Dynamic Spectral Shifts of Molecular Anions in Organic Glasses

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Time-dependent spectra of the radical anions of pyromellitic dianhydride and p-dinitrobenzene have been observed after formation by pulse radiolysis in frozen 2-methyltetrahydrofuran and triacetin glasses. At temperatures near the glass transition, the spectra shift toward the blue over the entire observed time range 100 ns-100 s), while at temperatures well below the glass transition, the spectral shifts can be stopped or greatly slowed. The magnitudes of the shifts are not large (typically ≈ 10 nm), but because they are larger than the vibrational line widths, dramatic kinetics may be observed: the absorbance grows or decays by more than a factor of five at some wavelengths. The observations are consistent with a solvent molecule reorientation mechanism for spectral shifts of molecular ions in low-temperature organic glasses.

Introduction

Molecular electronic spectra can be highly sensitive to environmental effects. It is well-known that in solution the position of an absorption band is often dependent on the nature of the solvent. This will be the case if the relative energies of the ground and excited states depend on the dielectric constant of the medium or on more specific solvent interactions such as hydrogen bonding.¹⁻⁵

Solvent effects may also be of a dynamic nature. If the structure or charge distribution of a species in solution is suddenly altered, the surrounding solvent will, in all probability, be in a nonequilibrium configuration until relaxation processes can occur.¹ Spectral changes due to the dynamics of solvent-molecule interactions have been observed in liquids following rapid creation of species by optical excitation^{6,7} or pulse radiolysis.^{8,9} Typically, the development of the absorption spectrum of a charged species in a liquid far from its melting point is complete in tens of picoseconds.⁷⁻⁹ This observation can be understood in terms of relatively unhindered reorientation of solvent molecules in liquids, where the solvation rates correlate with known dielectric relaxation times.^{8,9} In general, as the temperature is lowered, solvent molecule reorientation becomes more difficult and the solvation process will slow down.

In rigid media, it is often possible to observe relatively slowly varying spectra. Absorption spectra of trapped electrons (e_t^{-}) produced by irradiation in low-temperature organic glasses are known to undergo shifts to shorter wavelengths as a function of time¹⁰⁻¹⁷ which can often be

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essentially stopped by lowering the temperature to a few degrees Kelvin.¹⁸⁻²⁰ At intermediate temperatures, the spectral shifts are solvent and temperature dependent and may continue to occur over many orders of magnitude in time.¹³ In contrast to the behavior of trapped electron spectra, Kevan¹¹ observed that a number of molecular anions do not exhibit time-dependent spectra in 2-propanol glass at 77 K; the spectra are apparently fully developed by 100 ns after the pulse. However, time-dependent spectra have been observed for the anions of a few aromatic ketones, both in cold ethanol liquid²¹ and in alcohol glasses.^{22,23}

Here, we report continuous (in time) measurements of spectral shifts of the anions of rather structurally different molecules, pyromellitic dianhydride and p-dinitrobenzene, in low-temperature organic glasses. Both anions exhibit sharp absorption features.^{24,25} This is in contrast to the broad, structureless time-dependent bands seen in the case of trapped electrons or aromatic ketone anions. Attention has been paid to the dependence of the spectral changes on the solvent matrix, the temperature, the structure and electronic states of the molecular anion, and the neutral solute concentration. These observations add to the relatively short list of molecular ions that are known to show time-dependent spectra in rigid media. The results shed some light on, but by no means fully resolve, the question of the mechanism for time-dependent spectral shifts in glasses.

Experimental Section

All solvents were purified prior to use. The 2-methyltetrahydrofuran (MTHF) was distilled from lithium aluminum hydride under an atmosphere of argon and stored in the dark under argon. Absolute ethanol (EtOH) was

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distilled from sodium borohydride under argon. Triacetin was vacuum distilled. The solutes used in this study, pyromellitic dianhydride (PMDA, obtained from Fluka A.G.), p-dinitrobenzene (p-DNBz, Eastman Kodak Co.), and pyrene (Aldrich Chemical Co.), were the highest grades available and were used without further purification. Solutions were made up to give the desired concentrations upon freezing. The samples were carefully degassed and sealed under vacuum in Pyrex cells. Most of the experiments were done with cells with a 1-cm path length. For work at 4 K thinner cells (3 mm) were used to minimize the effects of cracking of the samples which inevitably occurred at the lower temperatures. Also, samples intended for cooling below 77 K were sealed with a small amount of helium to provide thermal contact between the sample and the cell walls. Previous experience had indicated that this precaution was necessary in order to ensure rapid cooling of the samples to liquid helium temperatures.

The pulse radiolysis setup has been described previously.^{13,26} The samples were held at the desired temperature inside of a continuously variable cryostat (Oxford CF204) with either liquid nitrogen or liquid helium serving as coolant. The reported temperatures are accurate to about ± 0.5 K, based on frequent calibrations with liquid nitrogen or liquid helium in the sample chamber at atmospheric pressure. A pulse from the Argonne electron linac (15 MeV, 7 A, 4-10 ns) created ionization in the sample. The matrix charges produced ($\approx 10^{-5}$ M of trapped electrons in MTHF or EtOH and solvent anions in triacetin) were rapidly captured by a high concentration of dopant molecules (0.075-0.3 M). Absorption by the molecular anion was monitored as a function of time at a number of wavelengths. The decay curves were replotted to produce time-resolved spectra over the range 10^{-7} - 10^{2} s. The spectral bandpass of the optical system was adjusted according to the width of the spectral feature being studied, but was typically 1-5 nm. The experimental setup had been designed specifically to minimize the effect of the analyzing light,¹³ a further reduction in the light intensity by use of neutral density filters did not alter the results, indicating that the analyzing light had no measurable effect on the kinetics.

The light detection and signal processing system included either a photomultiplier (Hamamatsu 928) or silicon photodiode (UDT PIN8LC), a Biomation 8100 transient digitizer, and a Xerox Sigma 5 computer. For most of the study, a Tektronics 7904 oscilloscope was used as a variable gain amplifier. It was subsequently noted that the output of the oscilloscope (signal out) showed a small delayed growth component ($\sim 5\%$) in response to a fast step function. The frequency response of the output amplifier of the 7904 is not flat but includes delayed components in the megahertz to subkilohertz region. The difficulties with the 7904 scope are restricted to the "signal out" and are apparently inherent to the design of the output amplifier, which also feeds the trigger circuits. The spectra reported here have been corrected where noted for the apparent delayed growth in absorption at short times caused by the oscilloscope amplifier response. The correction was determined from data taken at a few wavelengths without the oscilloscope in the signal-processing chain. The effect of the apparent delayed growth is negligible for times longer than 10^{-6} s. The estimated uncertainty in the absorption measurements is $\pm 6\%$, except at short times $(<10^{-6} \text{ s})$ where it should be considered to be ±10%.



Figure 1. Absorbance vs. log (time) curves at various wavelengths following pulse radiolysis of 0.15 M pyromellitic dianhydride (PMDA) in 2-methyltetrahydrofuran (MTHF) glass at 82 K.



Figure 2. Time-dependent spectra of the PMDA anion in MTHF at 82 K.

Results

Figure 1 shows the time dependence of the absorbance of a sample of 0.15 M PMDA in MTHF glass at 82 K for several wavelengths near the intense red absorption line of the PMDA anion. The absorbance is seen to grow at the shorter wavelengths and decay at the longer wavelengths over the entire observed time range $(10^{-7}-10^2 \text{ s})$ following creation of PMDA⁻ ions by ~ 10 -ns pulse radiolysis. Absorption vs. log (time) curves identical within experimental error were observed for 0.15 and 0.075 M PMDA samples, indicating that the spectral shift process is independent of the concentration of neutral PMDA molecules. The results have been replotted in Figure 2 to give time-dependent absorption spectra of the PMDA anion, where the results at 10^{-7} s have been corrected for the artificial delayed growth discussed above by scaling by a factor of 1.1. At 100 ns after the electron pulse, the absorption maximum lies near 680 nm, and it shifts roughly linearly in log (time) to 671 nm at 100 s.²⁷ significant feature of the spectra in Figure 1 is a substantial

⁽²⁷⁾ The position of the absorption maximum extrapolated to 2 min after the pulse (~ 669 nm) is still substantially to the red of that reported for a γ -irradiated sample at 77 K (666 nm, ref 24). This discrepancy can be explained by noting that the spectrum of a recently γ -irradiated sample agrees well with that predicted by using the data in Figure 2, but that photobleaching of the sample results in a further blue shift to 666 nm, presumably by locally heating the matrix through radiationless relaxation of the absorbed energy.



Figure 3. Time-dependent spectra of the PMDA anion in a triacetin glass at 215 K.

growth in the integrated intensity of the absorption, which is most pronounced at early times but continues to at least 0.1 s; from 10^{-7} to 10^2 s the oscillator strength of the band beyond 645 nm increases by $40 \pm 5\%$. The observed intensity growth is not attributable to delayed capture of matrix charges. On the basis of direct measurements of the disappearance of trapped electrons in a 0.025 M sample of PMDA in MTHF (monitored at 1000 nm) and the expected exponential concentration dependence for \mathbf{e}_t^- survival at a particular time,^{26,28-30} it can be concluded that more than 90% of the trapped electrons will be captured by 10^{-7} s after the pulse in a 0.15 M PMDA sample, and only 2% will be left at 10^{-6} s. At 77 K we observe a similar spectral shift accompanied by a smaller growth in intensity, with the corresponding spectra displaced slightly to longer wavelengths (supplementary material Figures S-1 and S-2; see paragraph at end of text regarding supplementary material).

Yields of trapped electrons in MTHF measured by their absorption at 1000 nm decreased exponentially with PMDA concentration from 0.025 to 0.15 M, providing evidence of the kind obtained earlier for other solutes²⁶ that aggregation of PMDA is insignificant. Concentration independence of the absorption spectra of the radical ions studied here also shows that aggregation does not occur.

This same line in the absorption spectra of the PMDA anion was also observed to show a time-dependent spectral shift in a triacetin matrix. Figure 3 shows spectra of PMDA⁻ in triacetin at 215 K. At this temperature, the spectrum shifts toward the blue and the peak absorbance grows, accompanied by some narrowing of the line, until 10^{-2} s. The contribution to the growth from delayed capture of matrix charges remains uncertain since there is no convenient wavelength to monitor the decay of the matrix charges in triacetin. Since the glass transition temperature of triacetin is ~ 205 K, diffusion occurs to a significant extent and PMDA⁻ disappears through ion recombination, causing the decay of the spectra in Figure 3 for times >0.1 s. At 195 K, little loss of the anion occurs and the spectral shift continues out to at least 10^2 s (supplementary material Figure S-3). By cooling to 77 Kthe spectral shift can be essentially stopped, although the growth in intensity persists (supplementary material Figure S-4). However, at 4 K the time-dependent spectra of PMDA⁻ in triacetin show a small blue shift (supplementary



Figure 4. Absorbance of the PMDA anion in triacetin at 666 nm vs. log (time) at various temperatures.



Figure 5. Time-dependent spectra of the PMDA anion in ethanol at 77 K.

material Figure S-5). At 10^{-6} s after the pulse, an asymmetric band which falls less steeply on the blue side and peaks at 684 nm is observed. Subsequently, this peak grows and shifts until roughly 0.1 s by which time it peaks at 681 nm and has become considerably more symmetric. From 0.1 to 100 s the spectrum decays by ~15% without shifting significantly. Apparently, the process which causes these spectral changes at 4 K is too fast to be observed at 77 K.

Figure 4 shows absorbance vs. log (time) curves for PMDA⁻ in triacetin at 666 nm over the range 195–230 K where the spectral changes are strongly temperature dependent. At the upper end of this range, the effect of translational diffusion is clearly seen, and the rate of loss of PMDA⁻ ion by recombination increases rapidly with increasing temperature. The rate of growth in absorbance at 666 nm at intermediate times due to the spectral shift process also increases as the temperature is raised. The initial growth in absorption from 10^{-7} to 10^{-5} s which appears much less strongly temperature dependent over 195–215 K is probably mostly due to delayed capture of matrix charge and apparent delayed growth caused by the oscilloscope amplifier.

The spectrum of PMDA⁻ was also studied in glassy ethanol. At 77 K no time-dependent spectral shift is observable; only a small growth is seen at early times, most of which is attributable to delayed capture of trapped electrons at the concentration used (0.075 M). However,

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Figure 6. Time-dependent spectra of the *p*-dinitrobenzene (*p*-DNBz) anion in MTHF at 77 K.

the long wavelength band now peaks at 536 nm, a much shorter wavelength than in MTHF or triacetin (Figure 5). Even at 4 K there is no dynamic spectral shift occurring over the accessible time range, and the spectrum is essentially identical with that observed at 77 K (supplementary material Figure S-6).

It may be that the large difference in the position of the absorption band of irradiated PMDA in EtOH from that observed in MTHF or triacetin is due to a distinct species in EtOH, resulting from a reaction such as rapid protonation by the solvent. In order to check this possibility, the absorbance at 530 nm was monitored as a function of time following pulse radiolysis of a sample of 0.075 M PMDA in EtOH to which a lower concentration (0.025 M) of trichloro-1,4-benzoquinone had been added to serve as an electron acceptor. The absorbance due to PMDA was seen to decay with the same kinetics as previously observed for electron transfer reactions in rigid media, which were shown to proceed by a long-range tunneling mechanism (hopping does not occur).^{23,26,28,29} The fact that this species can serve as an electron donor provides evidence that we are observing the PMDA anion.

Figure 6 shows spectral shift data for the long wavelength band of the anion of p-DNBz in MTHF at 77 K. This band is somewhat broader than the shifting band of PMDA⁻. Like PMDA⁻, the spectrum of *p*-DNBz shows a pronounced blue shift and an apparent growth over a very broad range of times. However, in the case of p-DNBz⁻, the spectral shift is accompanied by a substantial spectral narrowing so that there is less than 20% real growth in integrated intensity, either over the region 850–965 nm or in the main peak at \sim 900–965 nm. Decay curves identical within experimental error were observed for both 0.15 and 0.30 M p-DNBz in MTHF. In triacetin at 205 K, the p-DNBz anion shows a time-dependent blue shift such that its absorbance peaks at 940 nm at 10^{-7} s and 933 nm at 10^2 s after the pulse (supplementary material Figure S-7). At this temperature, the peak absorbance grows and the spectrum narrows until $\sim 10^{-4}$ s after which time the absorbance decays at all wavelengths. The latter stages of this decay can be attributed to diffusive processes, based on the observations for PMDA⁻ at 205 K (Figure 4). No spectral shift was observable for p-DNBz in EtOH (0.04 M). Again, it was shown that the observed species could serve as an electron donor to trichloro-1,4benzoquinone, so that protonation by the solvent does not occur.

An attempt was made to observe a spectral shift for the anion of pyrene, which exhibits a very narrow absorption peak in MTHF at 77 K. No spectral changes were measurable over the range $10^{-6}-10^2$ s after the pulse.

Discussion

The spectral shifts observed here display the following common features:

(1) The shifts are always toward the blue.

(2) They occur continuously over a range of many orders of magnitude in time.

(3) They are strongly temperature dependent, being stopped or greatly slowed at low temperature.

(4) The rates of the spectral shifts are independent of the neutral dopant concentration.

The spectral shifts may or may not be accompanied by changes in line width or intensity of the band. With respect to points 1–3 above, the observed spectral shifts for molecular ions are similar to those seen for trapped electrons in organic glasses, which have been extensively studied.^{10–20} The spectral shifts for both types of species can be given the following general interpretation: they are due to the process of stabilization of the ground state relative to the excited state of a species formed by introduction of charge into a partially rigid solvent framework.

The present observations are consistent with a matrix molecule reorientation mechanism for spectral shifts of molecular anions. Two alternative mechanisms can be ruled out on the basis of the experimental evidence: (1) charge hopping among the dopant molecules to reach more favorable solvation sites, and (2) diffusion of the anions to other sites in the matrix. The fact that the spectral shift kinetics are concentration independent rules out hopping. This was previously shown for spectral shifts involving the benzophenone anion in alcohol glasses.²³ A diffusion mechanism can be discounted since the effect of diffusion is clearly seen at the higher temperatures where loss by ion recombination occurs. The spectral shifts still occur even though the matrices are rigid with respect to translational diffusion at sufficiently low temperatures.

Each of the above four features common to the spectral shifts of molecular anions is consistent with the solvent molecule reorientation mechanism. Each of these points will be discussed in turn. Solvation of the charge by polarization in the surrounding medium would be expected to result in optimal stabilization of the ground state of the molecular ion. This polarization field should also lower the energy of excited states but by a lesser amount if the charge distribution differs in the excited state. The difference in stabilization of the ground and excited states leads to the observed blue spectral shift.

Not only are the spectral shifts observed to occur over many orders of magnitude in time, but in a number of systems, absorption vs. log (time) curves are rapidly changing at the ends of the observation region (PMDA/ MTHF at 77 or 82 K, PMDA/triacetin at 195 K, p-DNBz/MTHF at 77 K) without significant diffusion occurring. This implies that the spectral shifts may continue for orders of magnitude outside the observed time range (100 ns-100 s). The very broad time range over which the spectral shifts occur may be explained if there are several processes taking place at widely varying rates. The following distinct molecular reorientation processes would be expected to occur: (1) rotation around chemical bonds, (2) rotation of entire molecules or groups of molecules around different axes, (3) movement of solvent molecules toward or away from the ion, and (4) formation of hydrogen bonds between the ion and solvent molecules, where possible. In addition to the different rates expected for each of these processes, solvent molecules at different distances from the ion will see different field strengths and

are expected to relax at different rates. Also, there may be a range of rates for solvation at different sites for the ion due to either different initial solvent structures or a range of activation energies for molecular motions in the disordered glass; this would imply inhomogeneous broadening of the line and would serve to smooth out the observed time dependence of the spectral shift.

The results for PMDA⁻ in triacetin show clearly that the rate and extent of the spectral shift is strongly temperature activated, yet the shift occurs to some degree over a wide range of temperatures. Again, this is consistent with a matrix molecule reorientation mechanism in which there is a range of activation energies for different solvent relaxation processes. The observed temperature dependence can be interpreted on a molecular level in terms of hindered motions (vibrations and librations) with a distribution of frequencies. Sufficient thermal excitation of these vibrational and librational motions can lead to free displacements and rotations to achieve lower energy configurations which may be frozen in following vibrational relaxation. The fact that, in general, the spectral shifts can be essentially stopped at temperatures well below the glass transition implies that is is possible to freeze out the nuclear motions producing the shift. This, in turn, implies that there is a minimum activation energy or, equivalently, a lowest frequency for the molecular motions responsible for the shift. There is no evidence that nuclear tunneling contributes to the shifts. The results for PMDA⁻ in triacetin at 4 K show that, by lowering the temperature, two molecular relaxation processes can be separated; freezing out the spectral shift that occurs at higher temperatures allows one to observe another spectral shift process which is apparently too fast to see at the higher temperatures.

The lack of dependence of the spectral shift kinetics on dopant concentration is important evidence supporting the solvent reorientation mechanism. The observation of spectral shifts in low-temperature organic glasses in cases where hopping can be discounted (including the molecular ions studied here) suggests that spectral shifts of trapped electrons also proceed by a solvent reorientation mechanism.²³

The interesting result that no dynamic spectral shift is observed for PMDA⁻ or *p*-DNBz⁻ in EtOH could be due to either that an energetically favorable solvent structure for the anion already exists around the neutral before e⁻ capture or that the solvation process is very fast. The fact that no spectral shift can be seen for PMDA⁻ in EtOH even at 4 K argues against fast solvation. Formation of hydrogen bonds with the solvent may account for the substantial displacement toward shorter wavelengths of the spectrum of PMDA⁻ in EtOH from that in MTHF or triacetin.

The origin of the remarkable growth in integrated intensity which accompanies the spectral shift for PMDA⁻ in MTHF (and possibly in triacetin) is not clear. As noted above, the observed growth is larger than can be accounted for by delayed capture, and they continue to times when the capture should be complete. The growth must then represent an actual increase in the extinction coefficient as time proceeds. Two mechanisms for the growth are possible: (1) The solvation process might perturb the electronic wave functions of the anion and lead to a time-dependent transition dipole matrix element. However, the large ($\sim 50\%$) growth in intensity would require a large growth in the transition dipole. This would imply a substantial change in the electronic wave functions, which seems unlikely in view of the small observed spectral shifts. This mechanism would seem to be possible only

if the absolute energies of the ground and excited states change greatly, yet the change in their energy difference is small. (2) An alteration in the Franck-Condon factors through geometry changes caused by solvation could alter the intensity distribution among vibrational lines within the electronic band. In principle, one should see other peaks decrease in intensity as the major peak grows, but the measurements are not sensitive to the small changes expected if the intensity is spread over several small vibrational lines.

In general, in order to exhibit a spectral shift, a molecule must have differing charge distributions in the ground and excited states which are sensitive to the solvent environment. For PMDA⁻, the observed transition is of the socalled charge resonance type, corresponding to molecular orbital configurations which differ in their symmetry with respect to symmetry planes of the molecule but differ relatively little in their overall electron density distribution.²⁴ The transition does cause a small increase in electron density on the carbonyl carbons and moves density from the four substituted carbon atoms of the central aromatic ring to the other two aromatic carbon atoms, which are more exposed to the solvent. Likewise, the transition in p-DNBz⁻ studied here is of the charge resonance type and involves only relatively small changes in the electronic distribution where some density is removed from the substituted aromatic carbon atoms and placed on the nitrogen atoms.²⁵ Because of the symmetry of both PMDA⁻ and *p*-DNBz⁻, any changes in the bond dipoles of the polar groups cancel leaving no net dipole. That the transitions in PMDA⁻ and p-DNBz⁻ studied here represent rather minor changes in electron density distribution correlates well with the small magnitude of the observed shifts.

On the other hand, the 492-nm band of the pyrene anion, which does not show a measurable spectral shift, corresponds to a charge resonance transition with a seemingly comparable charge redistribution to that of PMDA⁻ or *p*-DNBz⁻. This conclusion is based on the assignment of the transition by Shida and Iwata³¹ and available Hückel molecular orbital calculations.³²

PMDA⁻ and *p*-DNBz⁻ form a sharp contrast to both the benzophenone anion and the trapped electron, which show much larger spectral shifts in a number of low-temperature glasses.¹⁰⁻²³ In the case of benzophenone, the transition involves a major charge redistribution between the carbonyl group and the aromatic ring.²⁴ In the case of trapped electrons, larger solvent rearrangements are probably occurring than for molecular ions, as evidenced by the fact that distinct spectral features, corresponding to different degrees of solvation of the trapped electron are often observable.¹⁶⁻²⁰ The spectral shifts observed here for PMDA⁻ and *p*-DNBz⁻ probably involve much more subtle changes in the solvent environment.

Whether or not time-dependent shifts of charged species in organic glasses are observable will depend on the amount of charge redistribution accompanying the transition. Addition of a charge to a molecule in a polar medium leads to substantial reorientation of nearby solvent molecules to stabilize the ground state of the ion. This results in a spectral shift to the extent that the reorientation affects the ground and excited states differently. For transitions accompanied by very small changes in the charge distribution, little spectral shift will be observed. For at least some range of moderate amounts of charge

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redistribution, vibrational lines of the transition will still be resolved and dramatic spectral shifts can be seen. Presumably, PMDA⁻ and p-DNBz⁻ in MTHF or triacetin are in this class. For transitions involving larger charge redistributions, solvent reorientation will substantially affect the energy difference between the ground and excited states. However, spectral shifts may not be observable if larger coupling of low-frequency vibrational modes of the solvent washes out the vibrational structure of the absorption band. If the magnitude of the spectral shift is considerably less than the width of the envelope, the spectral changes will be subtle. For very large charge redistributions (e.g., the benzophenone anion), the entire envelope may shift noticably.

The experiments reported here provide the most clearly observable examples to date of dynamic spectral shifts of molecular ions. They confirm that these shifts have kinetics spread over at least nine decades in time in rigid media, and that the shifts are arrested at temperatures well below the glass transition.

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Supplementary Material Available: Additional timedependent absorption spectra (7 pages). Ordering information is given on any current masthead page.

Electrochemistry of Prussian Blue. An in Situ Mössbauer Effect Measurement

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The Mössbauer effect measurement on electrochemically prepared Prussian blue has been performed with an in situ method. The Mössbauer absorption (isotope enriched) obtained at 0.6 V vs. SCE is identified as coming from the high-spin Fe^{3+} ions of Prussian blue, whereas that at -0.2 V vs. SCE is interpreted as coming from the high-spin Fe^{2+} ions. This result indicates that only the high-spin Fe^{3+} ions are quantitatively reduced to the high-spin Fe^{2+} ions through the electrochemical reaction. That is, insoluble Prussian blue, $Fe_4^{3+}[Fe^{II}(CN)_6]_3$, can be reduced to Prussian white, $Fe_4^{2+}[Fe^{II}(CN)_6]_3$.

Introduction

It has been an interesting problem to show which form the two kinds of iron ions take (ferric ferrocyanide or ferrous ferricyanide) in Prussian blue.¹⁻³ The colloidal precipitate, made by adding a solution of Fe³⁺ ions to that of $Fe^{II}(CN)_6^{4-}$, has been called Prussian blue (PB).^{1,2} That this pigment is demonstrated to be an iron(III) hexacyanoferrate(II) has been shown by observations on the infrared absorption spectrum,⁴ the optical absorption spectrum,⁵ and the Mössbauer resonance spectrum.⁶⁻¹¹ However, whether "water-soluble PB" has a definite formula of $KFeFe(CN)_6$ still seems to be open to question. Efforts have been made to increase the particle size of several polynuclear transition-metal cyanides by very slow precipitation, inducing a modification of the original structural model proposed by Keggin and Miles.^{1,12-14}

In our previous papers,^{15,16} a new method for the preparation of a thin film of PB has been disclosed and the electrochemistry has been discussed. The reduction and the oxidation of the electrochemically prepared PB were observed at 0.2 and 0.9 V vs. SCE, respectively.^{15,16} The electrochemical reactions have been tentatively formulated in our previous paper, assuming that the formula of PB is the "water-insoluble one", $Fe_4^{3+}[Fe^{II}(CN)_6]_3$.^{15,16} An almost identical voltammogram has been reported with "a chemically prepared PB" by Neff et al.¹⁷

In the history of the Prussian blue problem, Weiser et al. claimed that PB was the ferrous salt of ferricyanide based on the redox potentials of $Fe^{2+/3+}$ and of Fe $(CN)_{6}^{4-/3-.18}$ Although it seems to be true that PB is a ferric salt of ferrocyanide, no one has been directly able to show the electron-transfer mechanism of PB. An in situ Mössbauer effect measurement is a more promising method for the elucidation of the problem.

In this paper, the details of the in situ measurement of the Mössbauer effect and the electrochemistry for the PB film on glassy carbon electrodes are presented.

Experimental Section

Enrichment of ${}^{57}Fe$. There was a need to increase the concentration of ${}^{57}Fe$ in the ferric ion in order to get a high S/N ratio and for distinguishing the overlapping Mössbauer spectra. A stock solution of enriched ⁵⁷FeCl₃

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