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Linkage Isomerization in $KCd[Fe(CN)_6]$ Induced by Ultrasound

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The effects of ultrasound on solids are many and varied.[1] It has been found that the rates of many homogeneous and heterogeneous inorganic reactions are accelerated by the application of ultrasound.[2] In the case of metal powders, there is considerable surface change in which the oxide coating is removed and aggregates are formed. Suslick and coworkers have studied these effects for nickel, zinc, and copper.[3–5] As a result of the effects caused by sonication, these metals have greatly increased effectiveness as catalysts.[6] Also, ultrasound plays an important role in a wide variety of synthetic processes.[6] When slurries of crystalline solids are sonicated, considerable fragmentation occurs. These changes in solids are believed to originate from collision between high speed particles caused by the jet directed at the solid surface when acoustic bubbles near the solid surface collapse.[3–5] There have been many studies on the effects of ultrasound on metal complexes and organometallic compounds.[7] However, there appears to be no case where ultrasound has been used to bring about isomerization in coordination compounds. Linkage isomerization occurs when $KCd[Fe(CN)_6]$ is heated at 130 °C in the solid state to convert Fe^{3+}–CN–Cd^{2+} to Fe^{3+}–NC–Cd^{2+} linkages.[8] The former gives rise to an infrared absorption at 2151 cm^{-1} while the latter results in an absorption at 2063 cm^{-1}. Heating the solid at 130 °C for about 2 hrs results in isomerization of two thirds of the original linkages at which point the reaction ceases.[8] As part of a study of the effects of ultrasound on solid state reactions, we have investigated the linkage isomerization reaction in $KCd[Fe(CN)_6]$ induced by sonication. This report presents the results of that study.

Experimental Section

The $KCd[Fe(CN)_6]\cdot 5H_2O$ used in this work was prepared as previously described.[8] A solution containing an excess of $CdCl_2\cdot H_2O$ in 50 ml of water was added to a solution of $K_3[Fe(CN)_6]$ in 30 ml of water. The solid product was separated by filtration and allowed to dry in air at room temperature.

Samples were sonicated using a Sonics and Materials Vibra Cell Model VC-60 ultrasonic generator with a $^1/_8$-in. horn operating at 20 kHz on a power setting of 20. Samples of 0.02 g were suspended in 1.5 ml of dioxane, dodecane, heptane, or hexane. The effects of variation in amount of liquid medium were also investigated by using 6.0 ml of dioxane. In order to control some heating, the ultrasound was pulsed using a 1 sec sonication followed by 0.1 sec lapse. The temperature of the suspension was monitored using an Omega Model 199-P2-A-DSS digital temperature probe. A sample was also suspended in dioxane and maintained at 60 °C for 2.5 hrs in an oven. Infrared spectra were obtained from mulls in Nujol between sodium chloride plates using a Nicolet 5SCX-FTIR spectrophotometer. Particle size distributions of the sonicated samples of $KCd[Fe(CN)_6]\cdot 5H_2O$ were determined using a Nikon metallurgical microscope with a calibrated ocular reticule. A minimum of 100 representative particles were selected for obtaining the size ranges and standard deviations.

Results and Discussion

A sample of $KCd[Fe(CN)_6]\cdot 5H_2O$ as prepared has the infrared spectrum in the region of CN stretch shown in Figure 1a. The peak at 2151 cm^{-1} corresponds to the CN stretching vibration in Fe^{3+}–CN–Cd^{2+} linkages. There are also peaks in the regions of OH stretch and H–O–H bending. It has been shown that when $KCd[Fe(CN)_6]\cdot 5H_2O$ is heated at 130 °C for two hours the water of hydration is lost and a linkage isomerization occurs in which only two thirds of the CN groups flip.[8] Figure 1b shows the IR spectrum of $KCd[Fe(CN)_6]$ which has been heated at 130 °C for 30 min. A new peak is seen at 2063 cm^{-1} which is due to the Fe^{3+}–NC–Cd^{2+} linkages, but the peaks attributable to water are not present.

Samples of $KCd[Fe(CN)_6]\cdot 5H_2O$ (0.02 g) were suspended in 1.5 ml of dioxane and sonicated for times up to five hours. In order to ascertain that the effects were not produced by bulk heating of the suspension, one sonicated cell was cooled in an ice bath, and another sample was also heated at 60 °C for 2.5 hrs in an oven without sonication. At various times during the sonication, the temperature was determined, and it was found to remain constant at 12–13 °C when the cell was kept in an ice bath. After sonicating the suspension, the solid was removed by filtration and the final traces of solvent were removed by evaporation. The IR spectrum of a Nujol mull of the material is shown in Figure 1c. The integrated peak intensities indicate that 9.4% of the cyanides had isomerized. Five runs using this procedure gave an average extent of isomerization of 10.0 ± 3.0%. A sample sonicated in dodecane gave results which were indistinguishable from those obtained when using dioxane. In all cases, the peaks in the 3600 cm^{-1} and 1625 cm^{-1} regions due to water were still present indicating that the linkage isomerization occurs without completely dehydrating the complex. A second batch of $KCd[Fe(CN)_6]\cdot 5H_2O$ was prepared to see if different preparations would behave similarly. When sonicated for 2.5 hrs using the procedure described above, it was found that approximately 10% of the CN linkages had isomerized in a sample of this batch also. The sample heated at 60 °C in an oven showed no isomerization.

In order to determine the effects of ultrasound when the suspension of the sample was not cooled a run was made in which the temperature of the cell was allowed to increase during sonication. After 2.5 hrs, the suspension had reached a temperature of 60 °C. The IR spectrum of the solid so treated indicated that 9.6% of the CN linkages had isomerized and that the water of hydration had not been lost. Therefore, there appears to be no difference in the extent of isomerization whether the suspension is maintained at 12 °C or 60 °C under these conditions. Any effects of heating of the suspension during sonication appear to be insignificant compared to the effects of the ultrasound itself. Isomerization appears to be due totally to the ultrasonic cavitation effects rather than bulk thermal effects.

Particle size distributions were determined for all of the sonicated suspensions as well as the original $KCd[Fe(CN)_6]\cdot 5H_2O$ and a heated sample of the material (Figure 2). Table I shows the particle size data as well as the percent of isomerization. It is readily apparent that heating $KCd[Fe(CN)_6]$ at 130 °C, which causes the isomerization of two-thirds of the CN linkages, does not cause a change in particle size. Sonication of suspensions of $KCd[Fe(CN)_6]$ causes a drastic reduction in particle size and the effect varies with sonication time. Further, the data show that dioxane and dodecane are equally effective as a medium for

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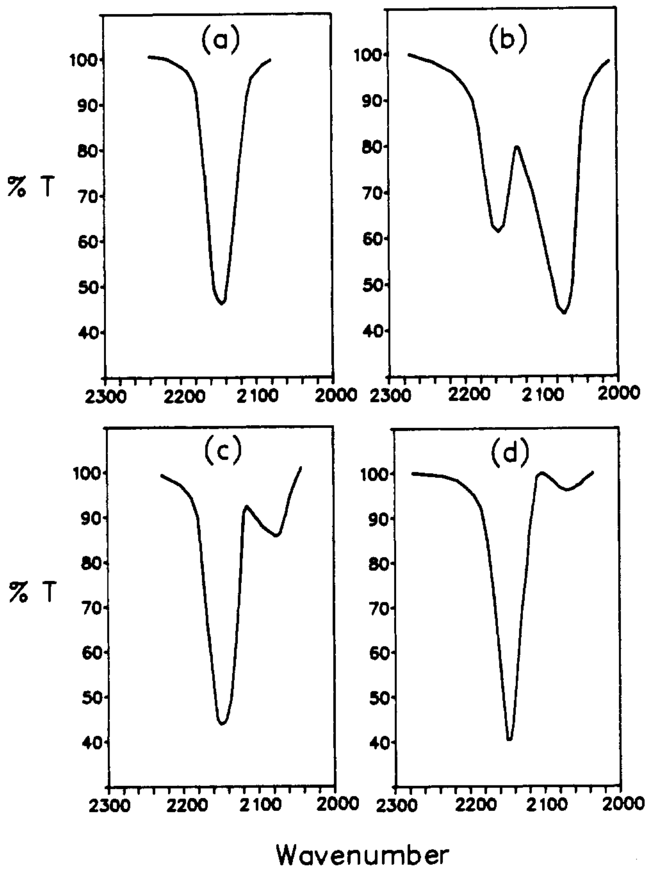

Figure 1. IR spectra of $KCd[Fe(CN)_6]$ in the CN region: (a) original sample; (b) after heating at 130 °C; (c) after sonicating 2.5 hrs in dioxane; (d) after sonicating 2.5 hrs in heptane.

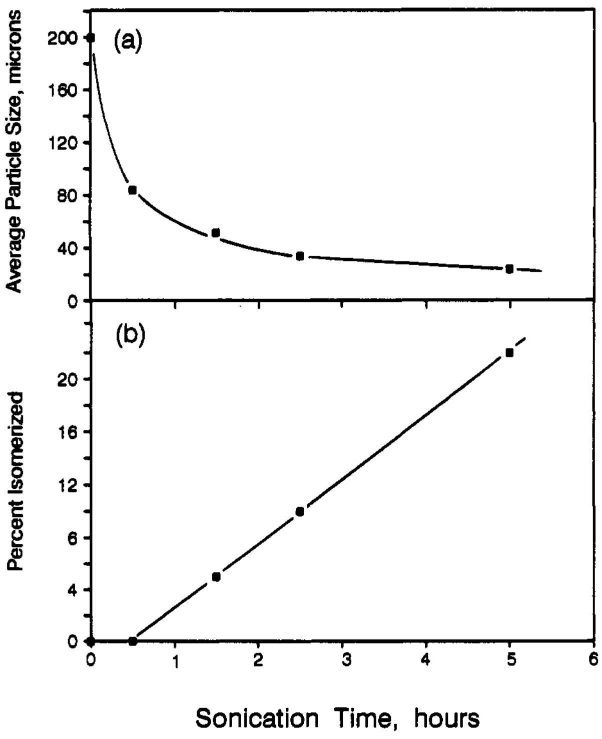

Figure 2. Particle size (a) and extent of isomerization (b) for $KCd[Fe(CN)_6]$ sonicated in dioxane.

particle size reduction and linkage isomerization. Hexane and heptane are less effective in allowing these processes.

The data shown in Table I indicate that as the time of sonication increases there is a decrease in average particle size and an increase in the extent of isomerization. After sonication for 5 hrs, 22% of the CN groups have changed bonding mode and since a complete reaction corresponds to two thirds of the CN groups flipping, this actually represents 33% of the process achieved thermally.

Table I. Effects of Sonication Conditions on Particle Size and Extent of Isomerization in $KCd[Fe(CN)_6]$

sample treatment[a]	av particle size, μm	std dev, μm	% isomerized
untreated	200	42.2	0.0
heated 130 °C, 30 min	179	36.4	67.0[b]
dioxane, 2.5 hrs	34	21.3	10.0
dodecane, 2.5 hrs	38	17.8	10.0
heptane, 2.5 hrs	49	21.5	4.8
hexane, 2.5 hrs	69	27.5	0.0
dioxane, 0.5 hrs	84	32.2	0.0
dioxane 0.5 hrs (ground sample)	59	25.6	0.0
dioxane, 1.5 hrs	52	21.8	5.0
dioxane, 2.5 hrs[c]	60	21.3	3.3
dioxane, 5.0 hrs	24	11.2	22.0

[a] All sonicate suspensions except one indicated prepared using 0.02 gram of solid $KCd\{Fe(CN)_6]\cdot 5H_2O$ with 1.5 ml of solvent. [b] This corresponds to the complete reaction. [c] This sample had 6.0 ml of dioxane.

Experiments were also carried out in which heptane and hexane were used as the suspending medium. It was observed that these solvents did not display the same heating effects that resulted when dioxane or dodecane was used. Dioxane suspensions eventually reached a temperature of about 60 °C while heptane and hexane suspensions reached temperatures of 50 and 40 °C, respectively. These results are in accord with the expected influence of vapor pressure on cavitation.[9]

Sonication of $KCd[Fe(CN)_6]$ for 2.5 hrs in heptane gave a solid whose IR spectrum (Figure 1d) indicated 4.8% isomerization. A similar sample sonicated for the same time in hexane gave an IR spectrum (similar to Figure 1a) which shows only one peak at 2151 cm^{-1} indicating no isomerization. These results are in accord with the fact that the effectiveness as a cavitation medium decreases in the order dioxane ≈ dodecane > heptane > hexane.[9]

The effect of using a larger volume of solvent during the sonication process was also investigated. A 0.02 g sample of $KCd[Fe(CN)_6]\cdot 5H_2O$ was sonicated for 2.5 hrs in 6.0 ml of dioxane with the cell cooled in an ice bath. The separated solid after sonication gave an IR spectrum which showed a small peak at 2063 cm^{-1} indicating some isomerization. The extent of isomerization was estimated to be about 3.3% compared to about 10% when 1.5 ml of the suspending liquid is used. This is believed to be due to the fact that cavitation takes place mainly at the focus of the ultrasound source. Since a solid is repelled by ultrasound, the solid is more dispersed in a larger volume of liquid. With the solid being more dispersed, there is less solid affected by cavitation and less isomerization occurs.

These results show that ultrasound conducted through an effective cavitation liquid can cause linkage isomerization in solid $KCd[Fe(CN)_6]$ at low bulk temperatures where the thermal process does not occur. The high speed jets resulting from acoustic bubble collapse and shock waves produce considerable energy at solid surfaces. It is probable that the localized, short lived hot spots exhibit temperaturs and pressures sufficient to produce linkage isomerization. We are currently investigating the effectiveness of ultrasound in causing other reactions of this type.

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