Novel Carrier Molecules for 'Up-hill' Transport of Metal Picrates

Shinji Tsuchiya,* Yutaka Yamada, and Manabu Senō
Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-Ku, Tokyo 106, Japan

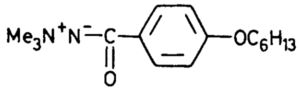
N–N Ylides have been synthesised for novel use as carrier molecules to transport metal picrates and organic anions through a liquid membrane; potassium picrate was successfully transported against its concentration gradient.

Metal ion transport across membranes is important in biology and is of great current interest.[1] Several functional carriers such as cyclic multidentate ligands or ionophores have been synthesised so as to mimic artificially the biological carriers.[2–5]

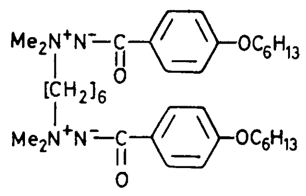
We report on an 'up-hill' transport system consisting of a liquid membrane containing an ylide as a novel carrier molecule. The ylides used here are carbonyl-stabilized aminimides, the electronic structures of which have been studied by *X*-ray photoelectron spectroscopy.[6,7] The oxygen atom of the carbonyl group is conjugated to the anionic nitrogen in the aminimide and can bind to metal ions. The anionic nitrogen in the aminimides can also form a salt with HCl and so their electronic structures are affected by the concentration of protons in solution. We have been interested, then, in the aminimides as novel pH dependent carriers of metal ions and to compare the efficiency of such transport with that by the electrostatic field of the oxygen atoms of, for instance, crown ethers.

The aminimides could also be used as carriers for organic anions in that they possess a quaternary nitrogen atom.

The aminimides (**1**) and (**2**) were synthesized from the corresponding hydrazonium salts. It is very important for the aminimide to have a long hydrocarbon chain as the concomitant insolubility in the aqueous phase protects the liquid membrane system from degradation. The structures of (**1**) and (**2**) were assigned from their i.r., n.m.r., and mass spectra and elemental analyses. For example, the ν(C=O) of (**1**) and (**2**) are 100 cm^{-1} lower than those of the corresponding hydrazonium salts and downfield shifts were observed for the methyl hydrogen atoms of the aminimides from those of the hydrazine derivatives in their respective ^{1}H n.m.r. spectra. The pK_a values of the aminimides are 4.0—5.0, though the exact values can not be ascertained owing to the insolubility of (**1**) and (**2**) in water.



(1)



(2)

Participation of the carbonyl oxygens of the aminimides in the complexation of KClO$_4$ was shown by ^{1}H n.m.r. and Fourier transform (F.t.) i.r. spectroscopy. The addition of KClO$_4$ to [^{2}H$_4$]methanol solutions of the aminimide caused significant changes in the chemical shifts of the methyl groups attached to the quaternary nitrogen [$\Delta\delta(Me_2N^+) = 0.10$ p.p.m.]. Furthermore, the carbonyl absorption in the F.t.-i.r. spectrum was broadened by the addition of KClO$_4$ to a methanol solution of the aminimide. The extraction of potassium ion by the aminimides was examined using the equilibrium of potassium picrate between an aqueous phase and a chloroform phase. Assuming that the complexation between metal picrate and aminimide was 1 : 1, the ion extrac-

Table 1. Details of the transport of potassium picrate by (**2**).[a]

Time	Ratio (%) of K^+ picrate in each phase Source	Organic	Receiving
(pH 7.20)			
1 day	77.0	9.0	14.0
2 days	67.0	8.0	25.0
3 days	58.0	6.0	36.0
(pH 8.05)			
1 day	89.0	5.0	6.0
2 days	85.0	4.0	11.0
3 days	80·0	3.0	17.0

[a] The organic phase contained (**2**) (1×10^{-3} M) and the source phase contained K^+ picrate (1×10^{-4} M) and KCl (1×10^{-1} M).

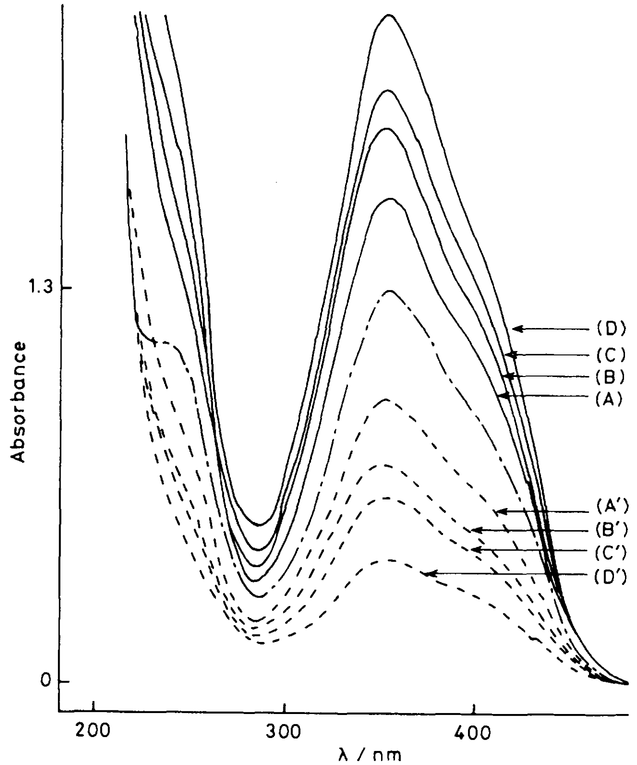


Figure 1. The change in concentration (by change in u.v. absorption) of K^+ picrate (initially 1×10^{-4} M) in the two aqueous phases with time (λ_{max} = 352 nm, log ϵ = 4.11). Absorption of K^+ picrate at initial concentration —·—·—; for outer aqueous phase (pH 8.05) with time ——; for inner aqueous phase (pH 7.20) with time - - - -; (A),(A'): after 1 day; (B),(B'): after 2 days; (C),(C'): after 3 days; (D),(D'): after 7 days.

tion constants of (**2**) at pH 7.20 and 8.05 were 637 and 313, respectively.

The metal ion transport of (**2**) was studied using a double cylindrical glass cell open at one end. A chloroform solution containing (**2**) (1×10^{-3} M) was placed at the base of the cell. A Tris buffer solution containing the metal picrate (1×10^{-4} M) and the metal chloride (1×10^{-1} M) was added carefully to the chloroform solution in the outer cylinder. A Tris buffer solution was placed in the inner cylinder and the organic phase was stirred magnetically at room temperature. Metal ion transport was examined by observing changes in the u.v. absorptions of the metal picrate. Results from atomic absorption analyses showed smaller amounts of transported cation than by u.v. methods. However, it is not clear whether the potassium picrate was carried as the picric acid or the values from atomic absorption analyses contain an error. The efficiency of transport by (**1**) is lower than that by (**2**)† and that of (**2**) with potassium picrate is shown in Table 1. This indicates that the ratio of potassium picrate in the organic phase to that in the aqueous phase is small. As the order of increasing transport efficiency follows that of the extraction constant, the ion uptake may be rate-determining. Conversely, it was found for 18-crown-6 that the ion release was rate-determining and that the concentration of potassium picrate in the organic phase was much higher.[8]

The most striking property of (**2**) as a carrier is the pH dependent transport of the metal picrate. The large difference between the efficiency of transport at pH 7.20 and that at pH 8.05 suggests an 'up-hill' transport of potassium picrate. To test this, a double cylindrical cell was set up with an inner aqueous phase of a Tris buffer solution (pH 7.20) and an outer phase of a Tris buffer solution (pH 8.05) both with the same concentration of potassium picrate (1×10^{-4} M). When 18-crown-6 was used as the carrier in this system, the concentrations of the two aqueous phases decreased together and no difference in concentration was observed. The potassium picrate passed from the two aqueous phases to the organic phase. With (**2**) as carrier, the concentration of the pH 8.05 solution increased with time, but that of the pH 7.20 solution decreased as shown in Figure 1. This indicates that the potassium picrate is transported against its concentration gradient by (**2**). One probable reason for this behaviour of (**2**) is the degree of interaction between the quaternary nitrogen and the anionic oxygen of potassium picrate.

Received, 17th May 1983; Com. 639

References

1 J. W. Westley, *Adv. App. Microbiol.*, 1977, **22**, 177; B. C. Pressman, *Ann. Rev. Biochem.*, 1976, **45**, 501.

2 R. M. Izatt and J. J. Christensen, 'Synthetic Multidentate Macrocyclic Compounds,' Academic Press, New York, 1978; J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351; J. S. Bradshaw, S. L. Baxter, J. D. Lamb, R. M. Izatt, and J. J. Christensen, *J. Am. Chem. Soc.*, 1981, **103**, 1821.

3 D. J. Cram, 'Application of Biochemical Systems in Organic Chemistry,' Wiley, New York, 1976; D. J. Cram, G. M. Lein, T. Kaneda, R. C. Helgeson, C. B. Knobler, E. Maverick, and K. N. Trueblood, *J. Am. Chem. Soc.*, 1981, **103**, 6228.

4 A. H. Haines and I. Hodgkisson, *J. Chem. Soc., Perkin Trans. 1*, 1983, 311; Y. Kokube, K. Hanji, K. Horiguchi, M. Asada, Y. Nakayama, and J. Furukawa, *J. Am. Chem. Soc.*, 1976, **98**, 7414.

5 M. W. Hosseini and J. M. Lehn, *J. Am. Chem. Soc.*, 1982, **104**, 3525; E. Graf, J. P. Kintzinger, J. M. Lehn, and J. LeMoigne, *J. Am. Chem. Soc.*, 1982, **104**, 1672.

6 M. Senō and S. Tsuchiya, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 165; M. Senō and S. Tsuchiya, *J. Chem. Soc., Dalton Trans.*, 1977, 751; M. Senō, S. Tsuchiya, and S. Ogawa, *J. Am. Chem. Soc.*, 1977, **99**, 3014; S. Tsuchiya and M. Senō, *Chem. Phys. Lett.*, 1978, **54**, 132; 1982, **92**, 359; S. Tsuchiya, S. Mitomo, and M. Senō, *J. Chem. Soc., Chem. Commun.*, 1983, 340.

7 S. Tsuchiya and M. Senō, *J. Org. Chem.*, 1979, **44**, 2850; S. Tsuchiya, M. Senō, and W. Lwowski, *J. Chem. Soc., Chem. Commun.*, 1982, 875; S. Tsuchiya and M. Senō, *ibid.*, 1983, 413; S. Tsuchiya, M. Senō, and W. Lwowski, *J. Chem. Soc., Perkin Trans. 2*, 1983, 887.

8 I. Tajima, M. Okada, and H. Sumitomo, *J. Am. Chem. Soc.*, 1981, **103**, 4096.

---

† After 3 days at pH 7.20 and 8.05 the transport ratios of K^+ (Ca^{2+}) picrate with (**2**) were 36.0 and 17.0% (27.0 and 16.0%) respectively [transport ratio = (concentration of transported metal picrate)/(initial concentration of metal picrate)].