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OSCILLATIONS OF FLUORESCENCE FROM IRRADIATED ERIOCHROME CYANINE R AND ERIOCHROME BLACK T IN AQUEOUS SOLUTION

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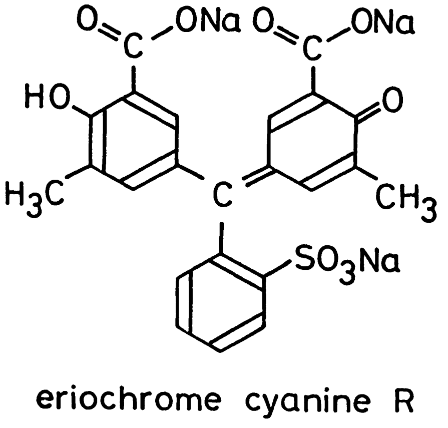
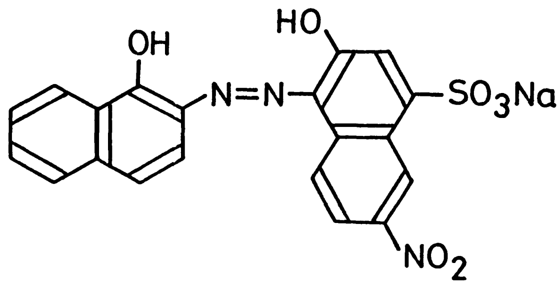
Rhythmic ocillations in fluorescence intensity were observed from irradiated organic fluorochrmoes, eriochrome cyanine R and eriochrome black T, in aqueous solution.

In the past few years, oscillatory chemical phenomena have attracted much attention.1) Despite the general interest in these phenomena, only a few examples of photochemical oscillations are known.2-7) Here, we report photochemical oscillation in an aqueous system.



eriochrome cyanine R



eriochrome black T

Figure 1 shows typical results on the periodic change of fluorescence intensities of eriochrome cyanine R (Fig.1 (a)) and eriochrome black T (Fig.1 (b)). Observations were made with a Hitachi 650-40 fluorescence spectrophotometer. In both cases, measurements were made in aqueous acetate/sodium acetate buffer (pH 7.7) containing 10% acetone. In these measurements, eriochrome cyanine R was excited at 319 nm (band width 10 nm) and fluorescence intensity was recorded at 420 nm (band width 5 nm), and eriochrome black T was excited at 309 nm (band width 10 nm) and fluorescence intensity was recorded at 410 nm. The characteristic features of induction of oscillations were as follows: (1) No oscillation or fluctuation of the fluorescence was observed in the absence of acetone. An aqueous solution of 10% acetone in the absence of fluorochrome also showed no time-dependent fluctuation in emission. (2) Oscillations were observed only when the solution was stood without stirring: when the sample was stirred, the intensity of the fluorescence did not fluctuate. (3) Oscillations were observed when the container of the solution was not sealed. (4) When other fluorochromes, such as 8-anilinonaphthalene-1-sulfonate (ANS) or 9-amino-acridine, were used instead of eriochrome cyanine R and eriochrome black T, no oscillation was observed.

In 1983, Epstein et al.[2,3] reported oscillation of emission intensity on illumination of biacetyl in acetonitrile. They also reexamined the emission of organic solutions of acetone, anthracene, and 9,10-dimethylanthracene, which were reported to oscillate by others.[4,5] They concluded that the observed oscillations did not result from cyclic dynamic photochemical changes, but from time-dependent convective motion of the fluid in the optical cell. This conclusion has been supported by M. Gimenez, et al. in a recent paper.[7]

In the present study, the oscillations ceased when the solution in the cell was stirred. This suggests the importance of convective motion of the solution. However, when 8-anilinonaphthalene-1-sulfonate or 9-aminoacridine was used as fluorochrome, no oscillation was observed even when the solution was stood without stirring. Thus the oscillations can't be explained simply by convective motion due to local heating induced by illumination. In other words the observed oscillations do not seem to be simply artifacts due to the temperature gradient induced by the excitatory light source.

Nemzek and Guillet[4] studied the temporal fluctuations in emission from

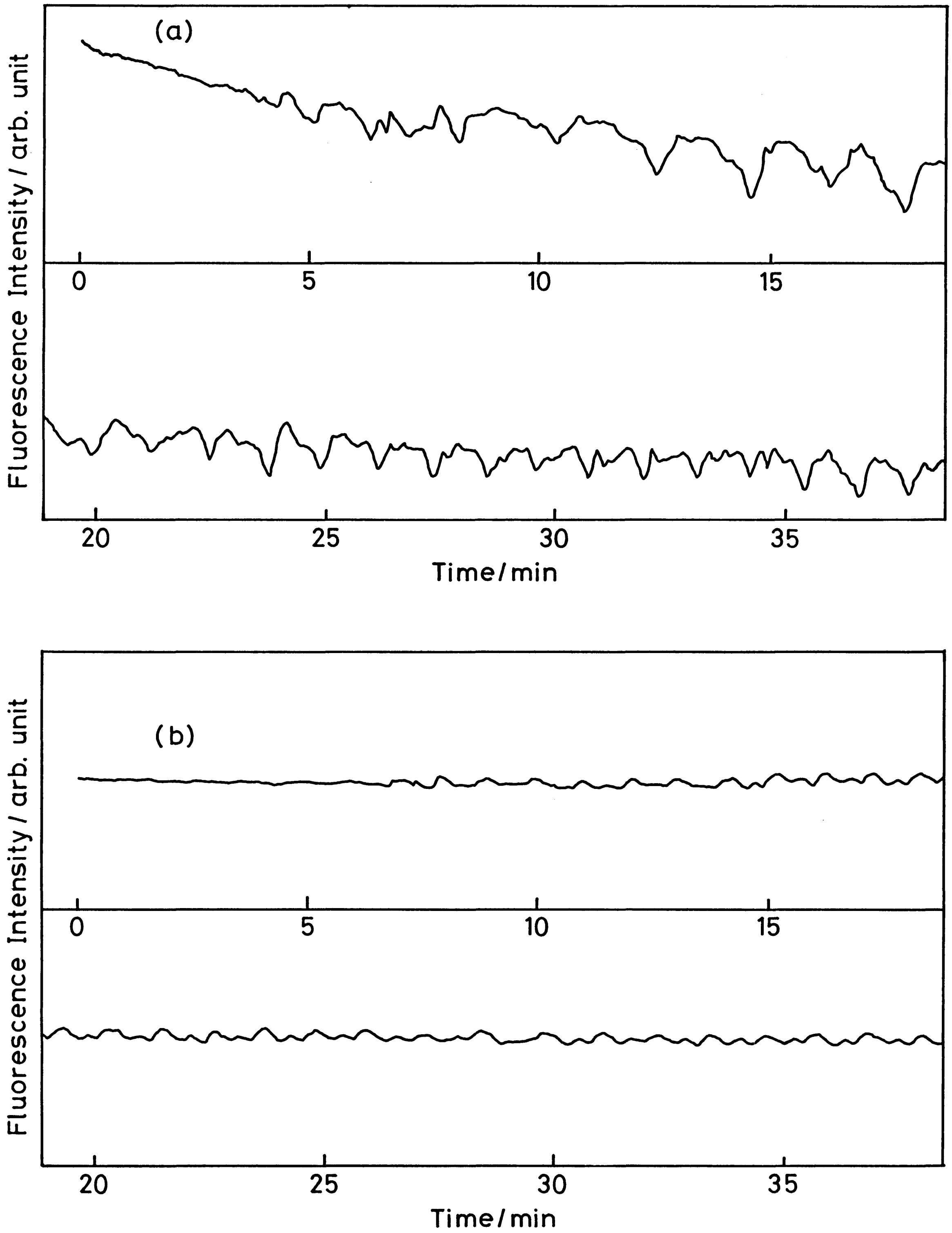


Fig. 1. Oscillations of fluorescence intensity of eriochrome cyanine R (a) and eriochrome black T (b). Fluorescence is shown in arbitary units.

irradiated acetone solution and concluded that they were due not to acetone, but to biacetyl, which was produced photochemically during illumination. We examined this possibility in our system by monitoring the emission at 515 nm of biacetyl excited at 310 nm, but did not observe any oscillation or fluctuation of the emission. This indicates that in our photochemical oscillator, neither emission from acetone nor from biacetyl contributes to the oscillation, although acetone may contribute to the time-dependent convective motion of the solution in some way.

The solution in the photo-cell may be heated by the excitation light in two ways: by direct conversion of light to heat energy and by release of heat through non-radiative transition of excited molecules. However, in our system, the former may be negligible because infra-red light was omitted during the measurement. We found that eriochrome cyanine R or eriochrome black T was essential for induction of oscillations. This suggests the importance of a non-radiative process in generation of this time-dependent phenomenon. In this sence, the observed oscillations can be regarded as caused by the coupling of chemical (non-radiative transition) and physical (convective motion) processes.

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