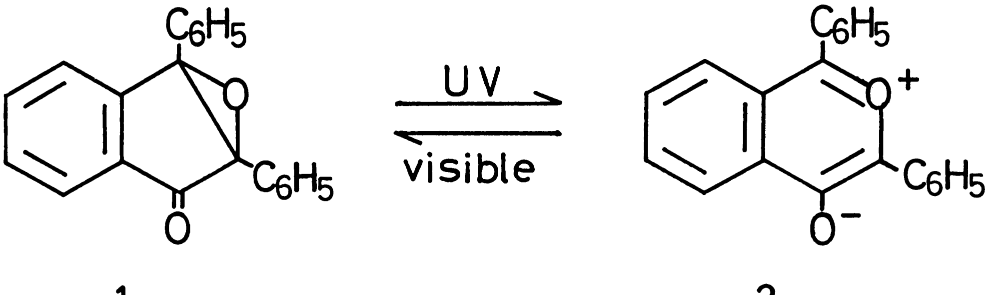
CHEMISTRY LETTERS, pp. 529-532, 1987.

Photo-induced Potential Changes across Poly(vinyl chloride)/ 2,3-Diphenylindenone Oxide Membrane

Hiroshi SASAKI, Akihiko UENO, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

Membrane potential across Poly(vinyl chloride) entrapping 2,3-Diphenylindenone oxide was reversibly controlled by UV and visible light irradiation. The magnitude of photo-induced potential change depended upon the concentration of electrolyte solution.

Azobenzene and spirobenzopyran are well known photoresponsive compounds, and in recent years, many attempts have been done to use these compounds as photochemical switches for controlling various molecular phenomena.[1,2] We have already reported that Poly (vinyl chloride) (PVC) can be converted to photoexcitable membrane, in which photo-induced potential change occurs across the membrane, by entrapping azobenzene-modified crown ether,[3] spirobenzopyran,[4] or crown ether linked spirobenzopyran.[5] 4,5-Epoxy-2-cyclopentene derivatives are also photoresponsive,[6-9] but there has been no attempt to use these compounds as switching elements. We report here that potential change across PVC membrane entrapping 2,3-diphenylindenone oxide (**1**) occurs reversibly by UV and visible light irradiation.



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The compound **1** was synthesized according to the Clark's method.[10) PVC/**1** membrane was prepared by pouring the mixture of PVC (235 mg), dibutyl phthalate (0.54 ml), **1** (20 mg), and tetrahydrofuran (20 ml) onto flat petri dish (9.2 cm diameter) and allowing the solvent to evaporate. The prepared membrane has a thickness of ca. 0.1 mm. All measurements were carried at 25 °C. The system used for the membrane potential measurements is shown in Fig. 1. The composition of the system was as follows: Hg_2Cl_2 (s), Hg| KCl (sat.)| NaCl solution (c)| PVC/**1** membrane| NaCl solution (c)| KCl (sat.)| Hg_2Cl_2 (s), Hg. Electrolyte concentrations of both a and b parts were the same in all measurements. The electrolyte solution of the left side was earthed. Photoirradiation was performed with a 500 W xenon lamp using cut off filters Toshiba UV D-35 and Y-45 for isolating UV (320 nm < λ < 400 nm) and visible (450 nm < λ) light, respectively. Photoirradiation was done from right side.

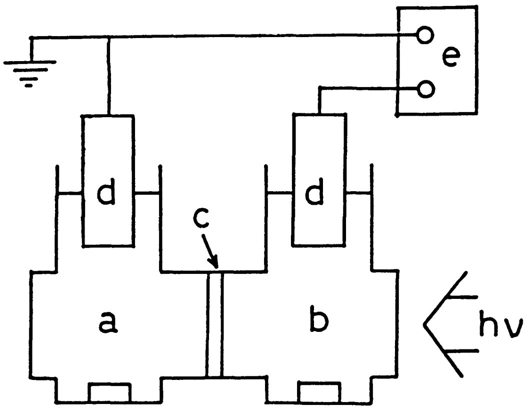

Fig. 1. Schematic sketch of the cell for membrane potential measurements. a and b: Electrolyte solutions, c: Membrane, d: Saturated calomel electrodes, e: Potentiometer.

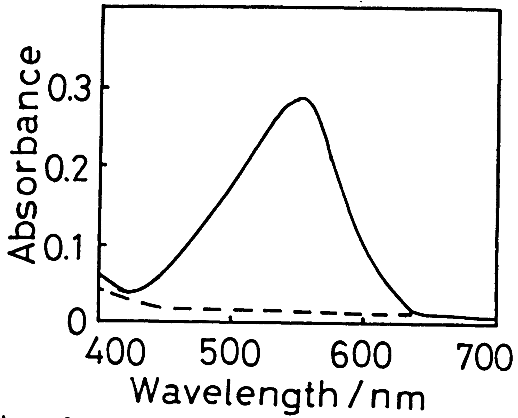

Fig. 2. Absorption spectra of PVC/1 membrane before (---) and after (——) UV light irradiation.

The isomerization of **1** in the membrane, which was once soaked in 1 mmol dm^{-3} NaCl solution, was checked by absorption spectra. The changes of the membrane absorption spectrum induced by UV irradiation are shown in Fig. 2. Before UV irradiation, the membrane showed no absorption in the wavelength region between 400 and 700 nm, so the membrane was colorless. After UV irradiation, the membrane turned purple, and a new absorption band appeared at 554 nm. This spectral change indicates that **1** was isomerized to pyrylium form (**2**).[8) By subsequent visible light irradiation, the original spectral pattern of **1** was recovered quickly, and the colorless membrane was again obtained (Fig. 3).

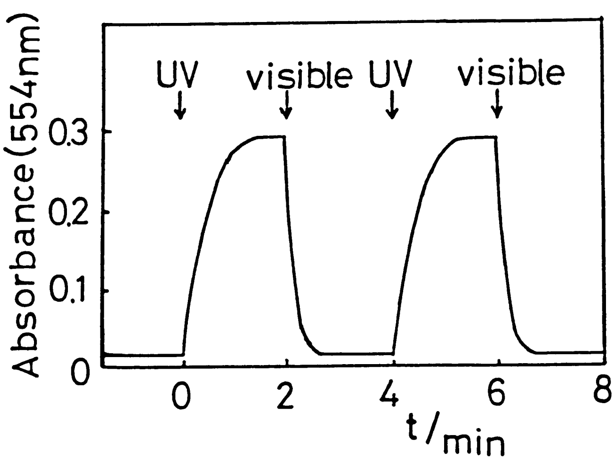

Fig. 3. The changes of the membrane absorbance (554 nm) induced by alternate UV and visible light irradiation.

Figure 4 illustrates the changes of the membrane potential induced by alternate UV and visible light irradiation. A negative shift of the membrane potential was induced by UV light irradiation ($\Delta(\Delta\Phi)$). The membrane potential reached steady state under UV light in ca. 2 min, and then returned to the initial potential by visible light irradiation in ca. 1.5 min. The phenomenon was similar to that of the membrane containing spirobenzopyran derivatives.[4,5,11-13)]

Figure 5 shows the effect of the concentration of NaCl solution (c) on the $\Delta(\Delta\Phi)$. The $\Delta(\Delta\Phi)$ value depended upon the concentration of NaCl. With increasing concentration, the $\Delta(\Delta\Phi)$ became less negative. The result contrasts to the photo-induced potential changes of the PVC/spirobenzopyran membrane, which are hardly affected by electrolyte concentration. In the case of PVC/spirobenzopyran membrane, the addition of proton to open-form of spirobenzopyrans was suggested to be prerequisite for causing photo-induced potential.[4,11-13)] The decreased photoresponse observed for PVC/**1** membrane at high NaCl concentrations suggests that the different mechanism operates in the present system. The incorporation of Cl^- into the membrane might occur at high NaCl concentrations, cancelling the positive charge of proton-added species of **2**.

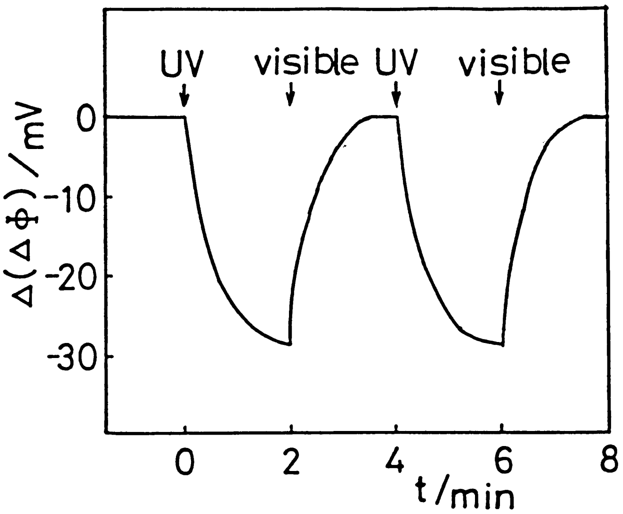

Fig. 4. The changes of the membrane potential induced by alternate UV and visible light irradiation. c= 1 mmol dm^{-3}

We are studying on the exact mechanism of the photo-induced system in our laboratory.

This work was supported by a Grant-in-Aid for Encouragement of Young Scientist (No. 61790179) from the Ministry of Education, Science and Culture of Japan.

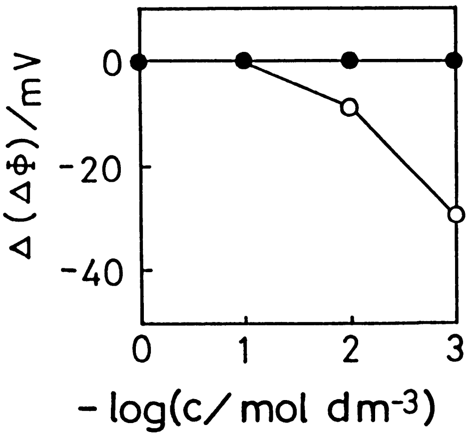

Fig. 5. Dependence of the membrane potential on NaCl concentration.
●: In the dark or under visible light irradiation.
○: Under UV light irradiation.

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(Received January 8, 1987)