Tetrahedron Letters No.28, pp. 3203-3206, 1968. Pergamon Press. Printed in Great Britain.

ALKALINE HYDROLYSIS OF YELLOW AZOMETHINE DYES

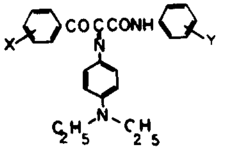
Kazuya Sano

Research Laboratories, Ashigara, Fuji Photo Film Co., Ltd.

Minamiashigara, Kanagawa, Japan

(Received in Japan 9 March 1968; received in UK for publication 15 April 1968)

The reaction of yellow azomethine dyes of the general formula I with hydroxide ion in 50 volume percent aqueous acetone has been studied.



(I)

Dyes employed were synthesized by a procedure similar to that of G. H. Brown et al (1). One volume of 10^{-4} M dye in acetone was mixed with 1 volume of aqueous sodium hydroxide of appropriate concentration to make 1.92 volumes, and the absorbance was followed in a thermostated optical cell.

The rate of fading is first order in dye but not in hydroxide unless dilute. At higher alkali concentration, the rate tends to converge to a limiting value specific to each dye (Fig. 1). Table I lists the logarithms of the pseudo-first order rate constants k at a fairly low concentration (0.026 M) of hydroxide ($k = -\frac{1}{D}\frac{dD}{dt}$, where D is the absorbance at a properly chosen wavelength and t is time in seconds). The data suggest that the rate determining reaction occurs at a site closer to the benzoyl group than to the other part of the molecule (2).

Dye extinction extrapolated to t = 0 (D_0) decreases with increasing hydroxide concentration and finally converges to a specific value in a manner similar to the rate. Indeed the reciprocal of ΔD ($= (D_0)_{[OH^-]=0} - D_0$) and that of k give two straight lines of an identical slope/intercept ratio when plotted against that of hydroxide concentration (Fig. 2).

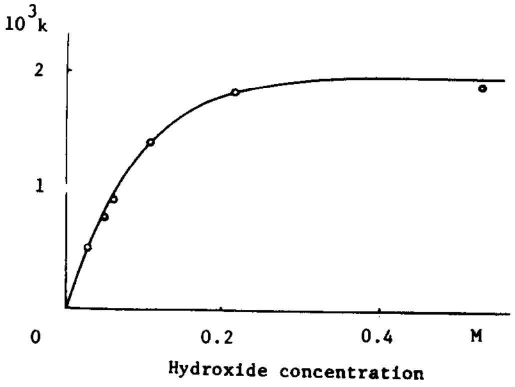


Fig. 1

Fading rates of dye No. 1
at various concentrations of sodium hydroxide

Table I

Pseudo-first Order Rate Constants of Fading of Dyes I at 25.0 °C
$[OH^-] = 0.026$ M

Dye No.	X	Y	log k	Dye No.	X	Y	log k
1	H	H	-3.31	4	$p\text{-}OCH_3$	H	-4.23
2	H	$p\text{-}OCH_3$	-3.20	5	$o\text{-}OCH_3$	H	-3.69
3	H	p-Cl	-3.28	6 a)	H	H	-3.19

a) $-C_6H_3(2\text{-}CH_3)[4\text{-}N\text{-}(C_2H_5)_2]$ instead of $-C_6H_4\text{-}[p\text{-}N(C_2H_5)_2]$

Fig. 3 compares the absorption spectra of dye No. 4 in the presence and absence of sodium hydroxide.

The initial dropping of the extinction was too rapid to be followed. The decrease of the extinction at elevated alkali concentration, e.g. 0.52 N sodium hydroxide in 50 volume percent aqueous acetone, depends on dye structure and varies within the range of 6 to 40 percent of the original extinction. This range and the decrease itself is too large to be accounted for by the change of the solvent composition.

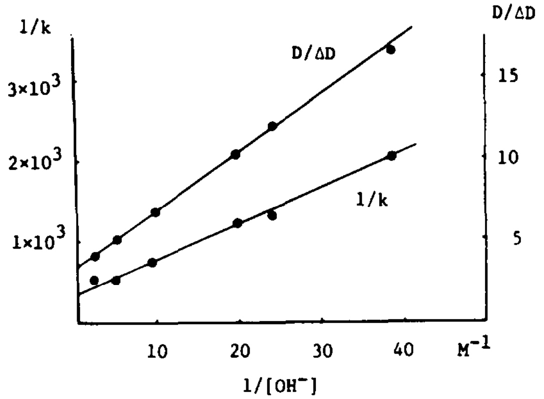


Fig. 2

Rate and D/ΔD of dye No. 1 as functions of $1/[OH^-]$
The absorbances measured at 440 millimicrons

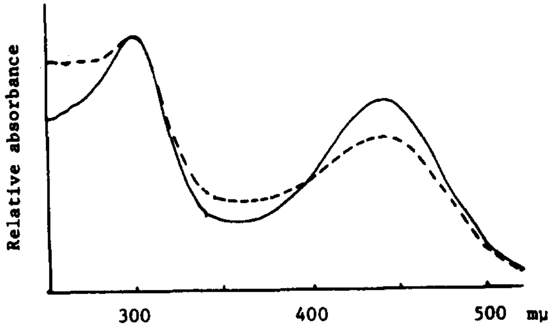


Fig. 3

The absorption spectra of dye No. 4 in ethanol-water mixture (——) and in ethanol-1N aqueous sodium hydroxide mixture (- - -) immediately after mixing (both 1:1 in volume)

Table II

Rate and Equilibrium Constants at 25.0°C, Calculated on Schemes A and B

Dye No.	10^3k (A)	10^3k (B)	k_1/k_2 (A & B)	Dye No.	10^3k (A)	10^3k (B)	k_1/k_2 (A & B)
1	3.0	23	7.5	4	0.43	2.6	6.0
2	4.3	24	5.4	5	3.6	22	6.2
3	1.7	28	16	6	5.0	28	5.6

The observations mentioned so far are explained by either of the following two mechanisms, in which ε_1 and ε_2 denote the extinction coefficients at a properly chosen wavelength.

SCHEME A

$$\begin{tikzcd}
\underset{(\varepsilon_1)}{\text{Dye}} \arrow[r, shift left, "k_1[OH^-]"] & \underset{(\varepsilon_2)}{\text{Dye}'} \arrow[l, shift left, "k_2"] \arrow[r, "k_3"] & \text{Product}
\end{tikzcd}$$

$$\frac{1}{k} = \frac{1}{k_3} + \frac{k_2}{k_1k_3[OH^-]}, \quad \frac{D}{\Delta D} = \frac{\varepsilon_1}{\varepsilon_1-\varepsilon_2}\left(1 + \frac{k_2}{k_1[OH^-]}\right)$$

SCHEME B

$$\begin{tikzcd}
\text{Dye} \arrow[r, shift left, "k_1[OH^-]"] \arrow[d, "k_3[OH^-]"] & \text{Dye}' \arrow[l, shift left, "k_2"] \\
\text{Product} &
\end{tikzcd}$$

$$\frac{1}{k} = \frac{k_1}{k_2k_3} + \frac{1}{k_3[OH^-]}, \quad \frac{D}{\Delta D} = \frac{\varepsilon_1}{\varepsilon_1-\varepsilon_2}\left(1 + \frac{k_2}{k_1[OH^-]}\right)$$

The constants calculated on these schemes are summarized in Table II. The equilibrium constants have been calculated fron 1/k curves and not from D/ΔD curves since the latter seem to be subject to greater experimental error at low hydroxide concentration where ΔD's are considerably small.

Although we have not reached the conclusion which scheme is correct, the observed susceptibility of the rate, rather than that of the equilibrium, to X substituent effect (according to whichever mechanism) implies that the two reactions, namely equilibration and hydrolysis, are taking place at different sites and hence that Dye' is not an intermediate in the hydroxide-independent C-C cleavage. Also the susceptibility of k_1/k_2 to Y substituent effect suggests the dissociation of the anilide proton.

A broader extension of the substituents for confirmation of the electronic effect and for testing of the steric influences is now under progress.

References

(1) G. H. Brown, J. Figueras, R. J. Gledhill, C. J. Kibler, F. C. McCrossen, S. M. Parmerter, P. W. Vittum, and A. Weissberger, J. Am. Chem. Soc., **79** 2919 (1957)

(2) cf. C. F. H. Allen, J. Van Allan, and C. V. Wilson, J. Am. Chem. Soc., **66** 1805 (1944)