Effect of Hydroxide Ion on the Cis–Trans Thermal Isomerization of Azobenzene Derivatives

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Azobenzenes can be photochemically transformed from the trans (*E*) form, which is thermodynamically more stable, to the cis (*Z*) form. In the dark, the latter reverts to the former. We report here a kinetic study of the thermal isomerization of methyl orange (**1**), 4-(dimethylamino)-4′-methoxyazobenzene (**2**), and naphthalene-1-azo-(4′-(dimethylamino)benzene) (**3**) in water or in water/cosolvent solution measured at different hydroxide ion concentrations. It was found that the reaction is strongly dependent on the hydroxide ion concentration. The observed rate constant for **2** changes from 1.43×10^{-2} s^{-1} at NaOH (1.0×10^{-3} M) to 7.7×10^{-4} s^{-1} at NaOH (0.10 M). These results can be interpreted in terms of the isomerization rate constant of the protonated substrates which is at least 10^8 times faster than that of the neutral compound.

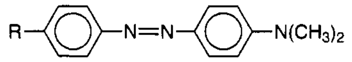
Introduction

Azobenzene derivatives exhibit photoinduced reversible cis–trans isomerism. The kinetics of the thermal cis–trans isomerization of azo compounds in solution has been intensively studied during the last 50 years.[1]

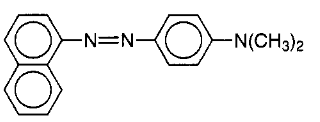
In recent years they have been employed as triggers[2,3] or probes[4,5] for the possible use of this type of compounds in image storage systems.[6]

Only a few systematic studies[7–9] have been reported about the acid catalysis observed for the cis–trans isomerization of azobenzenes, and almost all of them have been on azobenzene. Besides, it has been reported that the thermal photochromism of azobenzenes used as optical probes for proteins is highly dependent on the pH.[10]

The rate of the thermal cis–trans isomerization of azobenzenes is extremely solvent sensitive,[11,12] and many studies have been carried out in various media. We recently reported[13] that the rate of isomerization of methyl yellow, *p*-methyl red, and *o*-methyl red are strongly inhibited by hydroxide ion, and these results were attributed to the very fast rate of isomerization of the protonated azo compound which strongly contributed to the observed overall rate even under conditions where its effective concentration is very low. We have extended this study to compounds **1**–**3** in order to compare the results with those obtained previously. Compound **2** was chosen in particular because it has two electron donor groups and it is known that the mechanism of isomerization of azo compounds depends on the substituent.[14] The behavior of compounds **1**–**3** confirms the proposed mechanism and the results are reported here.



1: R = $-SO_3^-$, methyl orange
2: R = –OMe, 4-(dimethylamino)-4′-methoxyazobenzene



3: naphthalene-1-azo-(4′-(dimethylamino)benzene)

Results and Discussion

Compounds **1**–**3** were irradiated at constant ionic strength (0.20 M, NaCl), and temperature (25.0 °C) with a medium pressure Hg lamp (wavelength of maximum emission 365 nm) until the photostationary state was achieved. There was a bleaching of the solution at the wavelength of maximum absorption. The spectrum recovered its original shape in the dark. The solutions were irradiated several times and always reverted to the original spectrum which indicates that the reaction is completely reversible. The reaction rate is highly dependent on the HO^- concentration (Table 1), and there is a nonlinear dependence of the observed rate constant with the HO^- concentration (Figure 1). The concentration of hydroxide ion was changed between 10^{-3} and 10^{-1} M for compounds **2** and **3**, but for **1** it was not possible to carry out measurements at HO^- concentrations lower than 0.02 M because the reaction was too fast for our experimental technique.

We were concerned about the behavior of azo compounds in water solution though only substrate **1** was studied in pure water solution, **2** in acetonitrile/water, and **3** in ethanol/water solution because of solubility

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Table 1. Effect of Hydroxide Ion Concentration on the Cis–Trans Isomerization Rate of Compounds 1–3 at 25 °C[a]

$[HO^-]$, M	methyl orange k_{obs},[b] s^{-1}	4-(dimethylamino)-4′-methoxyazobenzene k_{obs},[c] s^{-1}	naphthalene-1-azo-(4′-(dimethylamino)-benzene k_{obs},[d,e] s^{-1}
0.001	0.0093[e]	0.0143	0.004 19
0.003		0.0048	0.002 88
0.006		0.0025	0.002 75
0.010	0.0029[e]	0.0018	0.002 50
0.020	0.290		
0.030		0.0011	0.002 30
0.050	0.251		0.002 06
0.060	0.241	0.000 98	
0.070	0.202		
0.075	0.187		
0.080	0.180		0.002 20
0.100	0.179 0.0022[e]	0.000 77	0.002 10
0.125	0.177		

[a] Mean values of three or four determinations, deviations less than 5%. [b] [Methyl orange] = 3.17 × 10^{-5} M. Solvent: H_2O unless otherwise noted. [c] [4-(Dimethylamino)-4′-methoxyazobenzene] = 9.8 × 10^{-6} M. Solvent: H_2O/ACN (80:20). [d] [Naphthalene-1-azo-(4′-(dimethylamino)benzene)] = 1.74 × 10^{-4} M. [e] Solvent: H_2O/EtOH (50:50).

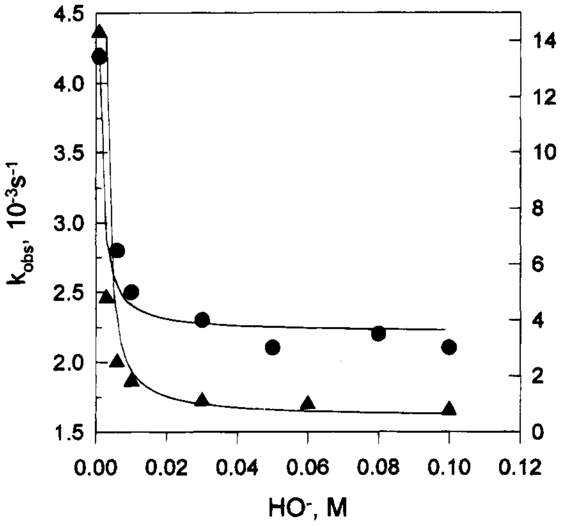
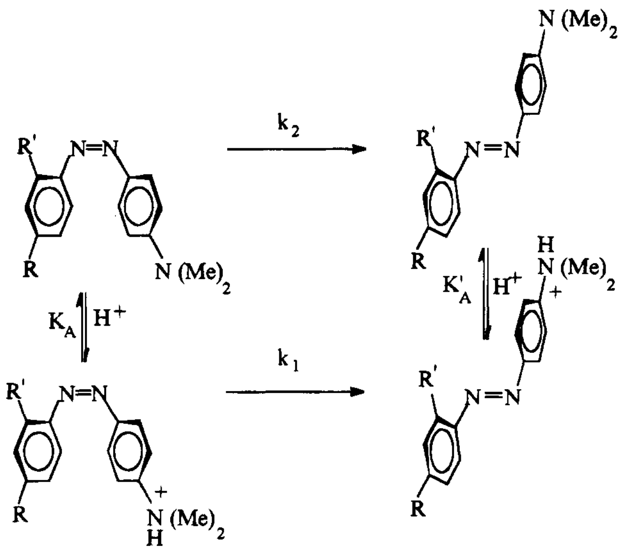


Figure 1. Effect of NaOH on the rate of isomerization of naphthalene-1-azo(4′-(dimethylamino)benzene), at an initial concentration 1.74 × 10^{-4} M in H_2O/EtOH (50:50) (left ordinate), ●, and 4-(dimethylamino)-4′-methoxyazobenzene, at an initial concentration of 9.8 × 10^{-6} M (right ordinate). Solvent: H_2O/ACN (80:20), ▲. Temperature: 25 °C; $\mu = 0.20$ M. Lines are calculated with eq 2, and the rate and equilibrium constants given in Table 2.

problems. The sensitivity of this reaction to the nature of the solvent is evident from the results reported in Table 1. It can be seen that for compound **1**, when the solvent is changed from water to 50% ethanol water the isomerization rate decreases 100 times. The effect of the change in solvent at constant OH^- concentration was studied for the isomerization of *o*-methyl red, and it was found that at 0.01 M NaOH the rate of thermal isomerization changes from 0.051 s^{-1} in water to 8 × 10^{-4} s^{-1} in 50% ethanol water.[13,15] This sensitivity of the reaction to the solvent polarity makes this reaction useful to measure micropolarity.[16]

Since it is very common that dyes associate when they are dissolved in water,[17] we determined the spectra of substrates **1–3** at several concentrations. There was no evidence for association in this range of concentrations, and there was a very good fit to the Lambert–Beer law.

Scheme 1



The results can be interpreted in terms of the reaction mechanism shown in Scheme 1.

The observed rate constant for this scheme is given by eq 1:

$$k_{obs} = \frac{k_1}{(K_A/K_w)[HO^-] + 1} + \frac{(K_A/K_w)[HO^-]k_2}{(K_A/K_w)[HO^-] + 1} \qquad (1)$$

Under our reaction conditions $(K_A/K_W)[HO^-] > 1$ eq 1 can be simplified to eq 2:

$$k_{obs} = \frac{k_1}{(K_A/K_w)[HO^-]} + k_2 \qquad (2)$$

The nonlinear fit of the data[18] with eq 2 gives the rate constants shown in Table 2. The values of the rate constants for the substrates previously studied[13] are also collected in Table 2 for comparison purposes. If we consider that K_A of these compounds in their cis form is similar to the K_A of the trans compounds, we can obtain the values of k_1. It should be noticed in Table 2 that the values of k_1 for methyl yellow and *o*-methyl red are different from those reported previously.[13] In that paper we used an estimated value of K_A (1.26 × 10^{-4} M) to calculate k_1 for *o*-methyl red whereas the value shown in Table 2 of this work was obtained using the K_A reported for the trans isomer, namely 10^{-5} M.[19] In the case of methyl yellow the values of k_1 have been calculated by fitting the experimental data with eq 1 with k_1 and K_A as adjustable parameters. Due to the fact that $(K_A/K_w)[HO^-] > 1$ under all our experimental conditions, eq 2 holds; therefore, the values of K_A/K_w and k_1 obtained in this type of calculation are very much dependent on each other and only the ratio $k_1/(K_A/K_w)$ can be obtained. Consequently, we have recalculated the latter value, and the result is shown in Table 2.

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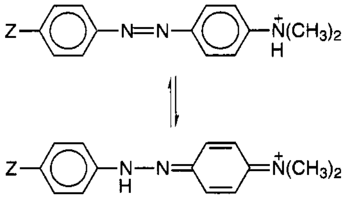
Table 2. Rate Constants for the Isomerization of the Protonated and Unprotonated Forms of 1–3[a]

substrate	k_2, s^{-1}	$10^{-9}k_1/K_A$	pK_a	k_1, 10^7 s^{-1}
methyl orange[b]	$(1.6 \pm 0.1) \times 10^{-1}$	270 ± 60	3.47[c]	9,36
4-(dimethylamino)-4′-methoxyazobenzene[d]	$(5.1 \pm 0.2) \times 10^{-4}$	1.37 ± 0.02	2.4[e,f]	0.54
naphthalene-1-azo-(4′-(dimethylamino)benzene)[f]	$(2.19 \pm 0.07) \times 10^{-3}$	0.20 ± 0.02	0.61[f]	4.9
methyl yellow[g,h]	$<1 \times 10^{-3}$	12 ± 0.7	3.19[i]	0.74
o-methyl red[b,h]	1.4×10^{-2}	280 ± 1	5[c]	0.28
p-methyl red[b,h]	9×10^{-2}		3.48[j]	

[a] Temperature 25.0 ± 0.1 °C, ionic strength 0.2 M. [b] Solvent: water. [c] *Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton, 1991–1992; pp 8–13. [d] Solvent: ACN/water 20:80. [e] Sawicki, E. *J. Org. Chem.* **1957**, *22*, 621–625. [f] Solvent: EtOH/water 50:50. [g] Solvent: EtOH/water 20:80. [h] Data from ref 13. [i] Kolthoff, F.; Sandell, E.; Mechan, E.; Bruckenstein, S. *Librería y Editorial Nigar SRL*, 6th ed.; 1972; p 718. [j] *Belsteins Handbuch der Organicher Chemie*; Edwards Brother Inc.: 1942, Band XVI, pp 164–165.

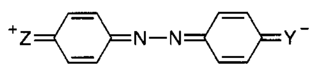
When the substrate is protonated, two tautomers form in equilibrium, i.e., the amonium and azonium (eq 3):[20]



(3)

The longest wavelength absorption is attributed to the azonium form whereas that at the shorter wavelength is attributed to the ammonium tautomers. In acidic solution the maximum wavelength absorptions for methyl orange are 507 and 318 in water and 513 and 319 in EtOH/water 50/50. The ratio of the absorbances in these two solvents are 5.86 and 4.95, respectively, indicating that equilibrium 3 shifts toward the amonium tautomer as ethanol is added to the solvent. Similar behavior is observed when the tautomerism azo–hydrazone of arylazonaphthols is determined in aqueous organic solvents.[21]

Two different mechanisms have been proposed for the cis–trans isomerization reaction, and these are rotation about the –N=N– bond[22] and inversion of one of the nitrogen atoms.[23] Compounds having an electron donor and an electron acceptor group are believed to react via a transition state involving rotation because structures of the type of **4** strongly contribute to the ground state stabilization of these substrates; these compounds also isomerize faster than those that have only one group.[24]



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The fact that the protonated azo compounds isomerize so much faster than the nonprotonated compound may be attributed to the presence of the azonium tautomer which can easily isomerize via rotation since there is a decrease of the double bond character between the nitrogens. The values of k_1 are 10^8–10^{10} higher than those of k_2, and it is evident that the nature of the substituent affects k_2 as well as k_1. However, we cannot draw any conclusions regarding the effect of the substituent on reaction rates because the solvents used were different so the observed changes in rates result from a combination of substituent and solvent effects.

Experimental Section

Materials. Methyl orange (Aldrich) was a commercial sample and was recrystallized from ethyl alcohol, whereas 4-(dimethylamino)-4′-methoxyazobenzene and naphthalene-1-azo-(4′-(dimethylamino)benzene) were synthesized as reported in the literature[25] from diazotized *p*-methoxyaniline and *N,N*-dimethylaniline and diazotized naphthylamine and *N,N*-dimethylaniline, respectively. Their purity was controlled by thin-layer chromatography and melting point and was identified by IR and NMR. The solutions were prepared using water obtained from a Millipore apparatus.

Several spectra were obtained in the range concentration 3×10^{-6}–1×10^{-5} M for **1** and **2** and 1×10^{-5}–1×10^{-4} M for **3**, respectively, to check for association of the substrate. There was a good fit to the Lambert–Beer law. Sodium hydroxide was standardized against primary standard potassium acid phthalate.

Kinetics. A solution in pure water or in ethanol water of the appropriate substrate was irradiated with a medium-pressure Hg lamp for 10 min, and then the cuvette was placed in the thermostated cell of a spectrophotometer (Shimadzu UV 260) and the absorbance at maximum of the substrate (461, 448, and 430 nm for **1**, **2**, and **3**, respectively) was measured as a function of time. The spectrum of the final solution matches that of the solution without irradiation. The temperature was controlled at 25.0 ± 0.1 °C.

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