Kinetics and Mechanism of Reduction of 4(p-Dimethylamino)- -Benzylidene-3-Methyl-1-Phenyl-2-Pyrazolin-5-one by Bisulphite Ions in Aqueous Ethanolic Media

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The kinetics of the title reduction studied in aqueous ethanolic media spectrophotometrically. The effect of hydrogen ion concentration on the reduction rate was investigated in buffer solutions at constant ionic strength of 1.0. The reaction was found to be of the first order in both reactants and inverse first order with respect to the hydrogen ion. The rate of the reaction decreased with increasing ethanol as well as hydrogen ion concentrations. The experimental data give a good fit to

$$- \mathrm{d}\,[dye]/\mathrm{d}t = k_{obs}\,[dye] = [dye]\,[bisulphite]$$
$$\left(\frac{k_a + k_b\,K_d\,[H^+]^{-1}}{1 + K_d\,[H^+]^{-1}} \right)$$

Pseudo-first-order rate constant, k_{obs}, was obtained by monitoring the disappearance of the [dye]. Activation parameters have been evaluated and a tentative reaction mechanism was discussed.

INTRODUCTION

Kinetics of the reduction of inorganic compounds by sodium bisulphite has been reported earlier.[1-3] However, much less attention has been focused on its application to organic compounds.[4,5] Pyrazolone dyes are of special interest because they have a wide application in different fields, particularly photographic industry,[6-8] electrophotography,[9] and in dyeing processes.[10,11] Kinetics of the reduction of the carbonyl group in pyrazolones has not been mentioned before. Therefore, we were prompted to undertake the present investigation on the title reduction using bisulphite ion in aqueous ethanolic media with a view of getting an insight into the reaction mechanism.

MATERIALS AND METHOD

Sodium bisulphite, ethyl alcohol and piperidine were of Analar (BDH) grade, whereas p-dimethylaminobenzaldehyde was of GR (E. Merck) grade. 4-(p-Dimethyl-amino)benzylidene-3-methyl-1-phenyl-2-pyrazolin-5-one was prepared by refluxing equimolar ratios of 3-methyl-1-phenyl-2-pyrazolin-5-one[12] and p-dimethylamino-benzaldehyde in ethanol containing piperidine as catalyst[13]. The obtained separated solid product was recrystallized from ethanol. The structure of the prepared dye is represented by the form
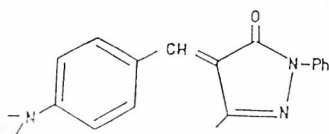
m.p. = 185 °C;
λ_{max} = 460 nm, ε_{max} = 70200 in pure ethanol.

The results of elemental analyses of this derivative were in accordance with its structure, Table I.

TABLE I

The Elemental Analysis Data of the Dye(I) and its Reduction Product (II)

Compound	Formula	Found (Calc.) %		
		C	H	N
I	$C_{19}H_{19}N_3O$	74.64 (74.73)	6.18 (6.27)	13.71 (13.76)
II	$C_{19}H_{21}N_3O$	74.01 (74.24)	6.76 (6.89)	13.54 (13.67)

Stock solution of the dye was prepared by dissolving an accurate amount of the dye in the appropriate volume of ethanol. Stock solution of sodium bisulphite was prepared by dissolving an appropriate weight of the recrystallized salt in doubly distilled conductivity water and standardized against iodine[14].

Kinetic Measurements

Kinetic experiments were carried out in a temperature-controlled (± 0.1 °C) water bath. The reaction was initiated by adding the requisite quantity of pre-equilibrated dye solution to an equilibrated mixture of sodium bisulphite, water and ethanol. The course of the reaction was followed by measuring the absorbance of the remaining dye at known intervals at the corresponding maximum absorption wavelength of the dye. The λ_{max} values were measured by rapid recording of the dye spectrum in the presence of the same percentage of EtOH—H₂O mixture and the same amount of NaHSO₃ as in the kinetic solutions. Absorption measurements were followed on a Shimadzu UV-200 S. double beam spectrophotometer, using the cell of 1 cm path length. The spectral change of the reaction is shown in Figure 1. It was verified that there is no interference due to other reagents or reduction product at λ_{max} of the dye. The reactions were usually followed up to not less than three half-lives. The pH measurements were carried out at 20 °C on WG PYE model 290 pH-meter accurate to ± 0.005 pH units.

The kinetics of the present work were conducted under pseudo-first-order conditions where [bisulphite] $\gg$ [dye]. Under these conditions, the rate equation can be written as follows,

$$-\frac{d[dye]}{dt} = k_{obs}[dye] \tag{1}$$

where k_{obs} is the observed pseudo-first-order rate constant, which may be expressed by the equation:

$$k_{obs} = k_2[bisulphite] \tag{2}$$

and k_2 is the second-order rate constant.

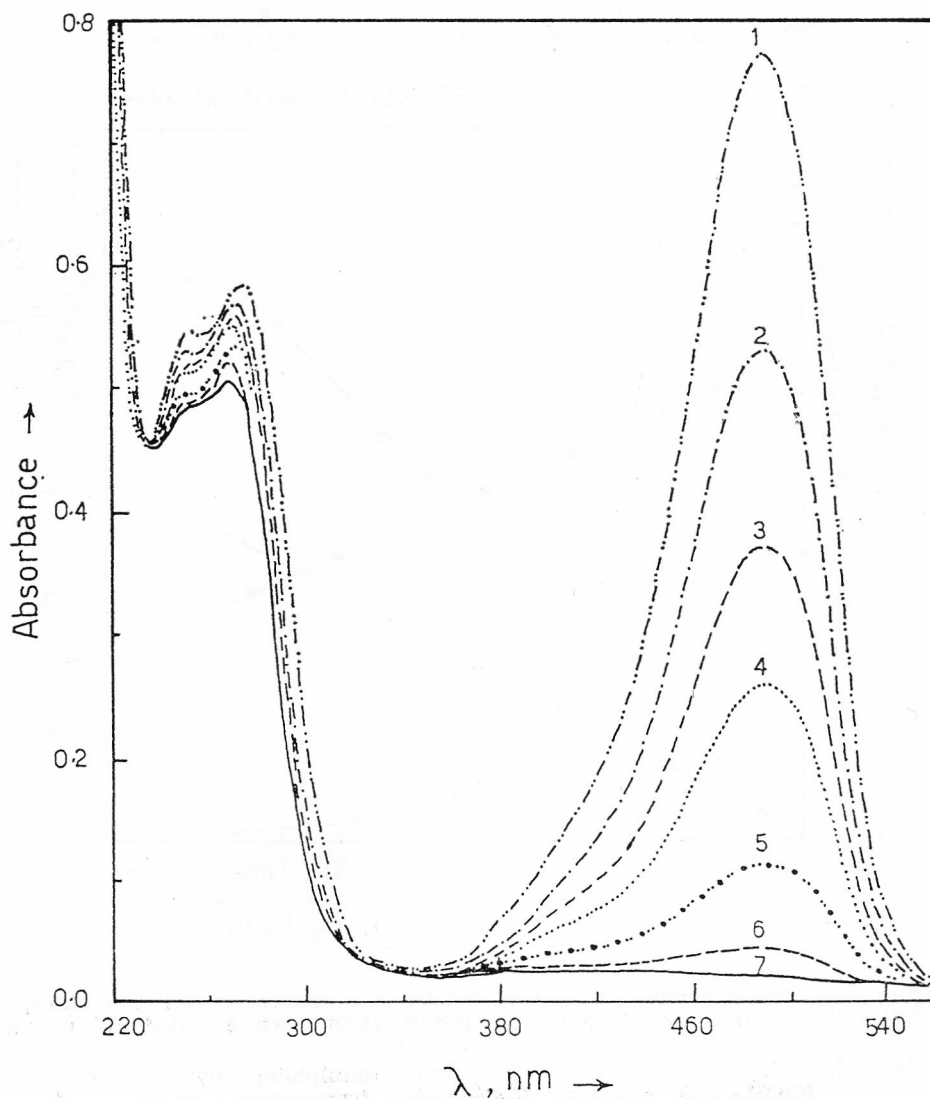Figure 1. Spectra change as a function of time of the reduction reaction: [dye] = = 2.77 × 10⁻⁵ M; [HSO₃⁻] = 1.0 × 10⁻³ M; (EtOH—H₂O) mixture = 34.6% (w/w); temperature = 28 °C. Time (min.): 1) 2.25; 2) 5.25; 3) 8.30; 4) 11.00; 5) 17.00; 6) 25.30; 7) after completion of the reaction.

RESULTS

a) Stoichiometry and Product Analysis

The stoichiometry of the overall reaction of bisulphite ions with excess of the dye was determined spectrophotometrically in terms of the consumption ratio ([dye]$_{consumed}$/[bisulphite]$_o$). The reaction mixture was placed in a ther-

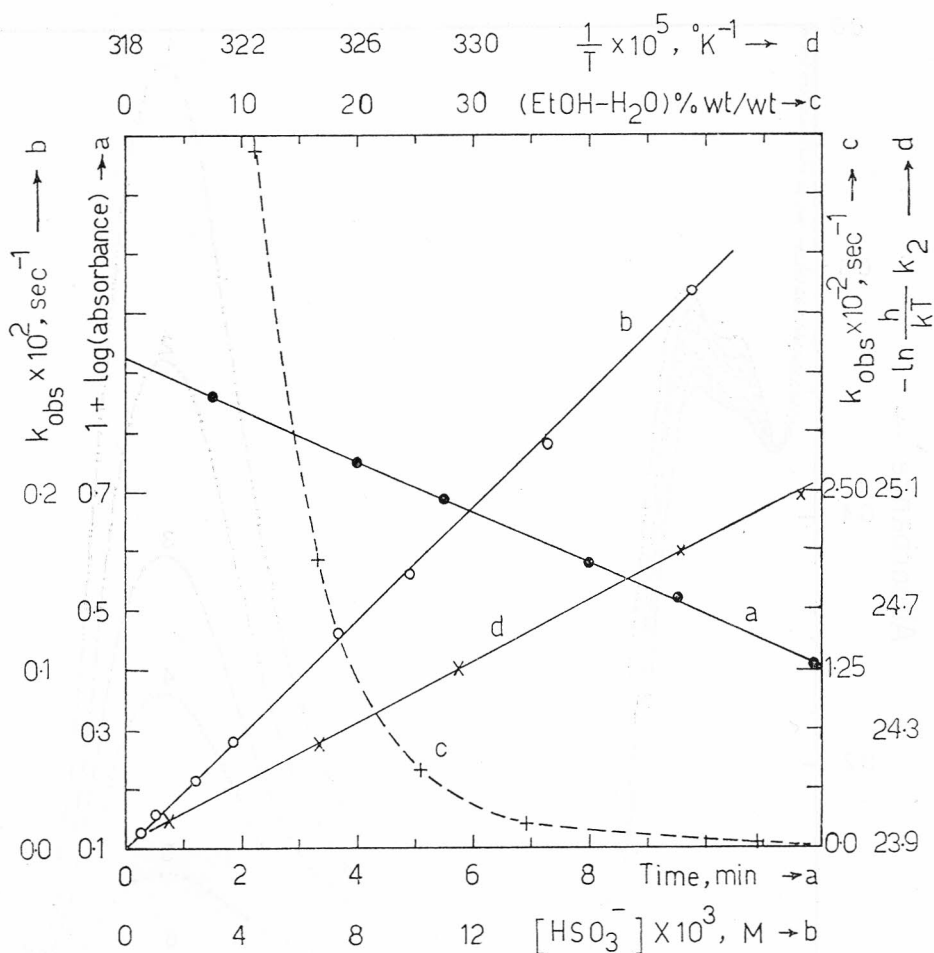Figure 2. a. Dye dependency. {Plot of $1 + \log$ (absorbance) versus time: [dye] $=$ $= 2.24 \times 10^{-5}$ M; $[HSO_3^-] = 1.0 \times 10^{-3}$ M; (EtOH—H_2O) mixture $= 34.6\%$(w/w); temperature $= 25\,°C$}.
b. Bisulphite dependency: {Plot of k_{obs} versus [bisulphite]: [dye] $= 4.4 \times 10^{-5}$ M; (EtOH—H_2O) mixture $= 34.6\%$ (w/w); temperature $= 25\,°C$}.
c. Effect of ethanol content on the reduction rate at $25\,°C$: [dye] $= 2.24 \times 10^{-5}$ M; $[HSO_3^-]$ 1.0×10^{-3} M.
d. The Eyring plot of $-\ln h/kT\, k_2$ versus $1/T$.

mostated water bath at 25 °C. The unreacted [dye] was estimated periodically till it attained a constant value. A stoichiometric ratio of 1 within experimental error was obtained in ten different initial concentrations of the dye.

The reduction product was isolated from the reaction mixture containing a large excess of bisulphite ions after completion of the reaction. A successive extraction with ether followed by drying over anhydrous sodium sulphate under N_2 gas gave a solid product confirmed by elemental (Table I) and i. r.

spectral analysis as 4 (p-dimethylamino)-benzylidene-3-methyl-1-phenyl-2-py-razolin-5-ol.

From the above results, the stoichiometry of the overall reaction can be represented by equation (3).

$$C_{19}H_{19}N_3O + HSO_3^+ + H_2O = C_{19}H_{21}N_3O + HSO_4^-$$ (3)
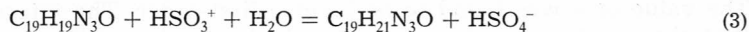
b) Rate Dependence on [Dye]

The order with respect to the dye was determined by studying the reaction at different initial concentrations of the dye with fixed [bisulphite]. The [dye] was varied in the range $(0.5—5.0) \times 10^{-5}$ M, whereas [bisulphite] suitable for kinetic measurements was 1.0×10^{-3} M, the ethanol-water mixture was 34.6% (w/w) at 25 °C. Under these conditions where [bisulphite] $\gg$ [dye], the plots of log (absorbance) versus time were linear, indicating the first-order dependence of rate on [dye], Figure 2 (a). The average value of k_{obs} was found to be $(1.64 \pm 0.05) \times 10^{--}$ sec^{-1}.

c) Rate Dependence on [Bisulphite]

The order with respect to HSO_3^- ion was deduced from the measurement of the reaction rates at several bisulphite and fixed dye concentrations. The [bisulphite] was varied in the range $(0.5—19.5) \times 10^{-3}$ M, [dye] $= 4.4 \times 10^{-5}$ M, ethanol-water mixture $= 34.6\%$ (w/w) at 25 °C. The plot of k_{obs}, versus [bisulphite] was found to be linear passing through the origin, Figure 2 (b). This indicates that the reaction is also first-order with respect to $[HSO_3^-]$ ion. Thus, the reduction of the dye using bisulphite ion follows overall second--order kinetics.

d) Rate Dependence on Ethanol-Water Mixture Composition

The effect of the medium content of ethanol on the dye reduction rates was investigated at 25 °C. The ethanol was varied in the range $(8.1—76.0)\%$ (w/w), [dye] $= 4.4 \times 10^{-5}$ M, [bisulphite] $= 1.0 \times 10^{-3}$ M. The reduction rates were found to decrease sharply with increasing the medium content of ethanol, Figure 2 (c).

e) Rate Dependence on [Hydrogen ion]

To clarify the influence of [H$^+$] on the reduction rates and to elucidate the reduction mechanism, the reaction of 2.02×10^{-5} M dye with 4.86×10^{-4} M NaHSO$_3$ in 34.6% (w/w) ethanol-water mixture at 22 °C was investigated in a series of citric acid-Na$_2$HPO$_4$ buffer solutions of different pH's and constant ionic strength of 1.0. The dependence of k_{obs} on [H$^+$] is presented in Table II. An increase in hydrogen ion concentration leads to inhibition of

TABLE II

Effect of Varying [H$^+$] on the Rate of Reduction: [dye] $= 2.02 \times 10^{-5}$ M; [HSO$_3^-$] $= 4.86 \times 10^{-4}$ M; (EtOH—H$_2$O) Mixture $= 34.6\%$ (w/w), Temperature $= 22$ °C

10^6 [H$^+$] (M)	0.11	0.20	0.40	1.38	3.70	6.59
$10^3 K_{obs}$ (sec^{-1})	2.56	1.45	0.81	0.25	0.09	0.05

the reaction rate. The power dependence of [H⁺] on k_2 was determined from the empirical equation:

$$\ln k_2 = \ln [H^+]^n \tag{4}$$

The value of n was found to be inverse first-order. The integer value suggests that the reaction involves only one hydrogen ion path. A plot of k_2 versus $[H^+]^{-1}$ gives a good straight line passing through the origin, Figure 3 (a).
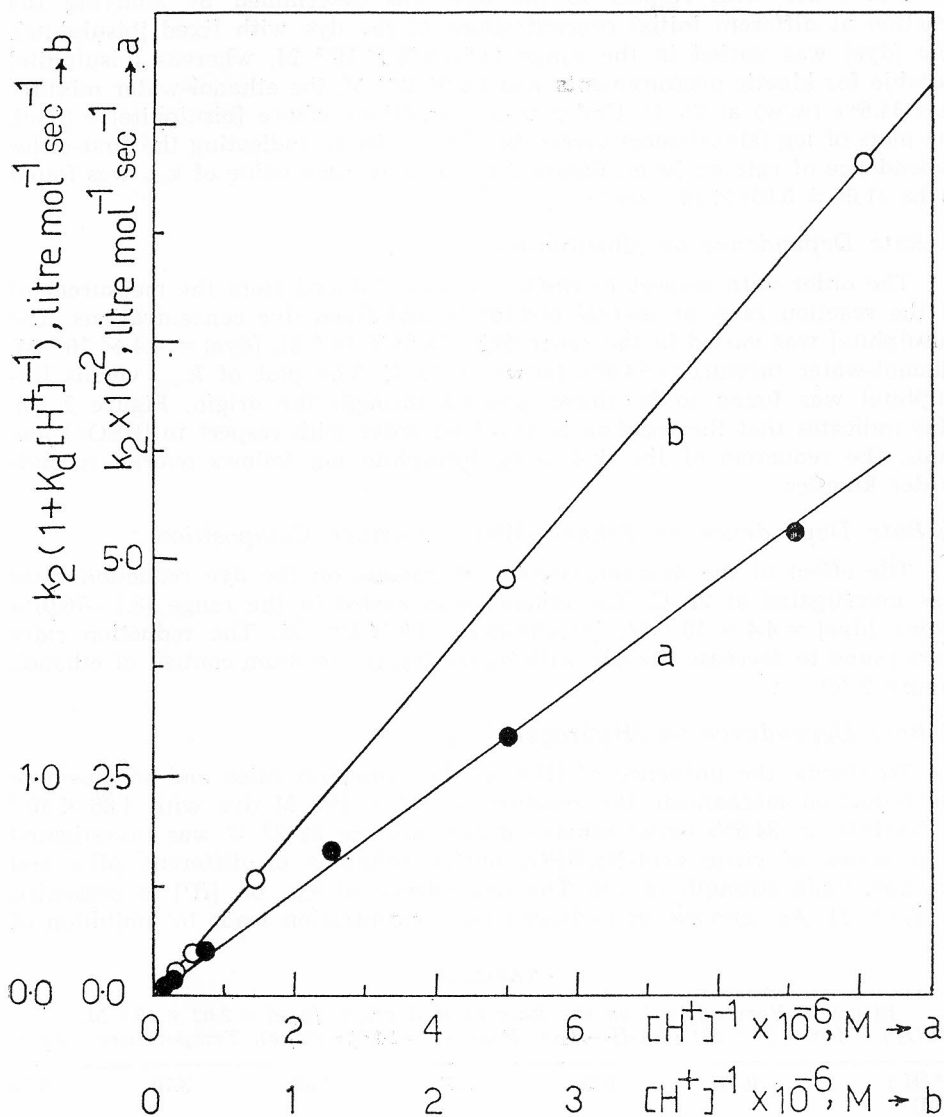

Figure 3. Effect of [H⁺] on the reduction rate at 22 °C: a. Plot of k_2 versus $[H^+]^{-1}$; b. Plot of $k_2 (1 + K_d [H^+]^{-1})$ versus $[H^+]^{-1}$: [dye] = 2.02×10^{-5} M; [HSO₃⁻] = 4.86×10^{-4} M; (EtOH—H₂O) mixture = 34.6% (w/w).

f) Rate Dependence on Temperature

The reaction was studied at 20; 23.5 30.5, 35 and 40 °C at [dye] $= 4.4 \times 10^{-5}$ M, [bisulphite] $= 1.0 \times 10^{-3}$ M, and 34.6% (w/w) ethanol-water mixture. The second-order rate constants (k_2) were calculated from rate expressions. The plot of $- \ln h/kT\, k_2$ against $1/T$ of Eyring Equation[15], gave a good straight line, Figure 2 (d). The values of the enthalpy and entropy of activations were determined from the slope and the intercept of the obtained straight line, respectively. These values are summarized in Table III.

TABLE III

Activation Parameters of the Reaction

Parameter	Value
$\Delta G \neq$ (kJ mol^{-1})	71.54 ± 3.59
$\Delta H \neq$ (kJ mol^{-1})	41.64 ± 2.23
$\Delta S \neq$ (kJ mol^{-1} deg^{-1})	-100.32 ± 4.56

DISCUSSION

The first-order dependence on both bisulphite and dye reactants lead us to formulate the following simple rate equation

$$-\frac{d\,[\text{dye}]}{dt} = -\frac{d\,[\text{bisulphite}]}{dt} = \frac{d\,[\text{product}]}{dt}$$

$$= k_2\,[\text{dye}]\,[\text{bisulphite}] \qquad (5)$$

Retardation of the reduction rate on increasing the ethanol content may be interpreted by the formation of a solvent cage between the dye and ethanol molecules via hydrogen bonding which retards the attack of HSO_3^- ions. On the other hand, increasing the amount of water may facilitate the reductant attack owing to the formation of hydrogen bonding as a bridge between the dye molecule and the solubilized reductant. This can be expressed as follows:

The large negative value of the entropy of activation obtained, c. f. Table III, can be explained in part by the necessity of the reductant ions to penetrate those cages in order to bring the pyrozolone dye into the reductant form.

Mechanism

From the inverse dependence of the second-order rate constant on [H$^+$] at moderately pH's used and from the linearity plot shown in Figure 3 (a), the mechanism can be visualized by a fast dissociation[16] of HSO_3^- prior to the rate determining step

$$HSO_3^- \overset{K_d}{\rightleftharpoons} H^+ + SO_3^{2-} \tag{6}$$

Introducing the dissociation constant (K_d), defined by Eq. (6), and the analytical concentration of bisulphite ions,
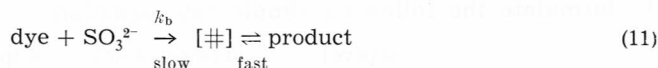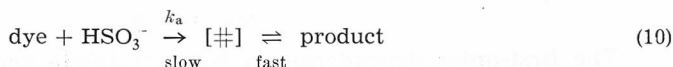
$$[HSO_3^-]_{Total} = [HSO_3^-] + [SO_3^{2-}] \tag{7}$$

the concentrations of HSO_3^- and SO_3^{2-} species may be expressed by the equations:

$$[HSO_3^-] = \frac{1}{1 + K_d [H^+]^{-1}} \approx [HSO_3^-]_{Total} \tag{8}$$

and

$$[SO_3^{2-}] = \frac{K_d [H^+]^{-1}}{1 + K_d [H^+]^{-1}} [HSO_3^-]_{Total} \tag{9}$$

When the following competitive reactions are considered for the rate determining step

$$dye + HSO_3^- \overset{k_a}{\underset{slow}{\rightarrow}} [\#] \underset{fast}{\rightleftharpoons} product \tag{10}$$

$$dye + SO_3^{2-} \overset{k_b}{\underset{slow}{\rightarrow}} [\#] \underset{fast}{\rightleftharpoons} product \tag{11}$$

the variation of the second-order rate constant with the change of hydrogen ion concentration would be expressed by the form

$$k_2 = \frac{k_a + k_b K_d [H^+]^{-1}}{1 + K_d [H^+]^{-1}} \tag{12}$$

From the experimental results, the value of k_a is nearly zero as shown in Figure 3 (a). Consequently, Eq. (12) can be recast in the form

$$\frac{1}{k_2} = \frac{[H^+]}{k_b K_d} + \frac{1}{k_b} \tag{13}$$

Eq. (13) indicates that the plot of $(k_2)^{-1}$ versus $[H^+]$ should be linear with the slope corresponding to $(k_b K_d)^{-1}$ and intercept corresponding to $(k_b)^{-1}$. The values of k_b and k_d were calculated and found to be 13.89 L mol^{-1} sec^{-1} and 5.1×10^{-8} M, respectively. The obtained value of the dissociation constant, K_d, is in good agreement with that reported in the literature.[16,3] On the other hand, on using the reported[16] value for K_d, 5.6×10^{-8} M, a plot of $k_2 (1 + K_d [H^+]^{-1})$ against $[H^+]$ gives a good straight line passing through the origin, Figure 3 (b), which in turn confirms the kinetic analysis of the present investigation.

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SAŽETAK

Kinetika i mehanizam redukcije 4(p-dimetilamido)-benzilidene-3-metil-1-fenil-2--pirazolin-5-ona pomoću bisulfitnih iona u vodenoj otopini etanola

M. M. Girgis, R. M. Hassan i Z. H. Khalil

Kinetika redukcije pirazolonskih boja bisulfitom proučavana je u vodenoj otopini etanola. Nađeno je da je brzina redukcije upravo proporcionalna koncentraciji reaktanata, a obrnuto proporcionalna koncentraciji vodikovih iona i etanola. Predložen je zakon brzine kemijske reakcije i mogući mehanizam redukcije.