even more difficult.

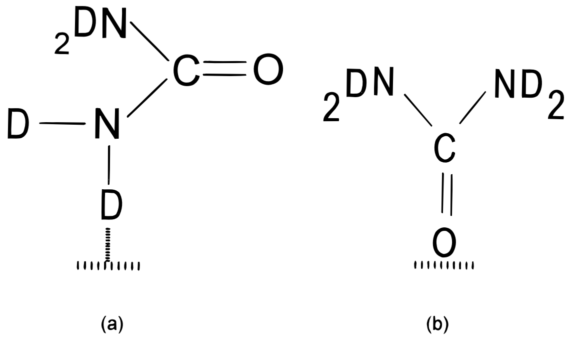

Figure 11. Schematic representation of the most probable structure for adsorbed urea on platinum electrodes in alkaline solution. Structure (a) is for potentials below −0.40 V and structure (b) for potentials above −0.40 V.

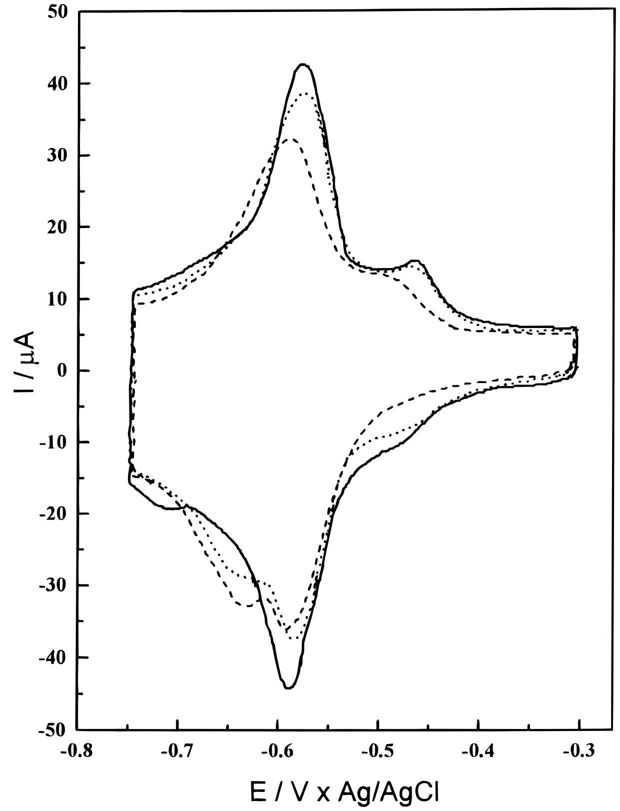

Figure 12. Cyclic voltammogram at 50 mV s^{-1} of the polycrystalline platinum electrode in 0.1 M NaOH (solid line) and 0.1 M NaOH containg 6 × 10^{-3} M H_2NCONH_2: first cycle after urea introduction (•••) and second cycle (---).

In Figure 9, urea is adsorbed *via* one of the NH_2 groups at potentials lower than −0.4 V, and for potentials higher than −0.4 V the molecule rotates to be adsorbed *via* oxygen atoms, according to the scheme of Figure 11.

In the case of acidic media, the proposed adsorption structure includes a charge transfer with the loss of two protons per molecule. In the case of alkaline media, unfortunately, it is not possible to detect charge transfer by cyclic voltammetry as can be seen in Figure 12. Furthermore the total hydrogen adsorption/desorption charge decreases with time, indicating that probably adsorbed CO is formed. This indication is supported by the small bands in the spectra of Figure 9. In conclusion, it is difficult to assert if charge transfer takes place or not when urea is adsorbed in alkaline media.

In the spectra of Figure 8, a weak feature can be seen at *ca.* 1750 cm^{-1}. This band is not potential-dependent, and in Figure

9 it appears as an upward pointing band in the spectrum with s-polarized light. The most likely explanation for this band is that it is due to some instrumental drift. In the spectrum of the beam splitter, a strong band is observed at this position. Note that the other spectral features observed are located in zones free of the beam splitter bands.

4. Concluding Remarks

The products and intermediates during the electrochemical oxidation of urea are strongly pH-dependent. In acidic and alkaline solutions the presence of CO resulting probably from the slow hydrolysis is detected even at very low potentials.

A reversibly adsorbed urea molecule is also observed for acidic and alkaline solutions. The adsorption geometry depends on pH. In acidic media the urea is probably adsorbed through the nitrogen, following a charge transfer with the loss of two protons. In alkaline solutions the urea is first adsorbed through one of the two NH_2 groups, producing a tilted molecule on the surface. At more positive potentials (possibly more positive than the point of zero charge) the molecule is flipped, and the final adsorption is an oxygen-end-down adsorbed urea molecule. The main products observed in acidic media are CO_2 and N_2. In neutral media no adsorbed molecule has been detected, possibly due to the high reference potential used. The main products are CNO^- and $[N_2O_2]^{2-}$ ions in solution for lower potentials and NO_2 and NO_3^- when the potential is made more positive.

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