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RETARDING EFFECT OF Ce(IV), Ce(III), CU(II) AND Zn(II) AS ACCEPTOR CENTERS ON THE HYDROLYSIS RATE OF H_2 SALEN

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The rates of hydrolysis of N-N`-salicylidene-ethylenediamine (H_2salen), have been investigated in the pH range 1.50-11.30 at 25°C in aqueous media containing 7% V methanol. It was observed that the rates of hydrolysis were dependent on pH values more basic than pH 9.20. The rate-limiting step in such media was suggested to be the attack of hydroxide ions on the H_2salen as a keto-form. The pH-independent reactions occured at pH region 9.20-6.35. At pH values more acidic than 6.50, the hydrolysis rates became pH-dependent again and were correlated with the conversion of the substrate to its conjugate acid. Under these conditions the predominant reaction was attack of water molecules on the protonated substrate. Furthermore, effects of certain transition metal ions viz Ce(IV), Ce(III), Cu(II) and Zn(II) on the hydrolysis reaction rate have been examined and interpreted on the basis of formation of tricyclic chelate rings. Thermodynamic parameters have been also determined and discussed.

Key words:Retarding effect, Hydrolysis rate, H_2 salen.

Introduction

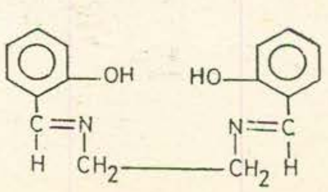
The present work is a continuation of our investigation on the N-N`-salicylidene-ethylenediamine (H_2salen) to collect more information about it because of its significant role in many of azomethine compounds in pharmacological and biological aspects (Morton and Pitt 1955; Chohen *et al* 1961; Witkop 1961; Cordes and Jencks 1962; Fridoviteh and Westheimer 1962; Grazi *et al* 1962). Our previous study (El-Taher and Gaber 1994) has confirmed the possibility of existence of H_2salen compound in a tautomeric equilibrium of the Keto←→ enol form. Such type of tautomeric equilibrium originated from the ortho-position of hydroxyl group with respect to the azomethine one. The present investigation is aimed to study the effect of Thiel buffer solutions of varying pH values on the hydrolysis behaviour of H_2salen. And also it is devoted to explore the effects of certain transition metal ions viz, Ce(IV), Ce(III), Cu(II) and Zn(II) on the hydrolysis reaction of the same studied compound. Furthermore, effect of temperature and thus thermodynamic parameters have been calculated and explained.

Experimental

Kinetic measurements. The hydrolysis reaction of H_2salen was studied in a medium containing methanol-water (7% v/v) mixture, in a series of buffer solutions having varying pH 1.50-11.30. And also it was studied in the presence of selected transition metal ions, Ce(IV), Ce(III), Cu(II) and Zn(II), in the hydrolysis medium, with a constant ionic strength of 0.1 mol dm^{-3} using 1.0 mol dm^{-3} of KCl, at different temperatures.

The reaction rates were followed spectrophotometrically with a Shimadzu UV-Visible Recording UV-240 with 1 cm matched silica cells to measure the absorbance at wavelength 400 nm. The hydrolysis products did not exhibit any absorbance at this wavelength. The reaction mixtures designed for the kinetic measurements were immersed in an ultrathermostat controlled to ±0.1°C. The moment of mixing was taken as the zero reaction time. The amount of H_2salen hydrolyzed at different time intervals was evaluated by the Lambert-Beer law.

Solid H_2salen: (Campbell *et al* 1944) N-N`-salicylidene-ethylenediamine ($H_2$salen) employed in the present work was prepared by refluxing N-N`-ethylenediamine and salicylaldehyde (in 1:2 molar ratio) in absolute ethanol using one drop of piperidine as a catalyst. The separated solid Schiff's base was filtered off and recrystallized from ethanol. The structure of the synthesised compound was characterised by C, H, N analysis (Found: C, 71.72; H, 5.89; N, 10.33%, Calc. for $C_{16}H_{16}N_2O_2$; C, 71.64; H, 5.97; N, 10.45%). According to above microchemical analysis data the structure formula of the prepared compound can be represented as follows:



N-N`-Salicylidene ethylenediamine (H_2 Salen)

Materials. All other reagents and methanol were of analar or extrapure grade.

Solutions. Stock solution (1×10^{-2} mol dm^{-3}) of the Schiff's base was prepared by dissolving the requisite amount in pure methanol. Solutions of low molarity were prepared by appropriate dilution of the stock solution.

1×10^{-2} mol dm^{-3} stock solutions of each of the $Ce(SO_4)_2$, $Ce(NO_3)_3 . 6H_2O$, $Cu(NO_3)_2 . 6H_2O$ and $Zn(NO_3)_2 . 6H_2O$ and $Zn(NO_3)_2 . 6H_2O$, were prepared by dissolving accurately weighed amount of each in pure methanol. The metal ion solutions were standardized according to usual procedures.

Buffer solutions. A series of buffer solutions of pH 1.50-11.30 were prepared according to Thiel, Schulz and Coch (Britton 1956) by mixing the appropriate volumes (0.05 mol dm^{-3} of each of oxalic acid, succinic acid, sodium sulphate, borax, sodium carbonate and 0.2 mol dm^{-3} of boric acid) in a media containing methanol-water (7% v/v) mixture. The pH of these solutions were checked using a MV-87 digital pH-meter, accurate to ±0.05 pH-unit at 25°C.

To account for the difference in acidity, basicity, dielectric constant and ion activities in aqueous 7% (v/v) methanol solutions relative to a pure aqueous ones, the measured pH values of the former solutions were corrected according to Doheret equation (Doheret 1967):

$$pH^* = pH(R) - \delta$$

where pH* is the corrected reading and pH(R) is the meter reading obtained in a partially aqueous media; the pH-meter is standardized using standard aqueous buffer solutions. The value of δ(Doheret 1967), of the aqueous buffer solutions containing 7%(v/v) methanol is 0.004.

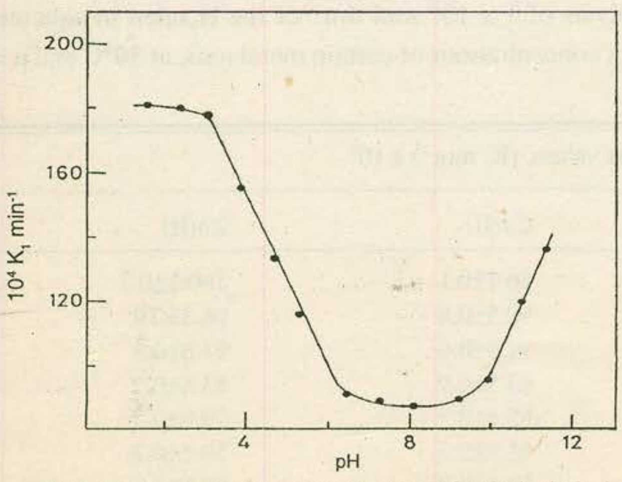


Fig 1. First-order rate constants versus pH for the hydrolysis of 1×10^{-4} mol dm^{-3} of H_2salen, in aqueous medium containing 7% v methanol at 25°C and $\mu = 0.1$ mol dm^{-3}.

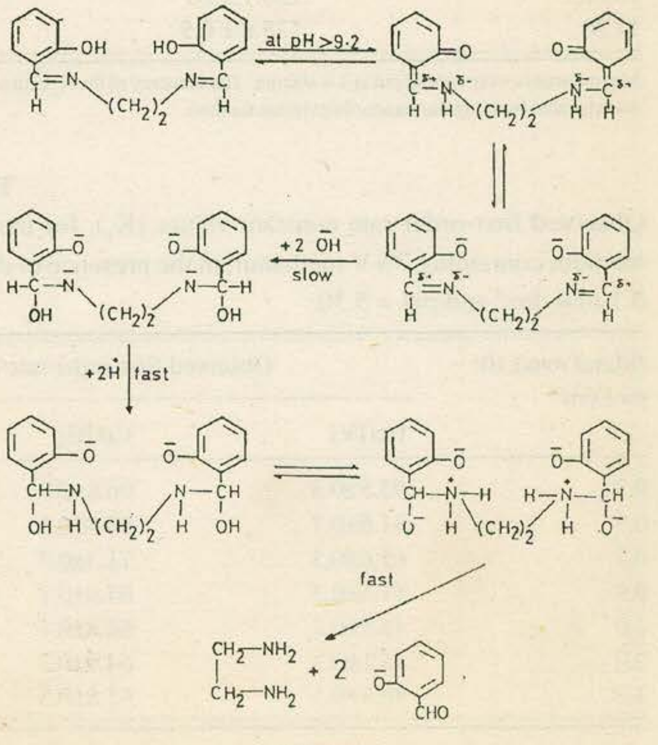
Results and Discussion

Effect of pH values on the hydrolysis reaction rates. In a series of buffer solutions of medium containing 7% (v/v) methanol-water mixture, the hydrolysis of 1×10^{-4} mol dm^{-3} of N-N`-salicylidene-ethylenediamine was investigated, at 25°C. The first-order rate constants for the hydrolysis reaction of Schiff's base are evaluated and plotted as a function of pH over the pH range 1.50-11.30 (see Table 1, and Fig 1). In light of Fig 1 it is evident that:-

The observed first-order rate constants for the hydrolysis of H_2salen, at pH values more basic than 9.20, slightly enhance with the rise of pH values in the hydrolysis medium. This refers to that the hydrolysis of the Schiff's base studied is pH-dependent in such alkaline region. These pH-dependent reactions may be accounted for in term of rate-determining attack of hydroxide ions on the ionized Schiff's base. Whereas, H_2salen exists as a keto-form (El-Taher and Gaber 1994) in alkaline media and it is expected to be hydrolysed as dianion imine (Dash *et al* 1983). Accordingly, the reaction mechanism in alkaline media can be proposed as Scheme I.

From the above hydrolysis mechanism, it is clear that a carbinolamine intermediate is formed in a slow step which decomposes with fast rate to products.

The pH-independent ractions which occur at pH region 9.20-6.35, are not subjected to detectable buffer catalysis. This is



Scheme I

attributed mainly to the usual transition from rate-determining attack of hydroxide ions at alkaline media to rate-determining raction of water molecules with the protonated Schiff's base which becomes the predominant reaction path as the pH is lowered. On the other hand, this pH region represents probably the tautomeric equilibrium of the keto←→enol form of Schiff's base (El-Taher and Gaber 1994), which transfers from keto-form in alkaline media to enol-form in neutral and acidic media.

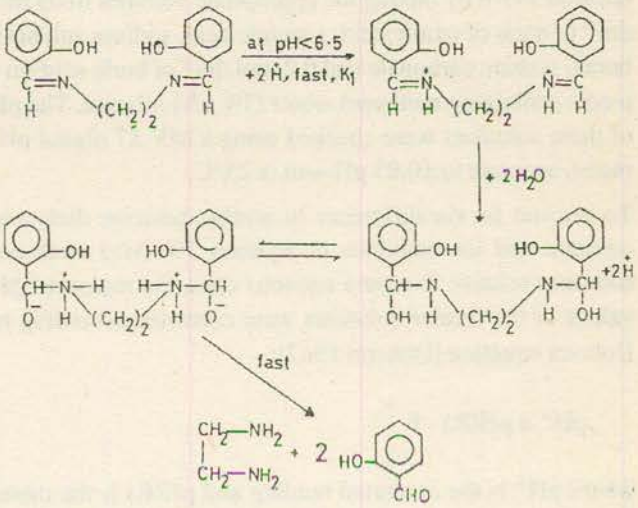
Table 1

Observed first-order rate constant values (K_1), for the hydrolysis of 1 x 10^{-4} mol dm^{-3} of the H_2salen in aqueous medium containing 7%V methanol at different pH values, 25°C and at $\mu = 0.1$ mol dm^3.

pH	Observed first-order rate constant values (K_1 min^{-1}) x 10^4
1.50	180.8 ± 0.9
2.35	178.9 ± 0.7
3.00	178.1 ± 0.7
3.71	155.3 ± 0.3
4.59	133.5 ± 0.1
5.26	115.8 ± 0.1
6.35	90.3 ± 0.6
7.22	88.9 ± 0.4
8.13	87.6 ± 0.8
9.20	88.5 ± 0.5
9.90	96.9 ± 0.1
10.68	120.1± 0.8
11.30	135.8 ± 0.5

Measurements were carried out at λ = 400 nm. The accuracy of the K_1 values was checked by using the standard deviation method.

At pH values more acidic than pH 6.35, the rates of Schiff's base hydrolysis become pH-dependent and are correlated with the conversion of the substrate to its conjugate acid ($-CH = N^+H- \longleftrightarrow -C^+H-NH-$) (Cordes and Jencks 1963). These observations suggest that, under these conditions the attack of water molecules on the protonated Schif'sf base (as enol-form) is the rate-determining step (Cordes and Jencks 1963). The mechanism pertinent to experimental observations can be suggested as Scheme II.



Scheme II

Table 2

Observed first-order rate constant values (K_1), for the hydrolysis of 1 x 10^{-4} mol dm^{-3} of the H_2salen in aqueous medium containing 7%V methanol, in the presence of different concentrations of certain metal ions, at 30°C and $\mu = 0.1$ mol dm^{-3} and pH = 5.30.

(Metal ions) 10^4 mol dm^{-3}	Observed first-order rate constant values, (K_1 min^{-1}) x 10^3			
	Ce(IV)	Ce(III)	Cu(II)	Zn(II)
0.3	93.5±0.3	96.8±0.9	96.1±0.1	100.1±0.7
0.5	81.8±0.7	89.5±0.5	90.5±0.8	96.8±0.9
0.7	65.6±0.3	71.3±0.7	71.0±0.6	91.6±0.5
0.9	51.5±0.3	65.9±0.1	62.3±0.9	83.6±0.3
1.0	48.5±0.1	64.8±0.1	65.5±0.3	79.8±0.3
2.0	45.1±0.2	64.9±0.3	61.9±0.2	70.1±0.2
3.0	46.8±0.1	65.8±0.5	62.5±0.2	68.5±0.3

Measurements were carried out at λ = 400 nm. The accuracy of the K_1 values was checked by using the standard deviation method.

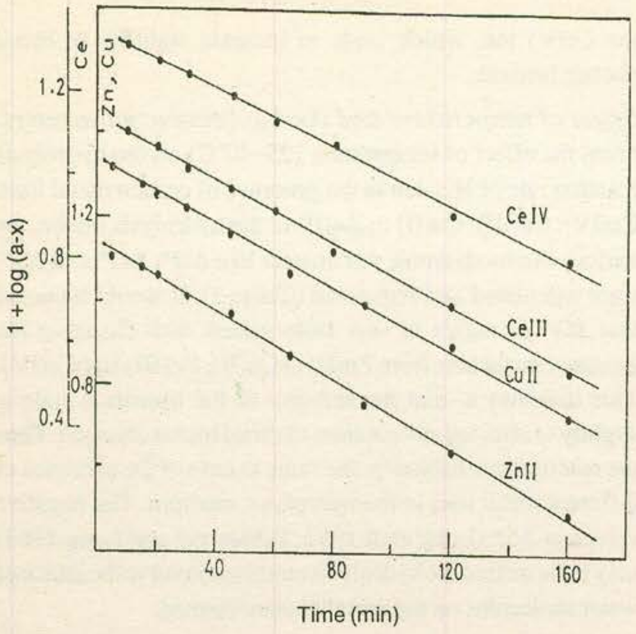
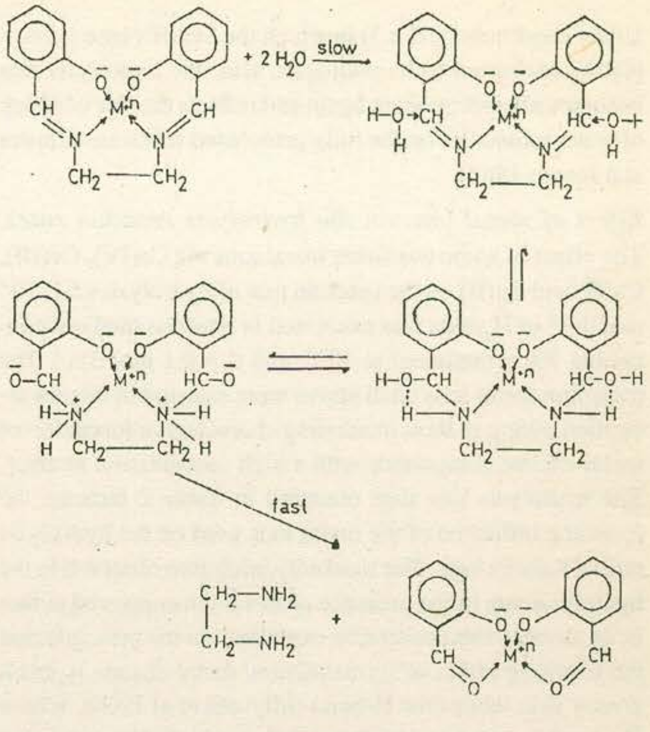


Fig 2. First-order rate plots for the hydrolysis of 1 x 10^{-4} mol dm^{-3} of H_2salen in aqueous medium containing 7% v methanol in the presence of 5 x 10^{-5} mol dm^{-3} of various transition metal ions at 30°C and μ = 0.1 mol dm^{-3}.



Scheme III

Table 3

Collective table for the first-order rate constant values (K_1) activation energy (Ea) and activation parameters (ΔG^*, ΔH^* and ΔS^*) for the hydrolysis of 1 x 10^{-4} mol dm^{-3} of H_2salen in aqueous medium containing 7% V methanol in the presence of 5 x 10^{-5} mol dm^{-3} of various transition metal ions at different temperatures and μ = 0.1 mol dm^{-3}.

Metal ion	Temp. (°K)	(K_{obs}(min^{-1}) x 10^4	Ea Kcal $mole^{-1}$	ΔH^* at 30°C Kcal $mole^{-1}$	ΔG^* at 30°C Kcal $mole^{-1}$	ΔS^* at 30°C cal $mole^{-1}$ deg^{-1}
Ce IV	298	65.3 ± 0.2				
	303	81.8 ± 0.7	13.73	13.12	18.30	-17.10
	308	120.1 ± 0.5				
	313	155.5 ± 0.3				
Ce III	298	70.1 ± 0.3				
	303	89.5 ± 0.5	12.20	11.59	18.24	-21.95
	308	130.3 ± 0.8				
	313	183.1 ± 0.8				
Cu II	298	71.5 ± 0.1				
	303	90.5 ± 0.8	11.82	11.21	18.23	-23.17
	308	131.9±0.1				
	313	185.3 ± 0.3				
Zn II	298	80.5 ± 0.8				
	303	96.8 ± 0.9	10.68	10.07	18.19	-26.80
	308	135.1 ± 0.7				
	313	199.6 ± 0.7				

Measurements were carried out at λ = 400 nm. The accuracy of the K_{obs} values was checked by using the standard deviation method.

Under conditions (pH < 3) in which the Schiff's base is completely converted to its conjugate acid, the hydrolysis rate becomes pH-independent again and reflects the rate of attack of water molecules on the fully protonated substrate (Cordes and Jencks 1963).

Effect of metal ions on the hydrolysis reaction rates. The effect of some transition metal ions viz Ce(IV), Ce(III), Cu(II) and Zn(II) on the reaction rate of hydrolysis of 1×10^{-4} mol dm^{-3} of H$_2$salen was examined in aqueous medium containing 7% v methanol at 30°C and $\mu = 0.1$ mol dm^{-3}. The transition metal ions cited above were selected in this investigation owing to their interesting characters in formation of metal chelate compounds with a high coordination number. The hydrolysis rate data recorded in Table 2 indicate the retarding influence of the metal ions used on the hydrolysis rate of Schiff's base. The markedly inhibition observed in the hydrolysis rate in the presence of metal ion compared to that in its absence can perhaps be explained on the principle that the retarding effect of six-membered metal chelate is much greater than that of the H-bond (Miyoshi *et al* 1966). Where H$_2$salen has a high tendency towards metal chelate formation as tetradentate ligand (Mahmoud *et al* 1985) through both the two azomethine nitrogen and two phenolic oxygen atoms forming tricyclic chelate rings (two six-membered and one five-membered). This tricyclic chelate structure imparts mainly kinetic stability to the imine linkage. In this context it is also worth mentioning that imines capable of forming bicyclic rings with metal ions have been reported to be strongly stabilized to hydrolysis (Eichorn and Marchand 1956). Since the rupture of two chelate rings is not normally favoured, our observation, that H$_2$salen which is capable of forming tricyclic chelate rings is stabilized towards hydrolysis in the presence of metal ions in hydrolysis medium, is uphold. The suggested mechanism in case of the presence of metal ions can be represented by the Scheme III.

On the other hand, it is noticed that the retarding effect of the metal ions on the hydrolysis reaction rate of H$_2$salen follows the following sequence:

$$\text{Ce(IV)} > \text{Ce(III)} > \text{Cu(II)} > \text{Zn(II)}$$

The smallest retarding effect of Zn(II), may be attributed to greater geometric flexibility permitted in its coordination of ligand (Dash and Nanda 1969). On the other hand, the high retarding effect observed in case of Ce(IV) relative to that of Ce(III), is probably due to the higher positive charge (+4) of the Ce(V) ion, which leads to increase stability of metal chelate formed.

Effect of temperature and thermodynamic parameters. From the effect of temperature (25–40°C) on the hydrolysis reaction rate of H$_2$salen in the presence of certain metal ions, Ce(IV), Ce(III), Cu(II) or Zn(II) in the hydrolysis media, the various thermodynamic parameters like ΔH^*, ΔG^* and ΔS^*, were calculated and registered (Table 3). It would be noted that ΔG^* increases in very little values with changing the nature of metal ions from Zn(II) to Cu(II), Ce(III) and Ce(IV). This indicates to that the stability of the transition state is slightly to affected as the nature of metal ions is changed. Thus the reaction mechanism is the same in case of the presence of different metal ions in the hydrolysis medium. The negative values of ΔS^* (Long *et al* 1957; Schalerger and Long 1963) may indicate that the hydrolysis reactions involve the attack of water molecules on the metal chelate formed.

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