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Ionization Reaction in Iodine/Pyridine Solutions: What Can We Learn from Conductivity Measurements, Far-Infrared Spectroscopy, and Raman Scattering?

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In nonpolar solvents, iodine interacts with pyridine to form a stable molecular complex Pyr*I_2. In binary mixtures, and more generally in polar solvents, the I_2/pyridine complex dissociates to form ionic species. Two different ionization mechanisms are proposed. It has been found that (1) the first reaction, fast (characteristic time ranging from picoseconds to nanoseconds), is reversible and favored by an increase of the polarity of the medium and/or a decrease in temperature and (2) the second process, which reaches equilibrium very slowly (few days), is irreversible and favored by an increase of the donor strength and/or of the temperature.

1. Introduction

The complexation reaction between iodine and pyridine in solution has been widely investigated in order to elucidate the reaction sequence in this sytem. It is well-known[4] that in nonpolar solvents, iodine reacts with pyridine to form a stable molecular complex. The chemical reaction can be written as

$$\mathrm{Pyr} + \mathrm{I_2} \rightleftarrows \mathrm{Pyr{*}I_2}$$

with an equilibrium constant, $K_c \approx 150\ \mathrm{dm^3\ mol^{-1}}$ at room temperature.

However, in the binary mixtures of I_2 and pyridine and more generally in polar solvents, this complex dissociates to form ionic species. Indeed, in 1933, Audrieth and Birr[1] showed that the binary mixtures of I_2 and pyridine displayed high electrical conductivity, probably due to the dissociation of the iodine molecule into ions whose concentrations slowly increase with time to asymptotic values. Since that time, several investigators have tried to elucidate the nature of these ionic solutions, which is, however, still not clearly established.

In 1952, R. S. Mulliken[2,3] suggested the following reaction sequence

$$\mathrm{Pyr} + \mathrm{I_2} \rightleftarrows \mathrm{Pyr{*}I_2} \quad \text{“outer complex”} \tag{1}$$

$$\mathrm{Pyr{*}I_2} \rightleftarrows \mathrm{PyrI^+{\cdots}I^-} \quad \text{“inner complex”} \tag{2}$$

$$\mathrm{PyrI^+{\cdots}I^-} \rightleftarrows \mathrm{PyrI^+} + \mathrm{I^-} \tag{3}$$

and, on the basis of experimental evidence, showed that reactions 1 and 3 reach equilibrium rapidly whereas reaction 2 involved an activation barrier of considerable height, and equilibrium was only approached after a period of days.[2,3]

A few years later, Mulliken and other investigators showed, using UV−visible spectrophotometry[4,5] and conductivity measurements,[6] that when great precautions to exclude moisture were taken, the freshly prepared iodine solutions in pure pyridine gave only a small conductivity. So the ions $\mathrm{PyrI^+}$ and $\mathrm{I^-}$ were formed immediately but in relatively small proportions via reactions 2 and 3. Moreover, to explain the formation of the anion $\mathrm{I_3^-}$ observed in the freshly made solutions, Mulliken proposed adding a fourth reaction:

$$\mathrm{Pyr{*}I_2} + \mathrm{I^-} \rightleftarrows \mathrm{Pyr} + \mathrm{I_3^-} \tag{4}$$

In addition, it was suggested that the subsequent slow increase in ionic concentration could be due to a very slow iodination of the pyridine ring. This should liberate $\mathrm{I^-}$ ions, which may form $\mathrm{I_3^-}$ ions with I_2.[7]

Finally, in 1966, a number of authors[8−14] suggested that in binary (I_2/pyridine) or ternary (I_2/pyridine/polar solvent) mixtures, reactions 2−4 could be replaced by the following equilibrium:

$$2\mathrm{Pyr{*}I_2} \rightleftarrows \mathrm{Pyr_2I^+} + \mathrm{I_3^-} \tag{5}$$

The anion formed was identified by both UV[7] and far-infrared spectroscopy[9,10] as the triodide ion $\mathrm{I_3^-}$. It has been suggested by Popov and Pflaum[8] that the corresponding cation formed is the iododipyridinium ion, $\mathrm{Pyr_2I^+}$. This centrosymmetric cation has been identified by Xray examination[15] in the crystalline material that deposits from alcoholic pyridine/iodine solutions. The presence of the cation $\mathrm{Pyr_2I^+}$ rather than $\mathrm{PyrI^+}$ in I_2/pyridine solutions has been reinforced using vibrational spectroscopic studies.[11,12,14]

Thus, for the I_2/pyridine system diluted in a polar solvent, the reaction sequence characteristic of the freshly made solutions can be written as

$$\begin{aligned} &\mathrm{Pyr} + \mathrm{I_2} \rightleftarrows \mathrm{Pyr{*}I_2} \\ &2\mathrm{Pyr{*}I_2} \rightleftarrows \mathrm{Pyr_2I^+} + \mathrm{I_3^-} \end{aligned} \tag{A}$$

It is still believed that the slow increase with time of the conductivity, and of the concentration of the anions $\mathrm{I_3^-}$, could be due to an irreversible substitution of an iodine atom in the ring of the pyridine.[12] However, as far as we know, these reactions have never been clearly established. This ionization sequence for the reaction between the iodine and the pyridine is still investigated from time to time particularly using electrochemical techniques, but the results are often contradicting.

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Thus, for example, Nigretto and Josefowicz[16] have shown that the iodine does not dissociate in pyridine solutions provided that the solvent is correctly purified and that the pH is lower than 5. However, Aronson and al.[17] concluded that the slow increase in conductivity of the I_2/pyridine solutions was due to the formation of the ions Pyr_2I^+ and I_3^- rather than a substitution of an iodine atom in the pyridine ring.

To try to elucidate the ionization sequence for the reaction between pyridine and iodine, we have combined conductivity measurements with a study by far-infrared spectroscopy and Raman scattering of freshly prepared binary and ternary I_2/pyridine/solvent mixtures as a function of the pyridine concentration and the temperature. In the case of the ternary mixtures, we have used nonpolar solvents (*n*-heptane, CCl_4, and CS_2) but also a polar solvent (CH_3CN). In each case, the interaction between the iodine and these solvents is very weak and negligible by comparison with the "specific" interaction between the iodine and the pyridine molecule.

This paper also reports a study of the slow evolution with time (up to 1 month) of the chemistry found in binary mixtures of I_2/pyridine as studied by conductivity and far-infrared spectroscopy.

2. Experimental Section

The conductivity measurements were made using a standard conductivity cell with platinum electrodes and a Solartron conductivity bridge. The cell constant was determined to be $0.90 \pm 0.01\ cm^{-1}$ using different solutions (0.01 and 0.1 M) of potassium chloride at 25 °C.

The far-infrared spectra were recorded on a Nicolet 20F interferometer equipped with a DTGS detector to cover the frequency range $50-650\ cm^{-1}$. Single beam spectra recorded at $4\ cm^{-1}$ instrumental resolution were obtained by Fourier transformation of 200 accumulated interferograms.

At room temperature, the cell was constructed from two polythene windows (thickness of about 2.5 mm each) with path lengths ranging from 200 μm to 3 mm depending on the nature and the concentration of the donor. The uncertainty of the path length was about $\pm 2\%$.

For the measurements between −100 and 100 °C, we used a Graseby-Specac Ltd P/N 21500 cell constructed from two silicon windows (thickness = 2 mm) for the studies in the range 25−100 °C or constructed of polythene windows for the measurements in the range −100−25 °C. The temperature control was achieved by a RKS REX C10 controller. The probe thermocouple was situated near the cell window to ensure that there was no temperature gradient. The temperature precision was about ±3 °C.

The Raman spectra were collected on a DILOR Z24 spectrometer comprising a triple monochromator and a standard photomultiplier. An argon ion laser was used as the source with a wavelength of 514.5 nm and a power of 200 mW. The spectral resolution was about $2\ cm^{-1}$. We recorded the "polarized" $I_{vv}(\bar{\nu})$ and "depolarized" $I_{vh}(\bar{\nu})$ spectra in the spectral range $80-220\ cm^{-1}$ with a step of $0.6\ cm^{-1}$. To improve the signal-to-noise ratio, we accumulated 10 $I_{vv}(\bar{\nu})$ spectra and 20 $I_{vh}(\bar{\nu})$ spectra. The far wing of the Rayleigh spectrum due to the solvent was approximated by a third-order polynomial and removed. Finally, we calculated the "isotropic" Raman spectra from the $I_{vv}(\bar{\nu})$ and $I_{vh}(\bar{\nu})$ spectra obtained, in the 90° geometry, using the equation

$$I_{iso}(\bar{\nu}) = I_{vv}(\bar{\nu}) - (4/3)I_{vh}(\bar{\nu})$$

The measurements have been performed using the usual spinning cell technique in order to prevent any local heating of the sample due the absorption of the laser light.

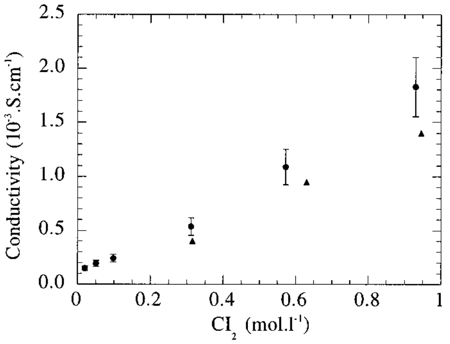

Figure 1. Evolution of the conductivity of the I_2/pyridine binary mixtures as a function of the iodine initial concentration: (●) our results; (▲) literature.

The iodine and the solvents used in this study were Aldrich spectroscopic grade (>99%). The liquids were dried over molecular sieves and used without further purification. Moreover, they were stored and handle under argon atmosphere in order to remove any trace of water. The argon used was of negligible (10 ppm) water content from "Air Liquide". It was further dehydrated by passing through a bank of columns containing molecular sieves. All the transfers to the cell were also performed under argon, and the cell itself was flushed using this gas. The iodine concentration was fixed at 0.2 M in the binary mixtures of I_2/pyridine but decreased to 0.05 M at high dilution because of limited solubility.

The spectra of freshly prepared solutions were measured approximately 15 min after preparation of the samples.

Solutions were contained in bottles surrounded by aluminum foils and kept in dark places in order to prevent them from being exposed to visible light. Under these conditions, any possible photochemical process that might contribute to the slow process reported further in this paper can be ruled out.

3. Results and Discussion

3.1. Study of the Freshly Prepared Solutions. *3.1.1. Conductivity Measurements of the I_2/Pyridine Binary Mixtures.* Figure 1 shows the electrical conductivity of I_2/pyridine binary mixtures as a function of the initial concentration of iodine (between 0.02 and 0.9 M). It is clear that our results are in good agreement with those reported in the literature.[18] For this concentration range, the conductivity is a linear function of the initial iodine concentration, which means that the ionization percentage is constant.

3.1.2. Far-Infrared Spectroscopy and Raman Scattering Study of the Binary and Ternary Mixtures I_2/Pyridine/"Inert" Solvent. The far-infrared spectra of the binary and the ternary mixtures of I_2/pyridine/(CS_2 or CCl_4) and the isotropic Raman spectra of the solutions of I_2/pyridine/n-heptane are reported respectively in the Figures 2 and 3 for different pyridine concentrations in the mixture. In each case, the spectrum of the mixture pyridine/"inert" solvent has been removed.

At low concentration of pyridine ($C_{Pyr} = 0.06-2.5$ M), the far-infrared spectrum (Figure 2) is composed of four bands centered approximatively at the frequencies 100, 180, 420, and $625\ cm^{-1}$. These can be assigned respectively to the intermolecular vibration ν_{D-I} of the complex, the stretching vibration ν_{I-I} of the complexed iodine, and the internal modes ν_{27} and ν_3 of the pyridine molecule complexed with the iodine.[12] The mode ν_{27} of the complexed pyridine is hidden by an internal mode of the "inert" solvent in the case of the I_2/pyridine/CS_2 mixtures.

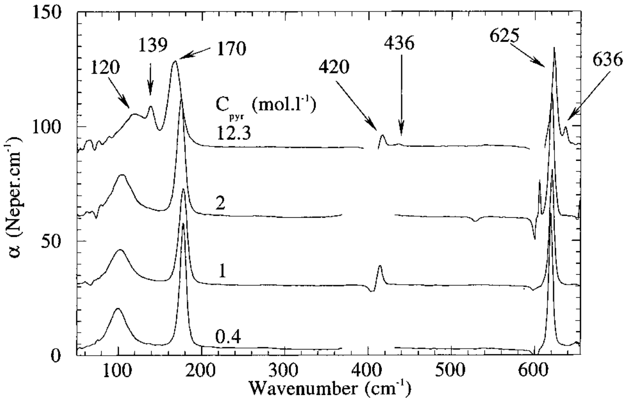

Figure 2. Far-infrared spectra of the binary and ternary mixtures I_2/pyridine/CS_2 (C_{Pyr} = 0.4 and 2 M) and I_2/pyridine/CCl_4 (C_{Pyr} = 1 M). The fourth spectrum is not drawn near 405 and 605 cm^{-1} because of the presence of very intense internal modes of the pyridine. The first and third spectra are not drawn in the spectral range 360−440 cm^{-1}, since the mixture I_2/pyridine/CS_2 has a negligible transmission in this region because of the presence of a very intense internal mode of CS_2.

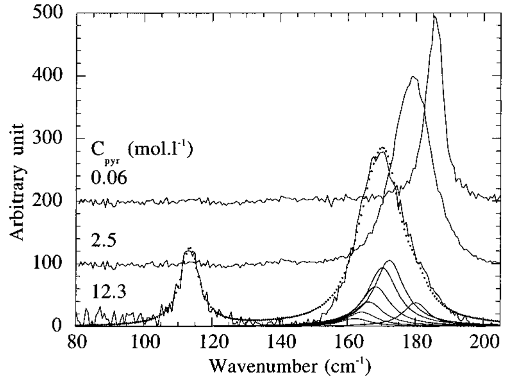

Figure 3. Evolution of the isotropic Raman spectra of the I_2/pyridine/*n*-heptane mixtures as a function of the pyridine concentration. For the binary mixture (C_{Pyr} = 12.3 M), the experimental profile (solid line) is compared to the calculated one (dashed line) (see text).

In Raman spectroscopy, the narrow band centered at 180 cm^{-1} corresponds to the stretching vibration ν_{I-I} of the complexed iodine (cf. Figure 3).

Since we observe in these spectra, only bands due to the molecular complex I_2/pyridine, then eq 1 in the reaction sequence is sufficient to account for the species in solution. However, in the case of the binary mixture (C_{Pyr} = 12.3 M), we observe, in the far-infrared spectra, three new bands of very weak intensity centered at 139, 436, and 636 cm^{-1}. These can be assigned respectively to the antisymmetric stretching vibration ν_3 of the I_3^- anion and to the normal modes ν_{27} and ν_3 of the ring of a cation, which could be Pyr_2I^+ or $PyrI^+$.[12] From these spectra, it is not possible to determine exactly the nature of the cation in solution because the frequencies of these modes, which involve essentially the pyridine ring motions, are expected to be very similar for these two cations. In Raman spectroscopy, there is a new band centered at 112 cm^{-1} that can be assigned to the symmetric stretching of the I_3^- anion. We have decomposed the profile centered at 170 cm^{-1} in a sum of six Lorentzian profiles corresponding respectively to the fundamental transition accompanied by five hot bands, the intensities of which are very important in this spectral range. The relative intensities of these bands were fixed according to the Maxwell−Boltzmann distribution, and their full width at half height (fwhh) were assumed to be identical. The band centers of the profiles are separated by $2\omega_e\chi_e$. The value of the anharmonicity constant $\omega_e\chi_e$ of the iodine molecule was fixed to 1 cm^{-1} according to the results obtained from our previous analysis on the stretching vibration of iodine in far-infrared spectroscopy, which was based on the same approach as the one reported here.[19]

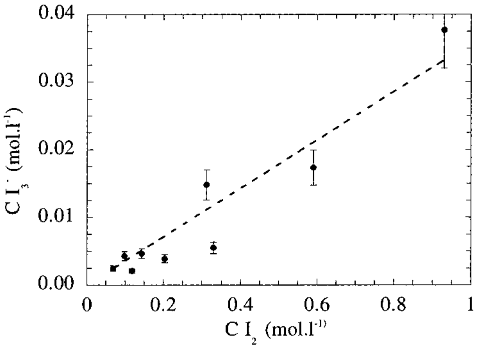

Figure 4. Evolution of the concentration of the I_3^- anion in solution as a function of the initial concentration of iodine in the I_2/pyridine binary mixtures.

The comparison between the theoretical profiles and the experimental one has been performed by fitting three parameters, namely, a general scaling factor and the values of the fwhh and the wavenumber of the band center of the fundamental transition, which have been found to be, respectively, 12 and 172 cm^{-1}. However, since this band is asymmetric at high frequency, it is not possible to account for the band shape of this profile even if we take into account the contribution of five hot bands. So we have added another profile centered at 180 cm^{-1} (see Figure 3). This band can be assigned to the symmetric stretching mode of the cation Pyr_2I^+.[11,14] Indeed, some previous infrared and Raman studies[14] on salts containing the Pyr_2I^+ cation have allowed the assignement of the different bands observed and have shown that the cation has a quasi-linear structure. We conclude that the cationic species in our binary mixtures is Pyr_2I^+ and not $PyrI^+$. This assignment is supported by the fact that if species such as $PyrI^+$ were present, we would observe, in the far-infrared spectrum, a new band corresponding to the intermolecular vibration of pyridine/I^+ centered near 280 cm^{-1}, as suggested by an ab initio calculation.[20]

Finally, in the case of the binary mixtures where pyridine plays both the role of a polar solvent and that of an electron donor, the ionic and molecular species involved in the reaction sequence A can account for all the bands observed in the Raman and the far-infrared spectra.

To determine the concentration of the I_3^- anion in solution, we have studied by far-infrared spectroscopy the salt *n*-Bu_4NI_3 in solution in pyridine. This salt was prepared using a method described in previous studies,[21] and it is known to dissociate in liquid pyridine according to

$$n\text{-Bu}_4\text{NI}_3 \rightarrow n\text{-Bu}_4\text{N}^+ + \text{I}_3^-$$

In the spectral range 100−200 cm^{-1}, there is no infrared absorption due to the cation *n*-Bu_4N^+ and we observe only a band associated with the antisymmetric stretching (ν_3) mode of the I_3^- anion centered at 139 cm^{-1}. Thus, by measuring the integrated area of this profile for different mixtures *n*-Bu_4NI_3/pyridine as a function of the initial concentration of *n*-Bu_4NI_3, we have evaluated the molar extinction coefficient ($\epsilon(\bar{\nu})$) of this absorption band centered at 139 cm^{-1}. We have found $\epsilon(\bar{\nu})$ =15 000 ± 1000 Np cm^{-2} mol^{-1} L.

Using this value, we have been able to determine the concentration of the I_3^- anion in solution in different I_2/pyridine binary mixtures as a function of the initial concentration of iodine (0.05−0.9 M). The results are reported in the Figure 4.It can be seen that the initial concentrations of iodine and of the I_3^- anion in solution are roughly linearly correlated over the whole concentration range studied. Moreover, the concentration of the I_3^- anion is always very low in comparison with the iodine concentration. Indeed, for the freshly made binary mixture, it appears that only 4% of the iodine dissociates to form the I_3^- anion. Thus, over the duration of a measurement (~15 min), the mid- and far-infrared spectra of the binary mixtures of I_2 in pyridine are essentially characteristic of the molecular complex formed in solution.

3.1.3. Far-Infrared Spectroscopy and Raman Scattering Study of the I_2/Pyridine/CCl_4/Acetonitrile Quaternary Mixtures. From the previous studies, it is difficult to know a priori whether the presence of ionic species in the binary mixtures is due to an increase of the "polarity" of the medium or an increase of the number of surrounding donor molecules in solution. Indeed, the pyridine molecule plays a dual role as solvent and donor, as mentioned already. So to evaluate the relative importance of these two functions and in particular the influence of the polarity of the medium, we have measured the far-infrared and Raman spectra of the quaternary mixtures I_2/pyridine/CCl_4/acetonitrile as a function of the relative proportions of CCl_4 and acetonitrile. The concentrations of the iodine and the pyridine were kept constant ($C_{I_2} = 0.1$ M, $C_{Pyr} = 1$ M). Since the acetonitrile is a high-polar molecule ($\mu = 3.3$ D) that forms only a very weak complex with the iodine ($K_c = 0.4$ L mol^{-1} at 298 °K),[22] it was possible to control the polarity of the medium.

The far-infrared and isotropic Raman spectra of the quaternary mixtures measured at different concentrations of acetonitrile in the mixture are reported respectively in Figures 5 and 6. At low concentrations of acetonitrile in the mixture, the spectra are identical as expected to those observed in the previous study at low concentrations of pyridine. These spectra are characteristic of the molecular complex I_2/pyridine. However, as we increase the concentration of acetonitrile in the mixture, bands characteristic of the anion I_3^- (Raman, 112 cm^{-1}) and of the cation Pyr_2I^+ (IR, 636 and 436 cm^{-1}; Raman, 180 cm^{-1}) appear progressively. The bands centered at 436 and 180 cm^{-1} are only observed in very concentrated solution ($C_{Aceto} = 17.1$ M) because of their very low intensity.

These results clearly show that the formation of the ionic species along the reaction sequence A is favored when the polarity of the medium is increased.

3.1.4. Far-infrared Spectroscopic Study of an I_2/Pyridine Binary Mixture at Low Temperature. The far-infrared spectra of a binary I_2/pyridine mixture measured at different temperature between 25 and −37 °C are reported in Figure 7 for the three spectral ranges of interest.

As the temperature of the solution is decreased, the intensity of the bands associated with the I_3^- anion (139 cm^{-1}) and the cation Pyr_2I^+ (436 and 636 cm^{-1}) are strongly enhanced. These observations support the previous results. Indeed, at lower temperature, a polar medium shows increased polarity. So equilibrium 5 is shifted toward the formation of the ionic species.

In addition, if we warm the sample up to room temperature, we can observe a decrease of the intensity of the band associated with the Pyr_2I^+ cation and the I_3^- anion (spectrum 25(a) in Figure 7). Thus, the final spectrum has exactly the same shape as the initial one. Moreover, it is no different from the spectrum of the solution, which has not suffered any thermal treatment (25(b) in Figure 7). This result is very important because it clearly shows that the reaction is reversible. We are using an increase in polarity of the medium to assist the formation of the Pyr_2I^+ and I_3^- ionic species.

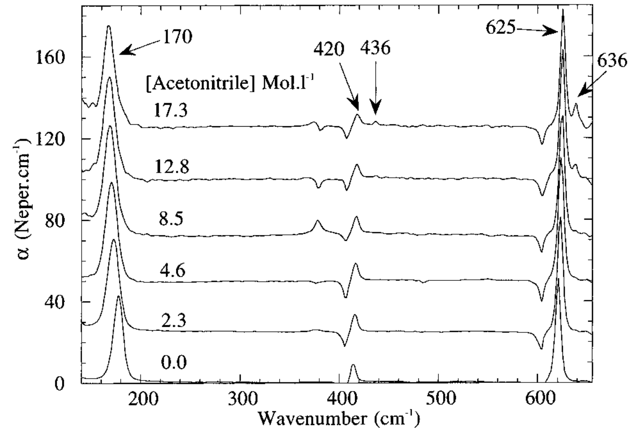

Figure 5. Far-infrared spectra of the I_2/pyridine/CCl_4/acetonitrile quaternary mixtures. In each case, the spectrum of the mixture pyridine/CCl_4/acetonitrile has been removed. The weak bands observed at 380, 405, and 605 cm^{-1} are due to poor compensation. The spectra are truncated at 140 cm^{-1} because acetonitrile, which is a high-polar molecule ($\mu = 3.3$ D), has negligible transmission in the spectral range 10−140 cm^{-1}, and so it is not possible to measure, even with a smaller path length, the band associated with the intermolecular stretching ν_{D-I} of the complex and the antisymmetric stretching of the anion I_3^-.

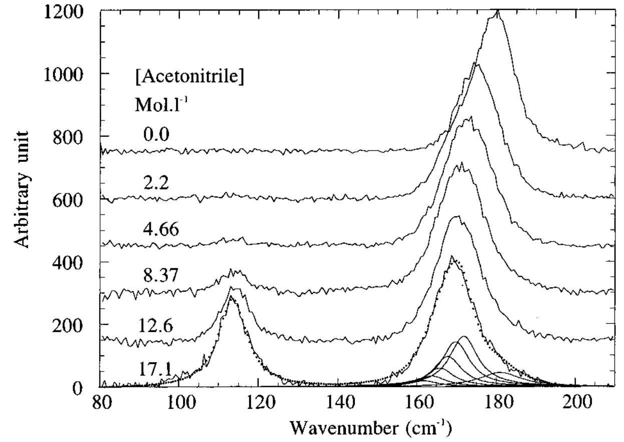

Figure 6. Isotropic Raman spectra of the I_2/pyridine/CCl_4/acetonitrile quaternary mixtures. For the ternary mixtures I_2/pyridine/acetonitrile ($C_{Aceto} = 17.1$ M), the experimental profile (solid line) is compared with the calculated one (dashed line) using the same method as that used for the I_2/pyridine binary mixture.

3.2. Evolution with Time of the I_2/Pyridine Binary Mixtures As Studied by Conductivity Measurements and Far-Infrared Spectroscopy. The evolution, with time, of the electrical conductivity of the I_2/pyridine binary mixtures with iodine concentration equal to $C_{I_2} = 0.1$, 0.3, 0.6, and 0.9 M is reported in Figure 8. For all solutions, we observe that the initial conductivity (measured approximatively 15 min after the preparation of the solution) is relatively high and that there is a very slow linear increase of conductivity with time. To explore the nature of the ionic species reponsible for this very slow increase with time, we studied the evolution, with time, of the far-infrared spectra of some I_2/pyridine binary mixtures in the spectral range 50−650 cm^{-1} (cf. Figure 9).

It appears that as the intensity of the band centered at 139 cm^{-1} (characteristic of the I_3^- anion) increases, we observe a decrease of the bands associated with the ν_{D-I}, ν_{I-I}, ν_{27}, and ν_3 modes of the molecular complex, centered respectively at the frequencies 100, 180, 420, and 625 cm^{-1}. However, the intensities of the bands centered at 636 and 436 cm^{-1} characteristic of the Pyr_2I^+ cation seem to be approximately constant over the period. We can conclude that the slow increase of the conductivity observed at longer times (>15 min) is due to a

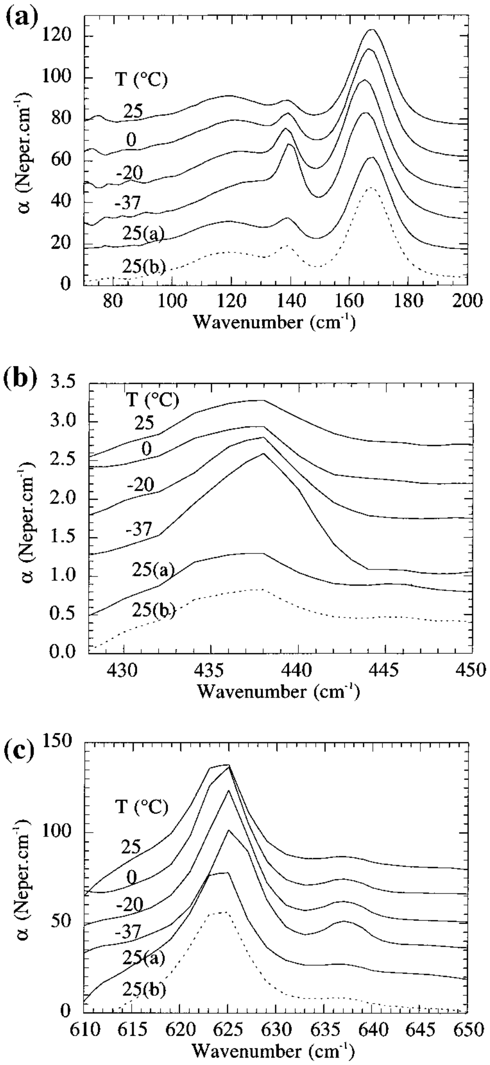

Figure 7. Evolution of the far-infrared spectra of an I_2/pyridine binary mixture (C_{I_2} = 0.3 M) as a function of the temperature. Spectra 25(a) and 25(b) are measured at 25 °C. The former corresponds to the solution contained in the cell that has been heated from −37 °C up to room temperature. The latter (dashed line) has been obtained by removing the solution from the cell and filling it with the initial I_2/pyridine mixture, which has not suffered any thermal treatment. The spectra are normalized to C_{I_2} = 0.2 M.

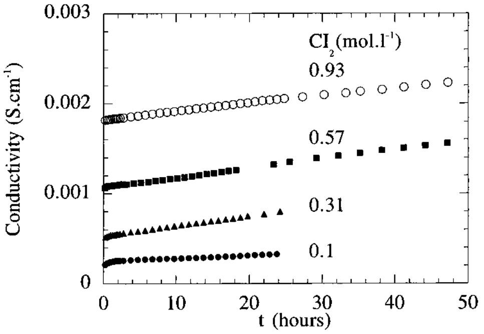

Figure 8. Evolution with time of the electrical conductivity of four I_2/pyridine binary mixtures.

second process that seems to be irreversible and leads to the formation of the I_3^- anion and to the observation of a continuum in the spectral range 200−650 cm^{-1}. We have not been able to assign this continuum, which, however, couldn't be characteristic of the normal mode of a molecular species. However, this very broad band has been observed in all our spectra and so can't be due to an experimental artifact.

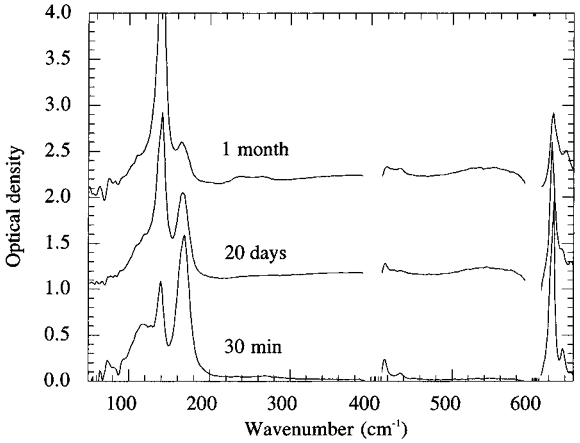

Figure 9. Evolution with time of the far-infrared spectra of an I_2/pyridine binary mixture (C_{I_2} = 0.98 M). The spectra are not drawn around the frequencies 405 and 605 cm^{-1} because of the negligible transmission of pure pyridine in these regions due to the presence of the very intense internal modes of the pyridine.

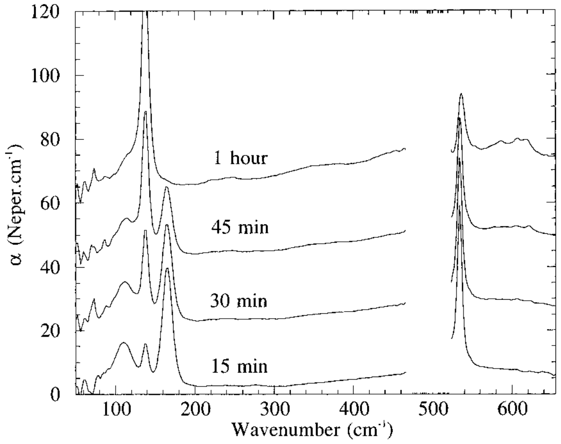

Figure 10. Evolution with time of the far-infrared spectra of an I_2/4-picoline/CCl_4 ternary mixture with $C_{4\text{-Pico}}$ = 9.3 M, C_{I_2} = 0.24 M. The spectra are not drawn between the frequencies 480 and 520 cm^{-1} because of the negligible transmission of the mixture in this region due to the presence of a very intense internal mode of the 4-picoline.

Furthermore, we have studied, by far-infrared spectroscopy, the evolution with time of solutions of iodine in a very concentrated solution of 4-picoline in CCl_4. This molecule has an electron donor character much stronger than that of the pyridine molecule, as can be seen from the equilibrium constant corresponding to the formation of the complex I_2/4-picoline (K_C = 480 ± 120 L mol^{-1} at room temperature).[23] 4-Picoline is a methyl derivative of pyridine (4-methylpyridine). As a function of time, we observe in the far-infrared spectra that there is formation of the I_3^- anion at the expense of the molecular species (decrease of the intensity of the bands centered at 120, 167, and 534 cm^{-1} associated with the modes ν_{D-I}, ν_{I-I}, and ν_{27} of the complex I_2/4-picoline (see Figure 10).

Moreover, we still observe a continuum and its intensity increases with time. Finally, after 1 h, the molecular species had disappeared (the bands centered at 120, 167, and 534 cm^{-1} are not present at all) at the expense of the ionic species (band centered at 139 cm^{-1} characteristic of the I_3^- anion). We have not been able to assign the residual band centered at 536 cm^{-1}, which does not correspond to a mode of the cation γ-Pic_2I^+ (the closest one being centered at 545 cm^{-1} [13,14]). Thus, the evolution with time of the spectrum is faster than in the case of the pyridine solutions, since the complex I_2/4-picoline is completely dissociated in about an hour.

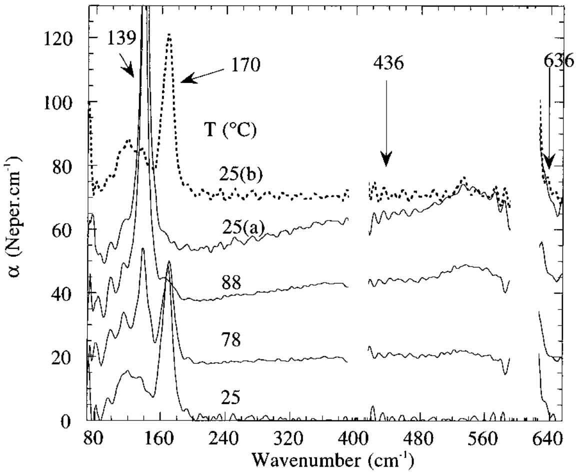

Figure 11. Evolution of the far-infrared spectra of an I_2/pyridine binary mixture ($C_{I_2} = 0.3$ M) as a function of the temperature. The spectra are not drawn around the frequencies 405 and 620 cm^{-1} because of the negligible transmission of pure pyridine in these regions and because of a strong absorption of the silicium window around 620 cm^{-1}. The residual noise observed in the spectra is coming from a nonperfect correction of the interference fringes due to a high reflection rate of the silicium windows. The two spectra at the top of the figure are recorded at room temperature; spectrum 25(a) corresponds to the solution contained in the cell that has been cooled from 88 to 25 °C, and the dashed line spectrum 25(b) has been obtained by removing the solution from the cell and filling it with the initial I_2/pyridine mixture, which has not suffered any thermal treatment. These spectra have been normalized to $C_{I_2} = 0.2$ M.

The dipole moments of pyridine and of 4-picoline are very similar ($\mu_{\mathrm{Pyr}} = 2.2$ D and $\mu_{\mathrm{Pic}} = 2.57$ D). So we can conclude that the kinetics of the irreversible process is strongly enhanced with the electron donor character of the solvent.

We have also measured the far-infrared spectra of a freshly made binary I_2/pyridine mixture as a function of the temperature between 25 and 88 °C (see Figure 11). It appears that as we increase the temperature of the medium, there is formation of the I_3^- anion at the expense of the molecular I_2/pyridine complex. Moreover, the bands centered at 636 and 436 cm^{-1} associated with the $\mathrm{Pyr_2I^+}$ cation are not detected, whereas a continuum appears with increasing intensity as the temperature of the medium is increased. It is important to note that if the solution is returned to room temperature, the far-infrared spectrum keeps the same shape that the one observed at $T = 88$ °C (spectrum 25(a) in Figure 11). This result clearly indicates the irreversible nature of the dissociation of the I_2/pyridine complex by an increase of the temperature. Finally, we conclude from this last study that the irreversible process responsible for the slow evolution with time of the binary mixtures I_2/pyridine is thermally favored.

4. Conclusion

In nonpolar solvents, the iodine interacts with pyridine to form a stable molecular complex:

$$\mathrm{Pyr} + \mathrm{I_2} \rightleftarrows \mathrm{Pyr^*I_2}$$

In the binary mixtures, and more generally in polar solvents, the I_2/pyridine complex dissociates to form ionic species. We have considered two different ionization sequences. The first reaction, fast (characteristic time ranging from picoseconds to nanoseconds[24]), can be written as follows

$$2(\mathrm{Pyr^*I_2}) \rightleftarrows \mathrm{Pyr_2I^+} + \mathrm{I_3^-}$$

It has been shown that this reaction is reversible and is favored by an increase of the polarity of the medium and/or a decrease in temperature. The second process, which reaches equilibrium very slowly (few days), is irreversible and favored by an increase of the donor strength and/or of the temperature . This reaction also leads to the fomation of the anion I_3^-. We have not been able to confirm the nature of the cationic species formed in this case, but we believe that neither of the cations $\mathrm{PyrI^+}$ or $\mathrm{Pyr_2I^+}$ are involved in this second reaction.

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