

Photostimulated Transport of Carboxylate and Phenolate Anions Across a Liquid-Liquid Membrane Using a Photochromic Cationic Copolymer as Carrier

Itamar Willner*, Sherbel Sussan and Shai Rubín

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Photostimulated transport of carboxylate and phenolate anions proceeds across a liquid-liquid membrane system using a styrene-vinyl Malachite green copolymer as carrier.

Development of transport systems for cations, anions and neutral substrates is a subject of continuous research efforts.^{1,2} Photochromic compounds linked to ion carriers, *i.e.* azobenzene-crown ethers^{3,4} and photochromic compounds undergoing light-induced isomerization to zwitterionic forms, *i.e.* spiropyran,⁵ have been applied as carriers in photochemically driven active transport of alkali ions and amino acids, respectively. Recent research activities are directed to the development of photostimulated macromolecules.^{6,7} Physical properties such as viscosity,⁸ density,⁹ tertiary structure¹⁰ and permeability,¹¹ have been photostimulated in photochromic copolymers. Catalytic properties of enzymes have been switched by light by anchoring photochromic components to the protein¹² or by immobilization in photochromic copolymers.¹³ Here we report the photostimulated transport of carboxylic acids and phenols in a liquid-liquid membrane system using the copolymer of styrene and 4-vinyl Malachite green¹⁴ **1** as carrier.

The liquid-liquid membrane system is composed of an aqueous solution, 2.5 ml, pH = 10, that includes the carboxylate, 0.1 mol dm⁻³, separated from a second aqueous phase, 2.5 ml, pH = 3, by a carbon tetrachloride solution, 5 ml. In the organic phase the photochromic copolymer styrene-**1**, (*M_r* = 25 000–35 000), 30 mg, is solubilized as carrier. The molar ratio of **1** to styrene in the copolymer **2a** is 1 : 200, respectively. The photostimulated transport of cinnamic acid, **3**, and *p*-hydroxycinnamic acid, **4**, is shown in Fig. 1. In the dark, the transport of the acids is slow. Upon illumination ($\lambda = 330\text{--}370$ nm) of the organic layer, a substantial enhancement in the transport rate of the acids is observed. For example, the transport of **4** is *ca.* three times faster upon irradiation of the organic phase. Illumination of the organic phase results in the dark-green colour of the triphenylmethyl cation, **2b**. Control experiments reveal that the transport rate of the carboxylic acids in the dark is very similar to the transport rate in the presence of polystyrene in the organic phase or to the

transport rate in the absence of any carrier. These results imply that photostimulation of the transport process results in the interaction of the cationic photochromic copolymer, acting as carrier, with the anionic substrate.

Fig. 2 represents schematically the photostimulated transport process. In the source phase, pH = 10, the carboxylic acid is in the anionic form. Upon illumination of the photochromic copolymer, the resulting cationic polymer acts as carrier by ion pairing of the anion. Transport across the membrane results in protonation of the acid in the sink aqueous phase. Thus, the transport of the carboxylate is followed by the concomitant antiport of an anion from the sink phase to the source aqueous phase. Similar photostimulated transport of phenolate anions; *p*-nitrophenol, **5**, and *p*-hydroxybenzaldehyde, **6**, is observed using the styrene-**1** copolymer as carrier. Table 1 summarizes the transport rates of the various anionic substrates in the dark and upon illumination of the organic phase. The switching

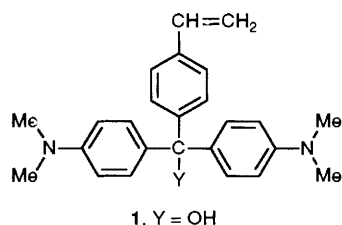


Table 1 Photostimulated transport rates of organic anions across a liquid-liquid membrane using styrene-**1** as carrier

Substrate	$v_{\text{dark}} / \text{mol dm}^{-3} \text{ min}^{-1}$	$v_{\text{illumination}} / \text{mol dm}^{-3} \text{ min}^{-1}$	Switching efficiency ^a
3	2.6×10^{-7}	7.0×10^{-7}	2.7
4	4.93×10^{-7}	1.61×10^{-6}	3.26
5	1.89×10^{-8}	7.43×10^{-8}	3.93
6	8.78×10^{-9}	7.53×10^{-8}	8.6

^a Switching efficiency is defined as $v_{\text{illumination}}/v_{\text{dark}}$.

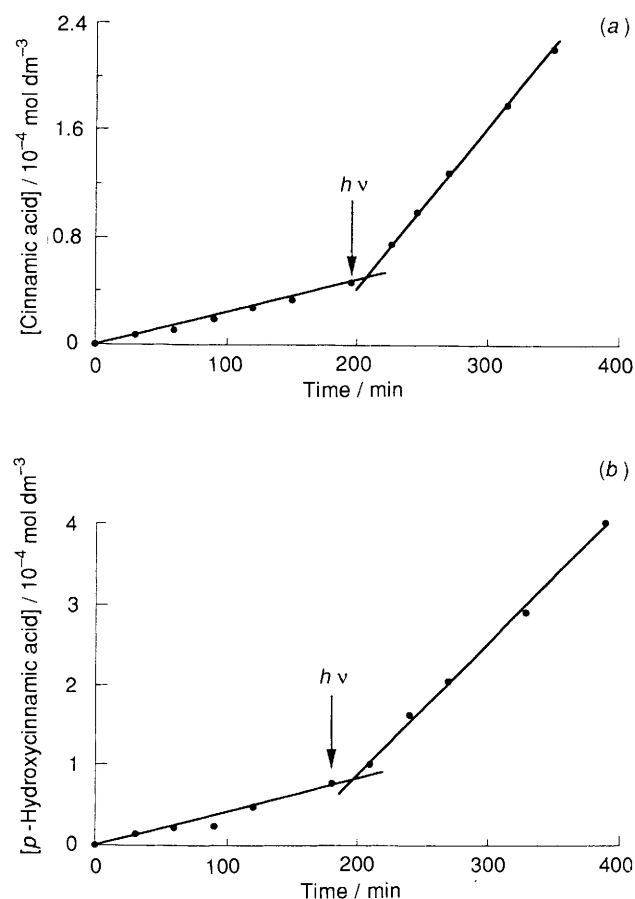


Fig. 1 Rate of carboxylate anion transport across a liquid-liquid membrane, [carboxylate] = 0.1 mol dm⁻³ in source phase, pH = 10, sink aqueous phase, pH = 3, styrene-**1** copolymer in organic phase, 30 mg/5 ml. (a) Transport of cinnamic acid, **3**. (b) Transport of *p*-hydroxycinnamic acid, **4**. The arrow indicates illumination of the organic phase on conversion of the carrier to the cationic photochromic form.

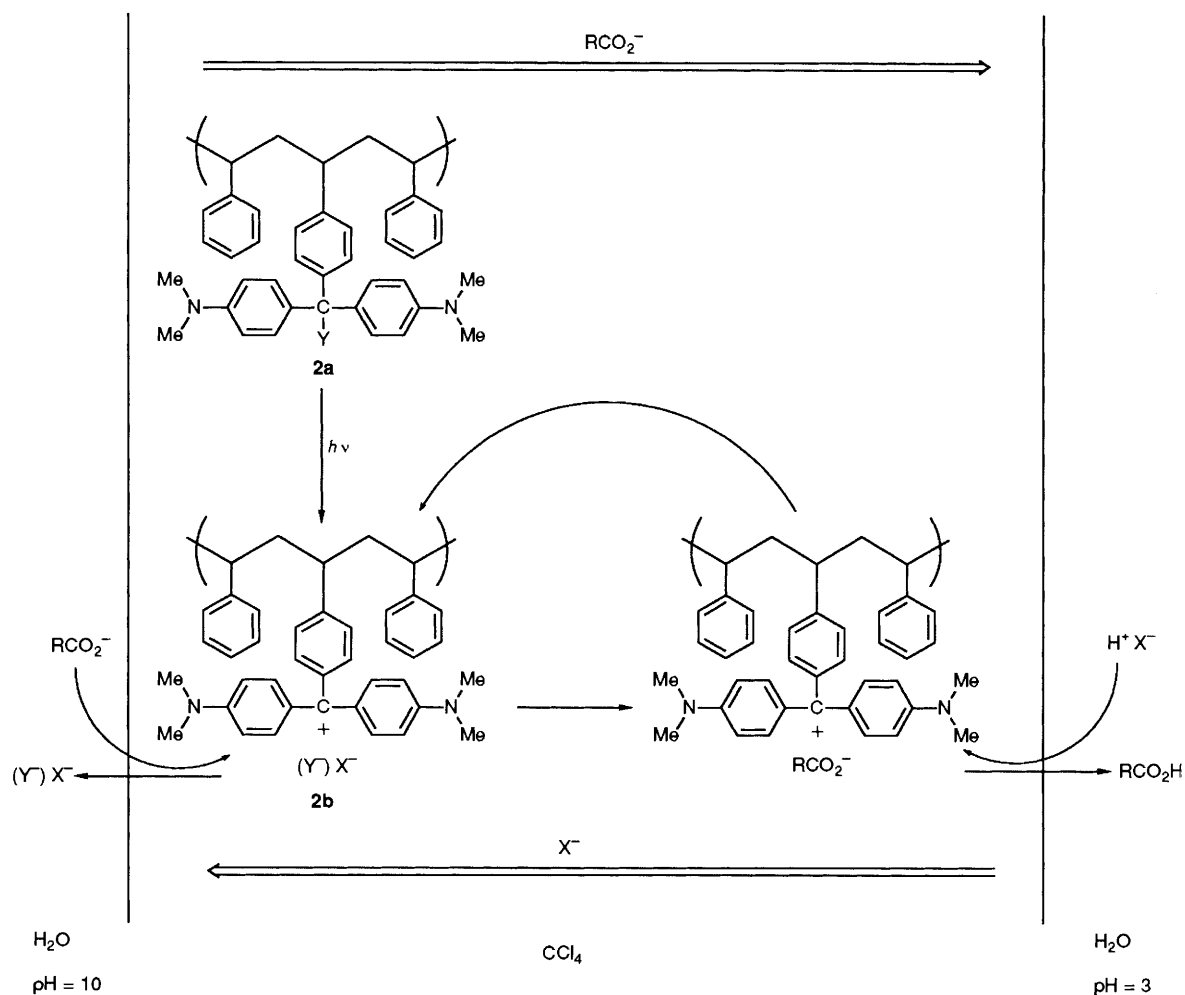


Fig. 2 Scheme for photostimulated transport of carboxylates and anionic antiport using styrene-1 copolymer as carrier, $Y^- = OH^-$; $X^- = Cl^-$

efficiency upon generation of the cationic polymeric carrier is tabulated for the various substrates. Although the transport rates of the various substrates is controlled by the transport of the polymeric carrier across the organic phase, different switching efficiencies, and consequently selectivity in substrate transport, are observed. This originates from different binding properties of the various anions to the polymeric cationic carrier. As a result, the actual concentration of the transported anion in the oil phase differs for the various substrates and selectivity is attained.

We thus conclude that transport of organic anions is photostimulated by the photochromic styrene-1 copolymer. Illumination of the assembly results in the cationic photochromic polymer that acts as a carrier and trigger in the transport process.

This research was supported by the Fund for Basic Research administered by the Israel Academy of Sciences and Humanities. The research was performed under the auspices of The Farkas Research Center for Photoinduced Processes.

Received, 29th August 1991; Cor. 1104511C

References

- 1 H. Tsukube, *J. Coord. Chem.*, 1987, **165**, 101; J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.

- 2 J. Rebek, Jr., *Top. Curr. Chem.*, 1988, **149**, 189; M. Okahara and Y. Nakatsuji, *Top. Curr. Chem.*, 1985, **128**, 37.
- 3 J.-I. Anzai, H. Sasaki, A. Ueno and T. Osa, *Chem. Lett.*, 1984, 1205.
- 4 J.-I. Anzai, H. Sasaki, A. Ueno and T. Osa, *J. Chem. Soc., Perkin Trans. 2*, 1985, 903; S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu and O. Manabe, *J. Am. Chem. Soc.*, 1981, **103**, 111.
- 5 J. Sunamoto, K. Iwamoto, Y. Mohri and T. Kominato, *J. Am. Chem. Soc.*, 1982, **104**, 5502.
- 6 M. Irie, in *Molecular Models of Photoresponsiveness*, ed. G. Ontagnoli and B. F. Erlanger, NATO ASI series, Section A, Vol. 68, 1982, p. 291.
- 7 M. Irie, *Adv. Polym. Sci.*, 1990, **94**, 27.
- 8 M. Irie and M. Hooda, *Makromol. Chem., Rapid Commun.*, 1985, **6**, 533; L. Matejka, M. Ilavsky, K. Dusek and O. Wechterla, *Polymer*, 1981, **22**, 1511.
- 9 C. D. Eisenbach, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 680; M. Irie and D. Kungwachakum, *Makromol. Chem., Rapid Commun.*, 1984, **5**, 829.
- 10 M. Goodman and A. Kossoy, *J. Am. Chem. Soc.*, 1967, **89** 3863; J. L. Houben, A. Fissi, D. Baccila, N. Rosato, O. Pieroni and F. Ciardelli, *Int. J. Biol. Macromol.*, 1983, **5**, 94.
- 11 M. Aoyama, J. Watanabe and S. Inoue, *J. Am. Chem. Soc.*, 1990, **112**, 4452.
- 12 I. Willner, S. Rubin and A. Riklin, *J. Am. Chem. Soc.*, 1991, **113**, 3321.
- 13 I. Willner, S. Rubin and T. Zor, *J. Am. Chem. Soc.*, 1991, **113**, 4013.
- 14 G. Manecke and G. Kossmehl, *Chem. Ber.*, 1960, **93**, 1899.