

A Molecular Reaction Cycle With a Solvatochromic Merocyanine Dye

An Experiment in Photochemistry, Kinetics, and Catalysis

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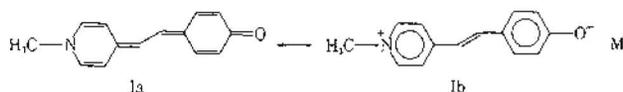
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Merocyanines of the stilbazolium betaine type, e.g., 1-methyl-stilbazolium 4'-olate¹ (see formula I), in the following abbreviated as M, are characterized by their extreme solvatochromic properties (1), i.e., their absorption spectra exhibit very large solvent effects which allow the polarity of a solvent to be judged by the color of the solution (2). For this reason M has been suggested as an interesting preparation for students in THIS JOURNAL (3).



In addition to its solvatochromy the compound M exhibits some remarkable chemical and photochemical properties (4) making it suitable to illustrate some important concepts in physical chemistry by simple experiments.

The resonance structure 1b represents an essentially stilbene-like structure, suggesting the possibility of cis/trans isomerism known for many stilbene derivatives (5), so that one should expect merocyanines of this type to exist likewise in cis and trans configurations. Recently we have identified the isomer M_{cis} (4) which represents the first example of a cis-stilbazoliumbetaine stable enough to be amenable to both spectral and photochemical characterization. However, M_{cis} cannot be obtained from M_{trans} directly. Instead one has to make use of the protonated form MH^+_{trans} , which is even more stilbene-like since resonance structure 1b is stabilized by the protonation. MH^+_{trans} may be transformed to MH^+_{cis} photochemically. Deprotonation of MH^+_{cis} yields the cis-betaine M_{cis} . Thermally as well as photochemically, M_{cis} can be completely reverted to the trans isomer M_{trans} .

The protolytic, photochemical, and/or thermal reactions described above can be combined to a complete molecular reaction cycle (Fig. 1), which is a one way cycle, however, since the step $M_{cis} \rightarrow M_{trans}$ is irreversible.

In this paper we describe three experiments with the merocyanine M, suitable as an integrated laboratory experience for undergraduates.

1) A simple experiment, demonstrating the complete molecular cycle composed of photochemical, thermal, and protolytic reaction steps. This molecular reaction cycle exhibits interesting aspects with relation to a model discussed in the literature for the mechanism of a light driven proton pump (6, 7).

- 2) A kinetic study of the thermal cis \rightarrow trans isomerization of the form M, which is a simple first-order reaction and is very sensitive to changes in temperature and solvent. This reaction is ideally suited for demonstrating the obvious significance of the activation parameters in Eyring's absolute rate theory (8).
- 3) An experiment, demonstrating the mechanism of base catalysis for thermal isomerization of $MH^+_{cis} \rightarrow MH^+_{trans}$.

Experimental

The merocyanine dye M may be synthesized as described in THIS JOURNAL (3). It is obtained as M_{trans} (5).

The reaction cycle depicted in Figure 1 is carried out in a 1-cm spectrophotometer cuvette, starting with a $2 \times 10^{-5} M$ solution of the dye (M_{trans}) in $10^{-4} M$ aqueous HCl, prepared freshly in the dark. The first absorption spectrum is measured at this stage. Then the cuvette

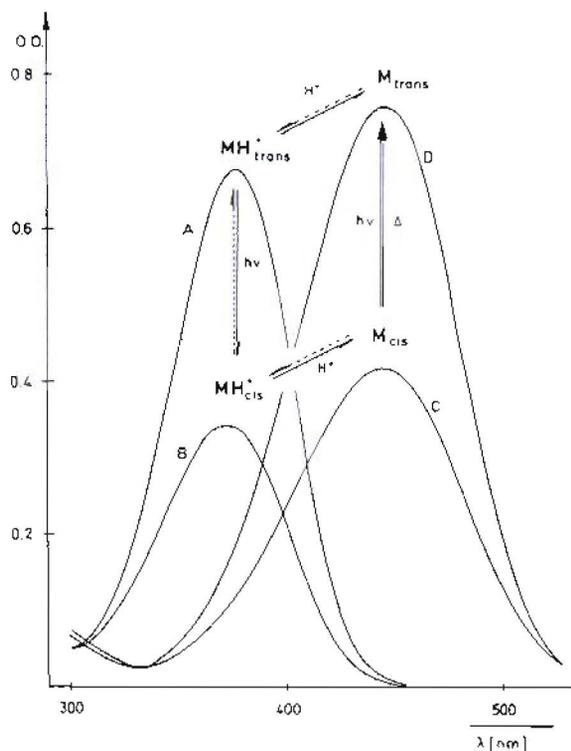


Figure 1. Absorption spectra representing the four stages of the reaction cycle A: Spectrum of a $2 \times 10^{-5} M$ aqueous solution of M, prepared in the dark, with $10^{-4} M$ HCl. B: After irradiating solution A with light of 366 nm until reaching the photostationary state, C: After addition of 1 drop of 1 N NaOH to the cuvette. D: After irradiating with light of 436 nm until reaching the photostationary state (volume of the cuvette 4 ml, optical pathlength 1 cm).

¹ Alternate names used in the literature are 1-methyl-4-(4'-hydroxystyryl)pyridinium betaine, 4'-hydroxy-1-methyl-stilbazolium betaine, and 1-methyl-4-[(oxycyclohexadienyldiene)ethylidene]-1,4-dihydropyridine.

is exposed to normal daylight or light from a halogen lamp. The progress of the conversion can be followed by measuring the absorbance at different stages of the reaction until the photostationary state is reached (approximately 2 hr at normal daylight). Addition of one drop of 1 *N* NaOH at room temperature yields a mixture of M_{cis} and M_{trans} with the same ratio as the photostationary state composition before the deprotonation. The cis/trans ratio of this mixture, if kept in the dark, is not changed significantly for 30 min, so there is enough time to record the absorption spectrum. The cis fraction is then isomerized to M_{trans} either photochemically or thermally. To follow the photochemical isomerization the solution must not be kept above room temperature. To measure the thermal isomerization, the reaction should be accelerated by heating in the dark (at 23°C, $t_{1/2}$ is 260 min, at 60°C only 1.2 min).

After the cis-trans isomerization of *M* has been completed, MH^+_{trans} is regenerated by adding 2 drops of 1 *N* HCl. This completes the reaction cycle. All the reactions described above can be followed by recording the absorption spectra as shown in Figure 1.

To measure the rate constant of thermal cis → trans isomerization of *M*, a thermostated cuvette holder is required. An irradiated acidic solution (HCl 10^{-4} *M*), which is thermally stable up to 100°C, is heated to the required temperature. A drop of 1 *N* NaOH is added to the cuvette, and after mixing, the isomerization is followed by measuring the change of absorption at a fixed wavelength, preferentially at 440 nm. This procedure is repeated at several temperatures between 20 and 60°C to determine the activation parameters.

To pursue the base catalyzed thermal isomerization $MH^+_{cis} \rightarrow MH^+_{trans}$, buffer solutions are used instead of NaOH. An irradiated 4×10^{-5} *M* slightly acidic solution (8×10^{-5} *N* HCl) of the dye is heated to the required temperature and then diluted to the half concentration with a given buffer solution, which has been previously adjusted in temperature to the irradiated solution. The rate of isomerization is measured as before.

Results and Discussion

Reaction cycle. The spectral change in going from a pure MH^+_{trans} solution to the photostationary state MH^+_{trans}/MH^+_{cis} is shown in Figure 1 (A → B). It should be noted that the photostationary state depends on the wavelength λ of irradiation. It is, however, not very sensitive to λ if $\lambda > 300$ nm. Deprotonation, which is achieved by addition of NaOH, transforms MH^+_{cis} to M_{cis} and MH^+_{trans} to M_{trans} , where the cis/trans conformation is preserved in the protolytic reaction. Therefore the cis/trans ratio of *M* obtained immediately after addition of NaOH (spectrum C) is the same as in the photostationary state of MH^+ . Subsequent irradiation of this solution transforms M_{cis} to M_{trans} with an increase of the main absorption band (spectrum D). The composition of the photostationary state obtained by irradiation with any wavelength above 254 nm corresponds to a pure M_{trans} solution. On acidifying this solution one obtains the original unirradiated MH^+_{trans} solution (spectrum A).

It can be seen from the reactions considered above that the cis-betaine M_{cis} constitutes an essential link of a complete photochemical, thermal, and protolytic reaction cycle. Since the step $M_{cis} \rightarrow M_{trans}$ is irreversible, the cycle can be traversed in one direction only. This peculiarity is of special interest with respect to a model for a molecular light-driven proton pump (cf. Fig. 2). This was recently suggested by Schulten and Tavan (6) to explain the role of the Schiff base of retinal in the light-driven proton pump, as discovered by Oesterheld and Stoerkenius (7) in the purple membrane of Halobacterium halobium.

Thermal isomerization. In contrast to MH^+_{cis} which is thermally stable up to 100°C, M_{cis} may be isomerized thermally. As expected, this is a first-order reaction with strong temperature dependence. Let A_0 be the absorbance observed at the beginning of the reaction, A_t at time t and A_∞ at infinity, corresponding to complete conversion to the trans isomer. The difference ($A_t - A_\infty$) is proportional to the concentration of cis isomer at any time t , and the integrated first-order rate equation is given by:

$$k_c t = \ln \frac{A_0 - A_\infty}{A_t - A_\infty} \quad (1)$$

A plot of $\ln(A_t - A_\infty)$ versus t is linear with slope equal to $-k_c$. The Arrhenius activation energy E^* and the frequency factor k_0 are determined from a plot of $\ln k_c$ versus $1/T$ (see Fig. 3) according to the equation:

$$\ln k_c = \ln k_0 - \frac{E^*}{RT} \quad (2)$$

The rate constant according to Eyring's theory (8) is given by:

$$k_c = \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (3)$$

where k is Boltzmann's constant, h is Planck's constant, ΔS^\ddagger is the entropy of activation, and ΔH^\ddagger the enthalpy of activation. For liquid phase reactions E^* and ΔH^\ddagger are related by:

$$\Delta H^\ddagger = E^* - RT \quad (4)$$

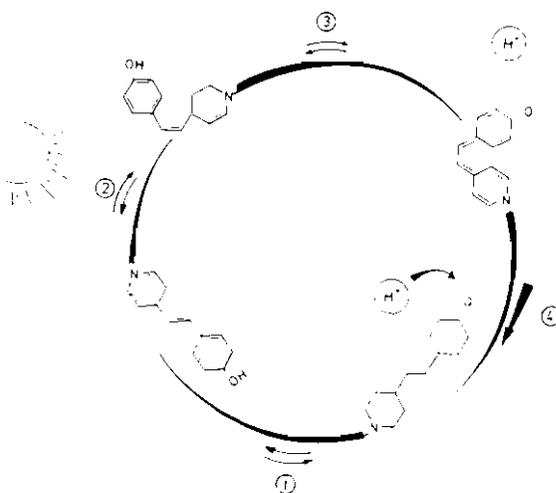


Figure 2. A model of a molecular light-driven proton pump according to (6). The merocyanine molecules are part of a closed membrane. By the reaction sequence 1, 2, 3, 4, 1, protons are accepted from carriers inside the vesicle, shifted across the membrane by the photochemical trans → cis isomerization and accepted by carriers outside the vesicle. The working direction of the pump is determined by the irreversibility of step 4.

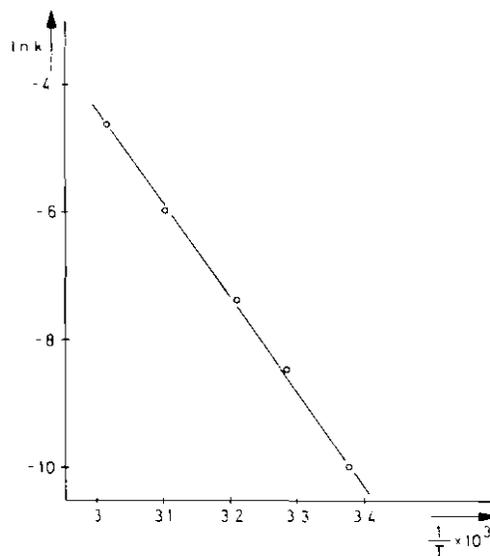


Figure 3. Arrhenius plot for the rate constant of thermal isomerization $M_{cis} \rightarrow M_{trans}$.

The following values are obtained for the thermal *cis* → *trans* isomerization of M:

$$k_0 = 7 \times 10^{16} \text{ s}^{-1}$$

$$E^{\ddagger} = 119.6 \text{ kJ mol}^{-1}$$

$$\Delta H^{\ddagger}_{298} = 117.1 \text{ kJ mol}^{-1}$$

$$\Delta S^{\ddagger}_{298} = 69.0 \text{ J mol}^{-1} \text{ K}^{-1}$$

These activation parameters are particularly useful in order to demonstrate that even though the activation energy is rather high, the actual reaction rate constant can be appreciably fast due to the influence of the activation entropy which is extraordinarily high in our case. Whereas the activation energy can be qualitatively accounted for by the strong contribution of resonance structure Ib giving the C—C bond essentially double bond character, the activation entropy can be related to an increasing disorder of the solvent shell in the course of the isomerization (cf. Fig. 4). While the planar state is very polar due to the strong contribution of resonance structure Ib, the dipole moment must be considerably smaller in the 90° twisted configuration where resonance structure Ia should be dominant. Polar solvent molecules which initially are highly oriented in the strong dipole field of the planar configuration can reorient rather freely in the activated twisted configuration. It is of interest to note that the observed entropy of activation corresponds to the entropy of melting about three moles of water.

Base catalysis MH^+ cannot be *cis/trans* isomerized thermally. From the spectra in Figure 1, however, it can be inferred that, by base catalysis, a thermal isomerization $\text{MH}^+_{\text{cis}} \rightarrow \text{MH}^+_{\text{trans}}$ becomes feasible through the reaction steps $\text{MH}^+_{\text{cis}} \rightarrow \text{M}_{\text{cis}} \rightarrow \text{M}_{\text{trans}} = \text{MH}^+_{\text{trans}}$. This offers the possibility of demonstrating the role of a base catalyst in reducing the energy barrier for MH^+_{cis} isomerization.

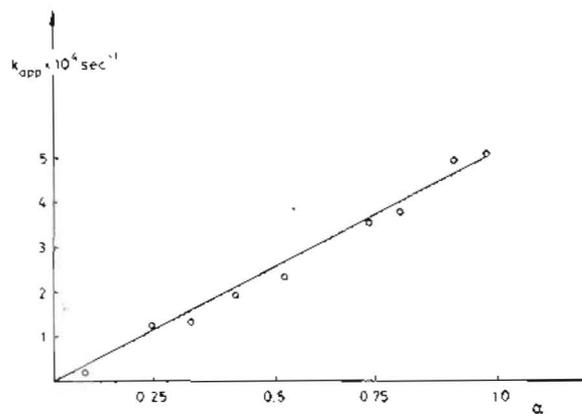


Figure 5. Apparent rate constant k_{app} of isomerization of MH^+_{cis} as a function of the degree α of protolytic dissociation ($T = 40^\circ\text{C}$)

$\text{M}_{\text{cis}} \rightarrow \text{M}_{\text{trans}} = \text{MH}^+_{\text{trans}}$. This offers the possibility of demonstrating the role of a base catalyst in reducing the energy barrier for MH^+_{cis} isomerization.

For a given pH a fraction α of MH^+_{cis} is dissociated. The value of α can be measured directly from the absorption spectrum or calculated using the relation (9):

$$\alpha = \frac{1}{1 + 10^{(pK_a - \text{pH})}} \quad (5)$$

The apparent rate constant for thermal isomerization is then given by:

$$k_{\text{app}} = \alpha k_c \quad (6)$$

k_c being the rate constant of the isomerization $\text{M}_{\text{cis}} \rightarrow \text{M}_{\text{trans}}$. The validity of this relation is shown in Figure 5 where the apparent rate constant k_{app} is plotted against α .

Acknowledgment

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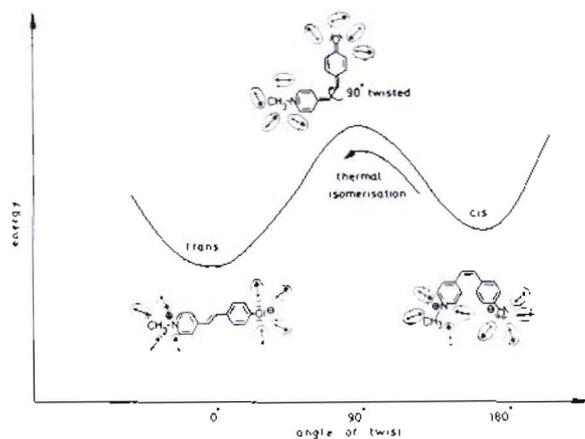


Figure 4 Interpretation of the positive entropy of activation for thermal isomerization of $\text{M}_{\text{cis}} \rightarrow \text{M}_{\text{trans}}$. Since the dipole moment of M is drastically decreased in the 90° twisted state there is a corresponding increase of the disorder of the solvent shell.