Table I. Reversible Migration of 2-Hydroxy-4-methylazobenzene (1) from Toluene to 1.0 N Aqueous NaOH

condition[a]	[azophenol 1] in toluene (M)	[azophenoxide 1] in aq phase (M)
after stirring in the dark, 3 min	4.45×10^{-5}	0.110×10^{-5}
after 3 min irradiation and stirring	3.23×10^{-5}	1.51×10^{-5}
after 3 min further stirring in the dark	4.21×10^{-5}	0.143×10^{-5}
after 3 min further irradiation and stirring	3.17×10^{-5}	1.43×10^{-5}

[a] Aqueous and organic phases, 50 mL each, in a 200-mL thermostated, round-bottomed flask at 25.0 °C, inside a Rayonet reactor equipped with 350-nm lamps.

Table II. Acidity Constant Values, K_a, Obtained with Use of Eq 3 for Azophenols 1, 2 and 3

compd	K_A(dark)	K_A(light)
1[a]	2.92×10^{-11}	5.47×10^{-10}
2[b]	1.54×10^{-10}	9.38×10^{-8}
3[c]	7.63×10^{-7}	5.70×10^{-7}

[a] The aqueous phase in the phase-transfer experiment was 1.0 M NaOH. [b] The aqueous phase in the phase-transfer experiment was 0.10 M NaOH. [c] The aqueous phase in the phase-transfer experiment was pH 9.0 borax buffer.

thermostated, round-bottomed flask inside a Rayonet reactor equipped with 350-nm lamps. When the stirring was stopped and the light was turned off, the yellow azophenol color in the toluene phase was found to be somewhat bleached, and the azophenoxide color in the alkaline aqueous phase was found to be considerably enhanced. Stirring for a few minutes in the dark restored the original situation, returning the bulk of the azophenol to the toluene phase. This migration was reversible and could be repeated any number of times. (It should be emphasized that the color observed in the aqueous phase is always that of the *trans*-azophenoxide. After the light is turned off the color persists, because, in the absence of stirring, migration across the water/toluene phase boundary is imperceptibly slow.) Using the absorbance maxima of *trans*-azophenol **1** and *trans*-azophenoxide **1**, at 400 and 475 nm, respectively, yielded the extent of the migration from one phase to the other which is reported in Table I.

The transfer of the azophenol from the organic phase to the aqueous alkaline phase is governed by two equilibria. The first equilibrium, (1), is the partition coefficient of the azophenol

$$(\text{Ar–OH})_{\text{tol}} \overset{K_{PT}}{\rightleftharpoons} (\text{Ar–OH})_{\text{aq}} \quad (1)$$

$$(\text{Ar–OH})_{\text{aq}} + (\text{OH}^-)_{\text{aq}} \overset{K_a/10^{-14}}{\rightleftharpoons} (\text{ArO}^-)_{\text{aq}} + \text{H}_2\text{O} \quad (2)$$

$$K_a = \frac{(\text{Ar–O}^-)_{\text{aq}} 10^{-14}}{(\text{Ar–OH})_{\text{tol}} (\text{OH}^-)_{\text{aq}} K_{PT}} \quad (3)$$

between toluene and water, K_{PT}. Equilibrium (2), or $K_a/10^{-14}$, is the reaction of the aqueous azophenol with NaOH to form the aqueous azophenoxide. Combination of eq 1 and 2 yields eq 3, the expression for the aqueous acidity constant of the azophenol, K_a. To evaluate K_a an additional experiment is required, namely the independent measurement of K_{PT}. This was done for azophenols **1**, **2**, and **3**, both in the dark and under irradiation, and the results are shown in Table II. It can be seen that the ratio of K_a (light)/K_a(dark) for compounds **1** and **2** is quite substantial, or 18.7 and 609, respectively. The ratio for compound **3** is near unity, evidently, because the acid-strengthening effect due to the loss of the intramolecular hydrogen bond is here counteracted by the acid-weakening effect due to the loss of conjugation to the 4′-NO_2 in the nonplanar cis isomer.

The K_a(light) value measured by this procedure is the *effective acidity* of the azophenol under the phase-transfer conditions described in this experiment. It may be smaller than the acidity constant of the transient *cis*-azophenol, K_a(cis), due to incomplete conversion to the *cis*-azophenol at the photostationary state. It is however the K_a value of interest when endeavoring to design an experiment utilizing this light-enhanced acidity phenomenon for the purposes of light-powdered membrane transport or any other purpose involving chemical work.

Registry No. 1, 109997-28-6; **2**, 109976-80-9; **3**, 109997-29-7.

Phototropic Molecules. 2. A Light-Powered Hydrogen-Ion Pump

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Received April 6, 1987

The photolysis of water using solar radiation has received much attention in recent years.[1-3] While the photoproduction of H_2 and O_2 by the splitting of water is an obviously desirable form of photochemical solar energy conversion, there is another possible way of "splitting" water, namely the hydrolysis reaction, $H_2O \rightarrow H^+ + OH^-$. The present communication reports the first example of a light-powered liquid membrane[4] which accomplishes the hydrolysis of water.

Figure 1 shows a schematic representation of the requirements for light-powered proton transport across a liquid membrane. What is required is a lipophilic, weak acid (*trans*-AH) which is converted by light into a stronger acid (*cis*-AH) but reverts rapidly to the weak acid in the dark. In the liquid membrane, one side of which is illuminated and the other side dark, the stronger acid on formation donates a proton to the illuminated aqueous compartment. The conjugate base of the stronger acid (*cis*-A^-) ultimately finds itself in the dark portion of the organic phase where it reverts to *trans*-A^-. *trans*-A^- is the conjugate base of a weak acid and hence a strong base, capable of abstracting a proton from the dark aqueous compartment. This reforms *trans*-AH which is now ready for the next cycle. Each cycle forms one H^+ in the illuminated aqueous compartment and one OH^- in the dark aqueous compartment. For simplicity of presentation the comigration of a counterion (to maintain electrical neutrality in the two aqueous compartments) has been ommited from this scheme.

In the previous communication[5] it has been shown that 2-hydroxyazobenzenes are good candidates for the kind of phototropic proton carrier envisioned above. The lifetime of the cis isomer is long enough to enable it to pass through a phase boundary[5] yet short enough to permit many proton transport cycles per second.[6] The compound found to be most suitable was 2-hydroxy-3,5,6-trichloro-4′-methylazobenzene. Tetrabutylammonium picrate (Bu_4NPic) was used to provide a lipophilic counterion for the conjugate base (the Bu_4N^+ ion) as well as a mobile anion to maintain electrical neutrality in the aqueous compartments (the Pic^- ion). In view of the pK_a values of the phototropic acid[5] an initial pH of 12 was used in the two aqueous compartments. In order to obtain suitable partition of all the migrating species between the two phases it was also found necessary to add a considerable amount of salt (1.5 M Na_2SO_4)

(1) Mau, A. W.-H.; Huang, C.-B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, M.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537.
(2) Tricot, Y.-M.; Fendler, J. H. *J. Am. Chem. Soc.*, **1984**, *106*, 2475.
(3) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376 and references cited therein.
(4) Light-powered proton pumps have been observed in biological systems, see, e.g.: Stoeckenius, W.; Bogomolni, R. A., *Ann. Rev. Biochem.* **1982**, *52*, 587.
(5) Haberfield, P. *J. Am. Chem. Soc.*, preceding paper in this issue.
(6) Wettermark, G.; Langmuir, M. E.; Anderson, D. G. *J. Am. Chem. Soc.* **1965**, *87*, 476. Gabor, G.; Frei, Y.; Gegiou, D.; Kaganowitch, M.; Fischer, E. *Isr. J. Chem.* **1967**, *5*, 193.

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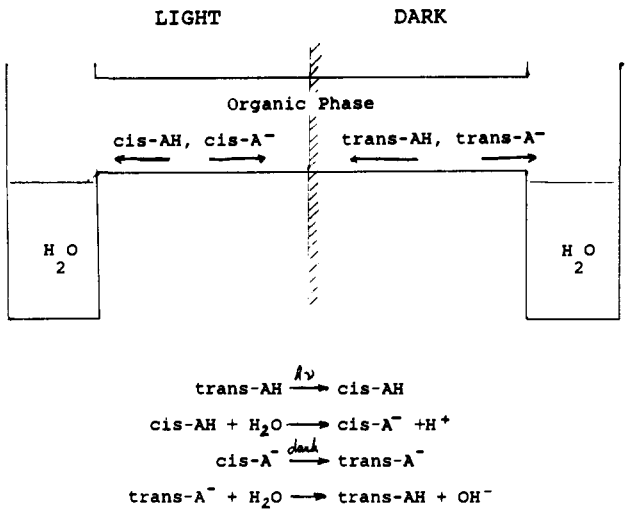

Figure 1. Schematic representation of light-powered proton transport across a liquid membrane.

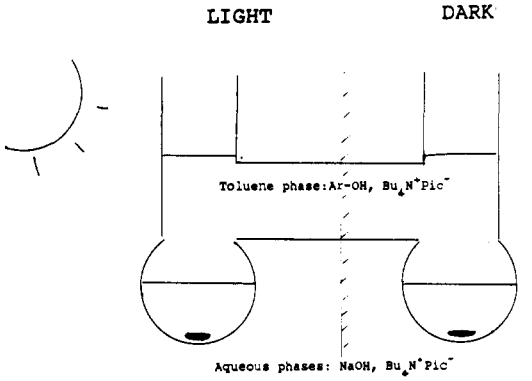

Figure 2. Liquid membrane.

to the aqueous phase. The complete scheme of reactions taking place in the liquid membrane is shown in eq 1–4.

$$trans\text{-}AH_{org} \xrightarrow{h\nu} cis\text{-}AH_{org} \quad (1)$$

$$cis\text{-}AH_{org} + NaOH_{aq} + Bu_4NPic_{org} \rightarrow cis\text{-}A^-Bu_4N^+_{org} + NaPic_{aq} + H_2O \quad (2)$$

$$cis\text{-}A^-Bu_4N^+_{org} \xrightarrow{dark} trans\text{-}A^-Bu_4N^+_{org} \quad (3)$$

$$trans\text{-}A^-Bu_4N^+_{org} + NaPic_{aq} + H_2O \rightarrow trans\text{-}AH_{org} + NaOH_{aq} + Bu_4NPic_{org} \quad (4)$$

After the *trans*-azophenol in the illuminated part of the organic phase is converted to the *cis*-azophenol (eq 1), it reacts with the aqueous NaOH forming a Bu_4N^+*cis*-A^- ion pair in the organic phase and forcing a Pic^- from the organic phase into the illuminated aqueous compartment (eq 2). The Bu_4N^+*cis*-A^- then reverts to Bu_4N^+-*trans*-A^- (eq 3) which then abstracts a proton from the H_2O in the dark aqueous compartment, generating an OH^- and allowing a Pic^- ion to enter the organic phase as $Bu_4N^+Pic^-$ (eq 4). The net result of each cycle is the appearance of one Pic^- and the disappearance of one OH^- from the illuminated aqueous compartment and the disappearance of one Pic^- and the appearance of one OH^- in the dark aqueous phase.

The liquid membrane consisted of two 100-mL, round-bottomed flasks joined by a bridge for the supernatant toluene solution (see Figure 2). Into the two round-bottomed flasks was poured 50 mL each of an aqueous solution containing 10^{-2} M NaOH, 1.18×10^{-4} M Bu_4N Pic, and 1.5 M Na_2SO_4. A toluene solution containing 6.17×10^{-4} M 2-hydroxy-3,5,6-trichloro-4′-methylazobenzene was then poured carefully on top to cover the two aqueous phases. The whole apparatus was immersed in a 25.0 °C constant temperature bath, the two flasks were subjected to vigorous stirring by means of two magnetic stirrers, and the left side of the liquid membrane was illuminated with a 275-W incandescent GE sunlamp. At the beginning of the experiment the contents of the two aqueous compartments were identical. At intervals aliquots of the two aqueous phases were assayed for picrate content. Figure 3 shows the increase in the picrate concentration of the illuminated aqueous compartment of the liquid membrane and the concomitant decrease in the picrate concentration on the dark side.[7] As can be seen from eq 1–4 the proton flux is exactly equal to changes in the picrate concentrations and is about 2×10^{-6} equiv per hour.

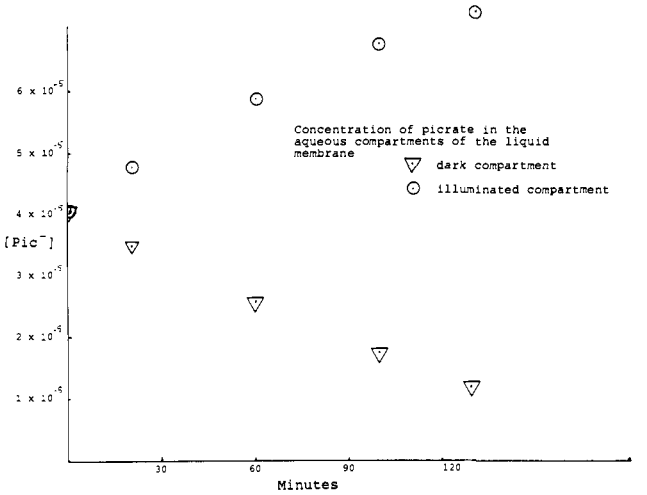

Figure 3. Change in the picrate concentration (M) in the illuminated and dark compartments of the liquid membrane vs. time (min).

Registry No. *trans*-AH, 109976-80-9; H_2O, 7732-18-5.

(7) The following controls should be noted: 1. When the illumination was placed on the other side of the liquid membrane the flow of picrate was reversed. 2. In the absence of illumination the two aqueous phases containing equal picrate concentrations maintained these concentrations without any change. No effort was made to exclude oxygen in these experiments.

The Biosynthetic Incorporation of [*methyl*-^{14}C,6-^{2}H,^{3}H]Trigonelline into Dioscorine in *Dioscorea hispida*

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Received April 23, 1987

Dioscorine (**4**) is the main alkaloid found in the tropical yam *Dioscorea hispida* Dennstedt. We have previously established that this novel isoquinuclidine alkaloid is derived from nicotinic acid[2] (**1**) and acetic acid.[3] A biogenetic scheme for dioscorine was considered[2b] which involved a condensation between 3,6-dihydronicotinic acid (**2**) and a branched eight carbon unit **3** derived from four acetate units, one of the terminal carboxyl groups being ultimately lost in the formation of dioscorine. In order to probe this proposed biogenetic scheme, feeding experiments have been carried out with [6-^{14}C,2-^{3}H]nicotinic acid and [6-^{14}C,6-^{3}H]nicotinic acid.[4] Both these precursors were incor-

(1) Contribution no. 205 from this laboratory. Presented at the 4th International Conference on Chemistry and Biotechnology of Biologically Active Natural Products, Budapest, Hungary, August 10–14, 1987.

(2) (a) Leete, E. *J. Am. Chem. Soc.* **1977**, *99*, 648. (b) Leete, E. *Phytochemistry*, **1977**, *16*, 1705.

(3) Leete, E.; Pinder, A. R. *Phytochemistry* **1972**, *11*, 3219.

(4) These ^{3}H labeled nicotinic acids were prepared as previously described by Dawson et al. (Dawson, R. F.; Christman, D. R.; D'Adamo, A.; Solt, M. L.; Wolf, A. P. *J. Am. Chem. Soc.* **1960**, *82*, 2628.) and were mixed with commercially available (Amersham) [6-^{14}C]nicotinic acid prior to feeding.

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