DETECTION OF SPARINGLY-SOLUBLE REACTION INTERMEDIATES IN SOLUTION
BY THE STOPPED-FLOW METHOD FOR THE SCATTERED LIGHT

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In the course of the reaction between Co^{2+} and 1-(2-pyridylazo)-2-naphthol (PAN) in aqueous dioxane media, the formation and the redissolution of neutral insoluble intermediate $[Co^{II}(PAN)_2]^0$ are observed in the stopped-flow signals for the light scattered by the reaction mixture. This approach for the detection of such invisible precipitates is also applied to the reaction of Ni^{2+} with PAN.

In the present paper, we report a sensitive and useful method for the detection of the formation and/or the redissolution of hardly visible precipitates in the course of fast reactions in solution.

The reaction of Co^{2+} with PAN (I) yields the trivalent cobalt complex with two ligand molecules $[Co^{III}(PAN)_2]^+$ (II) in aqueous dioxane media.[1,2] During the course of the reaction, the divalent cobalt complex is formed transiently. The intermediate $[Co^{II}(PAN)_2]^0$ [2] is neutral and is expected to be insoluble in aqueous media, while the cationic final product $[Co^{III}(PAN)_2]^+$ is more soluble. However, the reaction proceeds seemingly without forming insoluble species. The measurements of intensity of the light scattered by the reaction mixture clearly revealed the formation and the redissolution of insoluble reaction intermediates.

Figure 1 shows a disposition of the apparatus for the measurements. The apparatus was constructed simply by rearranging the position of the photomultiplier tube from B to A in a Union Giken rapid-scan stopped-flow spectrophotometer model RA-1300. The photomultiplier tube was disposed at right angle to the incident monochromatic light. A 2 mm cell with three windows was used.

Figure 2 shows the change in the intensity of the scattered light in the course of the reaction between Co^{2+} and PAN in a 5%(v/v) dioxane-water solution. A solution containing cobalt(II) perchlorate was rapidly mixed with a solution of PAN at pH 4.72 by stopped-flow technique. The intensity of the scattered light increases after
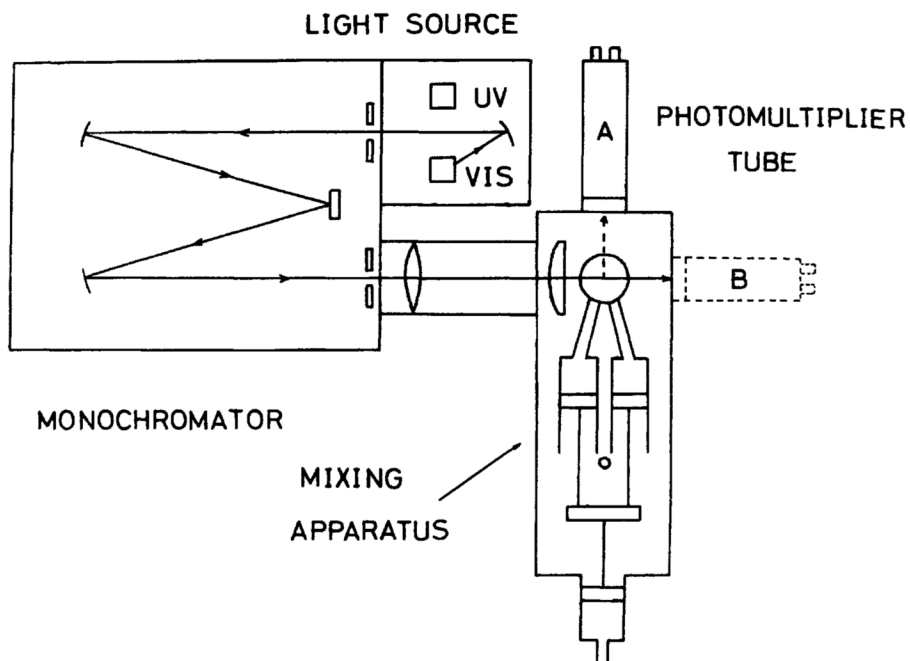
(I)

(II)

LIGHT SOURCE
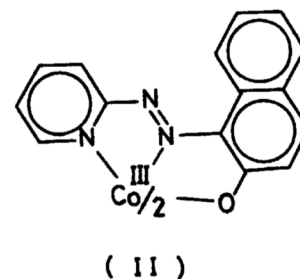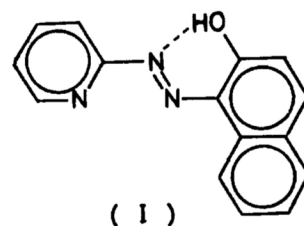
Fig. 1. Stopped-flow apparatus for the measurements of
scattered light. Photomultiplier tube at the position B
is for the conventional stopped-flow measurements.

short induction period and then decreases gradually. The feature of the signal was
essentially independent of the wavelength of the incident monochromatic light in
the range of 400-600 nm.

A flat, an increasing, and a decreasing portion of the signal shown in Fig. 2
would reasonably be explained as follows. The induction period appeared at the
initial stage of the reaction corresponds to the formation of cobalt(II)-PAN complex
prior to the crystal growth. The subsequent increase in the intensity of the
scattered light is due to the formation and the growth of insoluble crystals of
$[Co^{II}(PAN)_2]^0$. The final decreasing portion of the signal indicates the process of
redissolution of the insoluble intermediate. This corresponds to the step of oxida-
tion of $[Co^{II}(PAN)_2]^0$ by oxygen forming a more soluble $[Co^{III}(PAN)_2]^+$ complex.[2]

Similar experiments were carried out for the Ni^{2+}-PAN system. The reaction
of Ni^{2+} with PAN proceeds simply, yielding $[Ni(PAN)_2]^0$.[3] Figures 3(a) and 3(b)
show the stopped-flow signals of the scattered light for the reaction of Ni^{2+} with
PAN in 10 and 30%(v/v) dioxane-water solutions, respectively. The feature of the
signal shown in Fig. 3(a) is essentially the same as the first and the second part
of the signal shown in Fig. 2 and can be interpreted in the similar way. On the
other hand, no change in the stopped-flow signal for scattered light was observed for
the same reaction in a 30%(v/v) dioxane-water medium (Fig. 3(b)). These observations
suggest that the reaction product is insoluble in 10%(v/v) dioxane-water but is
soluble in 30%(v/v) dioxane-water.

The validity of this approach for the detection of an insoluble reaction
product was confirmed by the rapid-scan absorption spectral study and the analyses
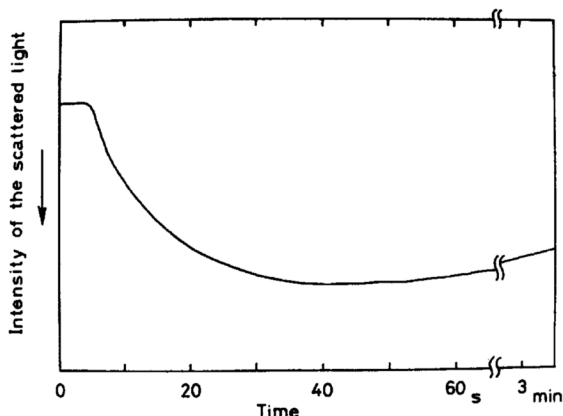of the conventional stopped-flow signals for the Ni^{2+}-PAN system.

Fig. 2. Stopped-flow signal of the scattered light for the reaction of 1.91×10^{-5} mol·dm^{-3} Co^{2+} and 2.99×10^{-5} mol·dm^{-3} PAN in a 5%(v/v) dioxane-water mixture at pH 4.72, I = 0.1 (NaClO$_4$) and 25 °C.
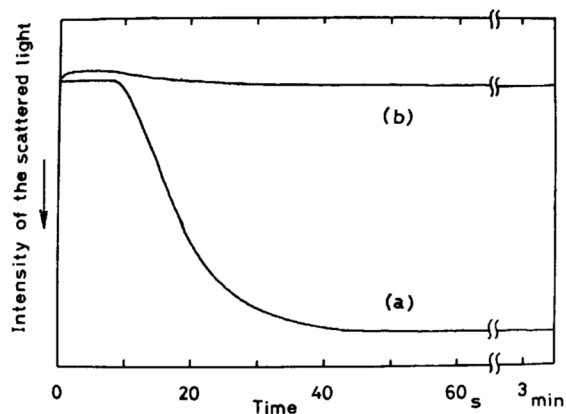
Fig. 3. Stopped-flow signals of the scattered light for the reaction of 9.06×10^{-4} mol·dm^{-3} Ni^{2+} and 2.99×10^{-5} mol·dm^{-3} PAN in 10 (a) and 30%(v/v) (b) dioxane-water mixtures at pH 4.72, I = 0.1 (NaClO$_4$) and 25 °C.

Figure 4 shows the rapid-scan spectra for the reaction of Ni^{2+} ion with PAN in a 10%(v/v) dioxane-water solution under the same conditions as in Fig. 3(a). Each spectrum was rapidly scanned (300 nm/0.5 s) at appropriate time intervals after a solution containing nickel(II) perchlorate was rapidly mixed with a PAN solution by stopped-flow technique. At the initial stage, the spectrum of the reaction mixture changes rapidly with an isosbestic point at 490 nm. The absorption around 470 nm due to the free ligand PAN decreases with the increase of a new absorption due to the complex around 555 nm. This rapid spectral change ceases in ca. 10 s after mixing. Then another relatively slow spectral change occurs with an increase of a new absorption around 600 nm. The final spectrum 6 was found to be very similar to the diffuse reflectance spectrum of solid [Ni(PAN)$_2$]^0 diluted with sodium chloride shown in Fig. 5.

On the other hand, when the experiment was carried out in a 30%(v/v) dioxane-water solution under the same conditions as in Fig. 3(b), only the spectral change with an isosbestic point at 490 nm was observed and no successive increase in absorption around 600 nm appeared. The final spectrum under this condition was essentially the same as the absorption spectrum of [Ni(PAN)$_2$]^0 in chloroform,[4] namely, the final spectrum corresponds to the spectrum of completely-dissolved [Ni(PAN)$_2$]^0.

These observations suggest that the solution spectrum is different from the solid spectrum, though the reason is uncertain. The absorption around 600 nm would be a characteristic band inherent to solid [Ni(PAN)$_2$]^0. Therefore, the increase in absorbance around 600 nm observed at the second stage of the reaction in a 10%(v/v) dioxane-water medium must correlate to the formation of crystalline [Ni(PAN)$_2$]^0. The change in absorbance at 590 nm during the course of the reaction in a 10%(v/v) dioxane-water solution is shown in the inset of Fig. 4, indicating the gradual formation of the crystals preceded by the homogeneous complexation reaction.
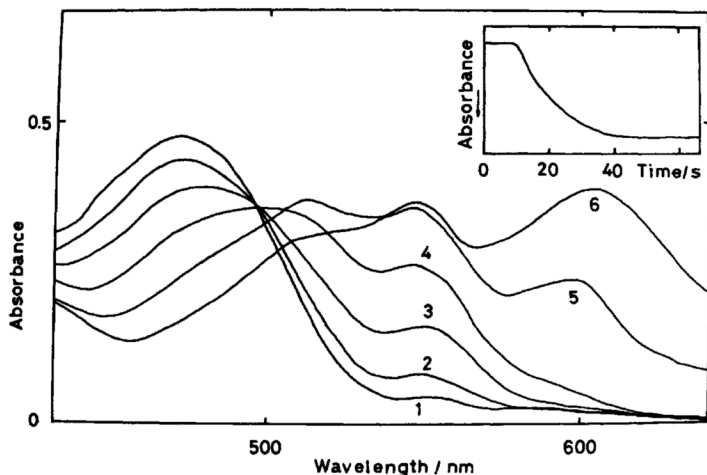
Fig. 4. Rapid-scan spectra for the reaction of 9.06×10^{-4} mol·dm^{-3} nickel(II) perchlorate and 2.99×10^{-5} mol·dm^{-3} PAN in a 10%-(v/v) dioxane-water mixture at pH 4.72, I = 0.1 ($NaClO_4$), and 25 °C, measured at 0 (1), 1 (2), 2.5 (3), 5 (4), 10 (5), and 25 s (6) after mixing. Inset shows the stopped-flow signal of the light absorption at 590 nm for this reaction.
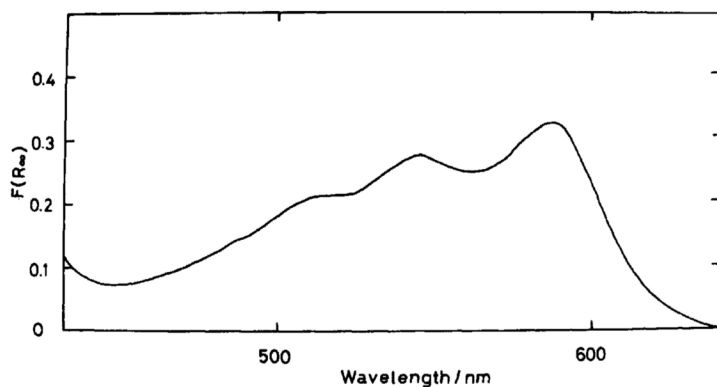

Fig. 5. Diffuse reflectance spectrum of $[Ni(PAN)_2]^0$ diluted with NaCl.

The feature and the length of the induction period of the signal shown in the inset of Fig. 4 are essentially the same as those of the stopped-flow signal observed for the scattered light shown in Fig. 3(a). For the reaction in a 30%(v/v) dioxane-water solution, no absorbance change was observed at 590 nm, indicating that no crystallization occurs as was found in the signal shown in Fig. 3(b).

On the basis of the analyses of the rapid-scan spectra and the stopped-flow signals for the light absorption, it is concluded that the stopped-flow signals for the scattered light shown in Figs. 2 and 3 reflect unambiguously the formation of very fine crystals in the course of fast reactions.

REFERENCES AND NOTES

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