

## Oscillation Found in Reaction between Permanganate and Oxalic Acid

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The temporal change in absorbance of the solution was observed after mixing permanganate and oxalic acid. The oscillating structure appeared continuing more than 1 h. This oscillation was not observed by mixing permanganate with the reducing agents other than oxalic acid such as  $\text{Ce}^{3+}$  and  $\text{As}^{3+}$ .

The reduction of permanganate by oxalic acid has been one of the most popular reactions of which mechanisms have been studied during latest 120 years.<sup>1)</sup> In spite of the long history of this study, chemical oscillation has not been yet reported, but the bistability of reaction kinetics.<sup>2)</sup> However, we would like to report here that, during the relaxation period after mixing the permanganate and oxalic acid solutions, some oscillatory structures appear under the spectrometric observation.

A stopped flow method was adopted for the simultaneous mixing of permanganate and oxalic acid solution, where a rapid reaction analyzer (Union Giken, model RA-1300) was employed with using a cell of 2 mm light path length. Reaction was followed by the absorption of the solution for visible light. The temperature of the solution and cell was controlled by a circulating water bath (Neslab Instruments Inc., model RTE-8). The output signal from the rapid reaction analyzer was recorded in a digital analyzing recorder (Yokogawa Electric Co., model 3655E).

The water used here was prepared by the redistillation of water with adding small amount of potassium permanganate. Potassium permanganate and oxalic acid were dissolved in this distilled water. Prior to the measurement, the reaction cylinder of the rapid reaction analyzer was carefully cleaned for eliminating  $\text{MnO}_2$  adsorbed in the cell.

Figure 1 shows a typical example of oscillation pattern observed in the reduction of permanganate solution (0.02 M (= mol  $\text{dm}^{-3}$ )) by oxalic acid (0.02 M) at 50 °C. In this figure, absorbance of the solution decreased just after the mixing, and then recovered due to the excess in amount of permanganate compared with that of oxalic acid. The oscillation of absorption of solution occurred during this recovery process and continued for about 1.5 hours. The oscillation pattern shown in Fig. 1 can be observed not only in the present stopped flow analyzer, but also observed in the ordinary spectrophotometer. After mixing the 0.01 M aqueous solution of permanganate with the 0.01 M aqueous solution of oxalic

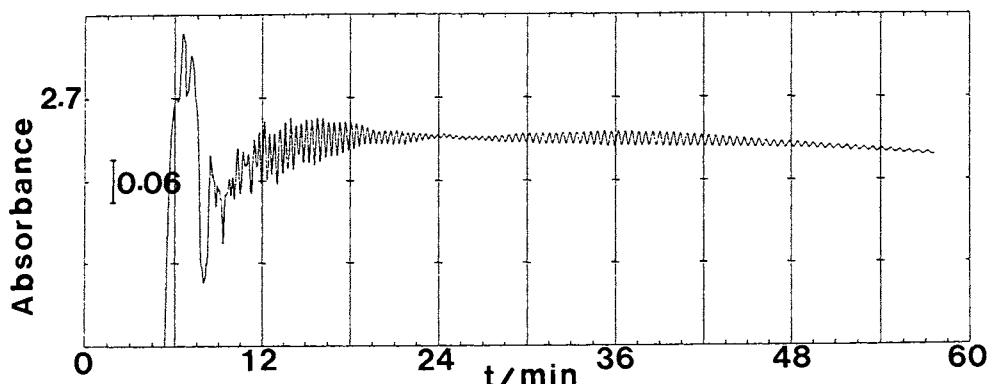


Fig. 1. Oscillation in absorption at 500 nm.

acid, the change of absorbance of this mixture was followed by the ordinary spectrophotometer with using 1 mm cell under the control of the temperature.

This oscillation was not observed when the concentration of oxalic acid is close to or exceeds the molar equivalent (neutralization equivalent) point. The oscillation was observed in the wavelength region from 400 to 700 nm. However, addition of 1% sulfuric acid to the oxalic acid solution provided the fast reaction, and did not induce the oscillation during the period of recovery of permanganate color in the solution. Differing from the case of reduction of permanganate by hydrogen peroxide,<sup>3)</sup> coexistence of more than 0.01 M of  $Mn^{2+}$  in the oxalic acid solution diminished the oscillation structure with rapid recovery of permanganate color under the same condition as Fig. 1.

When arsenite and cerium(III) sulfate were used as the reducing agent of permanganate instead of oxalic acid, their solutions did not produce oscillation for the reduction process of permanganate in any pH region. When the temperature of solution and cell becomes lower than 25 °C, the temporal change of absorption of solution was rather smooth losing the oscillation structure.

According to Fig. 1, it takes about 10 min for starting the oscillation: oxalic acid seems to be consumed at this moment. Therefore, it is considerable that this oscillation is not due to permanganate color but due to the formation of manganese dioxide although the formation of precipitate was not visually recognized in the cell after the measurement. Several mechanisms can be considered: the disproportionation of  $MnO_4^{2-}$  to  $MnO_2$  and  $MnO_4^-$ , or the reverse reaction of this process. Also, if  $Mn^{2+}$  appears during some stages,  $MnO_2$  is produced due to the reaction between  $Mn^{2+}$  and  $MnO_4^-$ .<sup>4)</sup> The fact that the oscillation appears under the condition in excess of permanganate rather than oxalic acid supports that  $MnO_2$  mediates the present phenomena. Several novel type chemical oscillating reactions have been recently studied by many scientists. The present type is, however, rather different from the general oscillating reactions in terms of its timing (short periodic time) and rather small amplitude of vibration.

#### References

- 1) S. J. Adler and R. M. Noyes, *J. Am. Chem. Soc.*, 77, 2036 (1955).
- 2) J. S. Reckley and K. Showalter, *J. Am. Chem. Soc.*, 103, 7012 (1981).
- 3) A. Nagy and L. Treindl, *Nature*, 320, 344 (1986).
- 4) Y. K. Gupta and S. Ghosh, *Z. Phys. Chem. (Leipzig)*, 208, 368 (1958).

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