Thermochimica Acta, 67 (1983) 17-22
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THE EFFECT OF TEMPERATURE AND THE KINETICS OF THE HYDROLYSIS OF SOME β-DIKETONE SCHIFF BASES

ALI A.H. SAEED *, M.H. WATTON and A.W.A. SULTAN

Department of Chemistry, College of Science, Basrah University, Basrah (Iraq)

(Received 25 January 1983)

ABSTRACT

The first order rate constants ($k_{obsd.}$) of the hydrolysis of Schiff bases derived from β-diketones were measured at different temperatures and pH in phosphate and acetate buffers. The results show that some molecules hydrolyze more slowly due to the existence of a high proportion of a hydrogen bonded enolimine tautomer, whereas the rates of hydrolysis of others are accelerated due to the formation of a species which has not been suggested previously containing two positive charge centres adjacent to each other. This species allows the rapid formation of the carbinolamine, the well-known intermediate during the hydrolysis of Schiff bases. From the effect of temperature, the activation parameters of the hydrolysis have been calculated although definite trends have not been established due to the random variation of their values with the nature of the substituent.

INTRODUCTION

The kinetics of the hydrolysis of aliphatic and aromatic Schiff bases in neutral, acidic and basic aqueous solutions have been studied extensively by many workers [1-4]. Conclusions regarding reaction pathways in acid medium involve conversion of the substrate into its conjugate acid which is stabilized by delocalization of the charge $-CH{=}\overset{+}{N}H- \leftrightarrow -\overset{+}{C}H-NH-$ [1,3,4], the carbonium ion is hydrolytically cleaved through the formation of the carbinolamine intermediate [1-3]. In neutral and alkaline solutions the pH-rate profiles exhibit pH-independent reactions which may be accounted for in terms of either rate-determining water attack on the free substrate or rate-determining hydroxide ion attack on the protonated substrate [1,5,6], as well as a pH-independent reaction under slightly acidic conditions in which the Schiff base is nearly completely converted to the conjugate acid, which may be accounted for as rate-determining attack of water on the protonated substrate [4,6]. The Schiff bases chosen for study in this work are derived from acetylacetone and benzoylacetone (I) which are of special interest

---

* To whom correspondence should be addressed.

0040-6031/83/$03.00

because of the possibility of neighbouring group effects. However, it is known that such Schiff bases exist mainly as a tautomeric mixture of both the enolimine and ketamine forms [7–10]. Their hydrolysis has not been attempted previously. A mechanism of their hydrolysis is proposed and compared with that of earlier studies for simpler Schiff bases.

EXPERIMENTAL

All the Schiff bases (I) used throughout this work were prepared and purified using the procedures described in the literature [7]. The UV–visible spectra and the decay curves of the hydrolysis reactions were measured on a Pye-Unicam SP8-200 UV–visible spectrophotometer which was connected to a circulator thermostat No. 2095 (Masterline Forma Scientific Maritta-Ohio) to control the temperature of the reaction cell. Standard phosphate and acetate buffers were used to prepare the solutions of the desired pH. The concentration of all Schiff bases was held constant (4.8×10^{-4}–1.2×10^{-4} mole dm^{-3}) throughout the measurements. In every case the ionic strength of the solution was kept constant at 0.49 mole dm^{-3} which was adjusted by the addition of Analar potassium chloride to the buffered solution. The hydrolyses were followed until 85% completion. The products of the hydrolyses were identified by comparison of their UV spectra with those of authentic samples. Calculation of $k_{\text{obs.}}$ from the decay curves has been discussed elsewhere [4].

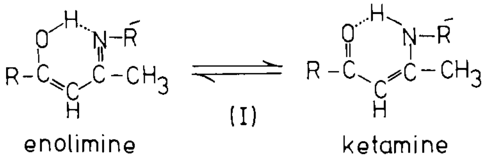
RESULTS AND DISCUSSION

The observed hydrolysis rate constants k_{obs} in acid solutions for the molecules Ic, Id, If, Ii, and Ij in phosphate and acetate buffers are plotted in the form of $(-\log k_{\text{obs}})$–pH in Fig. 1. The results indicate that changing the kind of buffer solution has a negligible effect on k_{obs}. The rate–pH profiles for these compounds are similar to those previously obtained for the hydrolysis of simpler Schiff bases such as substituted benzylideneanilines [11] and *p*-*N*,*N*-dimethylaminobenzylideneanilines [5,12] below pH 4.0, and they probably follow the same rate law in this pH range [5,11].

$$\text{Rate} = -(\mathrm{d}[\mathrm{BH}^+]_t/\mathrm{d}t) = k_1[\mathrm{BH}^+][\mathrm{H}^+] + k_2[\mathrm{BH}^+]$$

where $[\mathrm{BH}^+]$ is the concentration of the protonated Schiff base molecule, and k_1 and k_2 are constants. Accordingly, it can be concluded that acetylacetonylidene and benzoylacetonylideneanilines exist almost entirely as one species, possibly as hydrogen bonded chelate tautomers, namely, the ketamine and enolimine, where one of them appears to predominate.

To elucidate this point, we hydrolyzed a number of Schiff bases, mole-



Ia: $R=CH_3$, $R'=n\text{-}C_3H_7$
Ib: $R=CH_3$, $R'=C_6H_5$
Ic: $R=CH_3$, $R'=p\text{-}CH_3C_6H_4$
Id: $R=CH_3$, $R'=p\text{-}CH_3OC_6H_4$
Ie: $R=CH_3$, $R'=p\text{-}(CH_3)_2NC_6H_4$
If: $R=CH_3$, $R'=p\text{-}ClC_6H_4$
Ig: $R=CH_3$, $R'=p\text{-}HOOCC_6H_4$
Ih: $R=C_6H_5$, $R'=n\text{-}C_3H_7$
Ii: $R=R'=C_6H_5$
Ij: $R=C_6H_5$, $R'=p\text{-}CH_3OC_6H_4$
Ik: $R=C_6H_5$, $R'=p\text{-}HOOCC_6H_4$

cules Ia–k, in phosphate buffer at a single pH, namely 3.4, and different temperatures. The results are summarized in Tables 1 and 2. A comparison between the measured k_{obs} for different substituents allows a correlation between the effect of substituent on the rate of hydrolysis and the ratio of enolimine–ketamine forms in these Schiff bases to be established. The results indicate that compounds Ia–d and Ig hydrolyze faster than the corresponding compounds Ih and Ii, respectively. The presence of a phenyl group adjacent to the carbonyl group in the latter molecules may enhance enolization in a way similar to that of *β*-diketones [7,13], *β*-ketoesters [13,14], and *β*-keto-*N*-substituted amides [15]. Accordingly, the addition of a proton to the azomethine nitrogen of such Schiff bases, which represents the

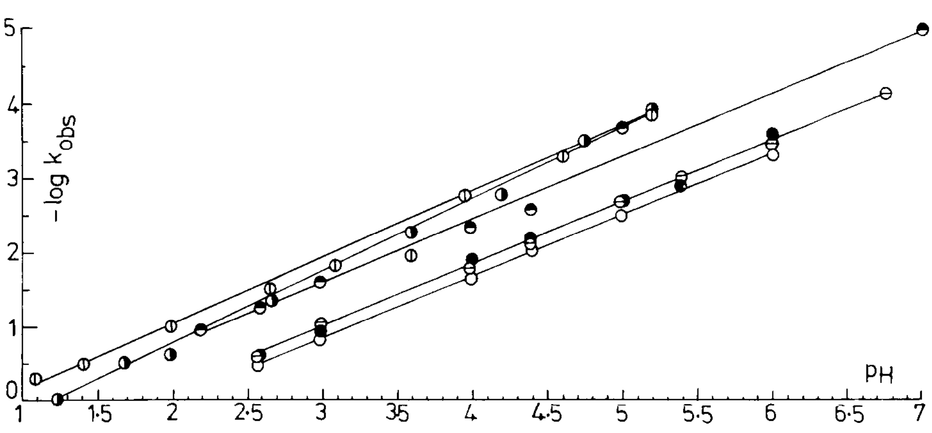


Fig. 1. Plots of $-\log k_{obs}$ vs. pH in buffered media. ◑, Molecule Ii in acetate buffer; ◓, molecule Ii in phosphate buffer; ⦶, molecule Ij in acetate buffer at 24 ± 0.5°C. ●, Molecule Ic; ⊖, molecule Id; ○, molecule If in phosphate buffer at 32 ± 1°C.

TABLE 1

$k_{obsd.}$ and the activation parameters of acetylacetone Schiff bases, molecules Ia–g, in aqueous phosphate buffer at pH 3.4

Molecule	Analytical wavelength (nm)	Temp. (K)	$k_{obs} \times 10^3$ (sec^{-1})[a]	ΔG^* (kJ mole^{-1})	ΔH^* (kJ mole^{-1})	ΔS^* (J mole^{-1})
Ia	310	290	1.86±0.35			
		298	4.30±0.30	86.3	52.8	−112.4
		312	9.80±0.50			
Ib	321	290	28.00±0.50			
		298	47.10±0.50	80.4	47.3	−111.0
		312	121.70±6.20			
Ic	320	290	25.50±0.40			
		298	44.40±1.70	80.6	44.0	−122.6
		312	118.10±3.40			
Id	312	290	24.00±1.10			
		298	42.30±1.50	78.2	49.0	−97.9
		312	107.80±5.80			
Ie	319	290	21.00±0.60			
		298	36.80±1.00	78.6	47.3	−104.8
		312	90.50±2.80			
If	324	290	28.50±1.80			
		298	49.10±2.10	76.6	49.7	−90.3
		312	133.30±9.10			
Ig	345	290	31.50±0.40			
		298	53.10±1.50	77.5	47.3	−101.2
		312	140.30±4.30			

[a] Each reading is the average of at least three measurements.

first step in the catalytic hydrolysis [1,3,5,12], will be hindered due to the intramolecular hydrogen bonding. A similar intramolecular hydrogen bonding structure has been suggested previously in the stabilization of cyclohexene-1-carboxylideneaminoacetic acid [3]. On the other hand, it is evident from the results that substitution of a phenyl group for the *n*-propyl group in molecules Ia and Ih, i.e. molecules Ib and Ii, accelerates the rate of hydrolysis markedly. This can be explained as follows. Upon protonation the positive charge is delocalized to form the carbonium ion (II) in Scheme 1 [1–5,12] in which the phenyl ring may create a positive charge on the nitrogen atom due to the conjugative interaction of its lone pair of electrons with the π-conjugated system of the ring forming the intermediate (III). Accordingly, the positivity of the adjacent carbon atom will increase, leading to a fast addition of OH, from the H_2O molecule, forming the carbinolamine intermediate (IV). The carbinolamine intermediate is hydrolyzed to the final

TABLE 2

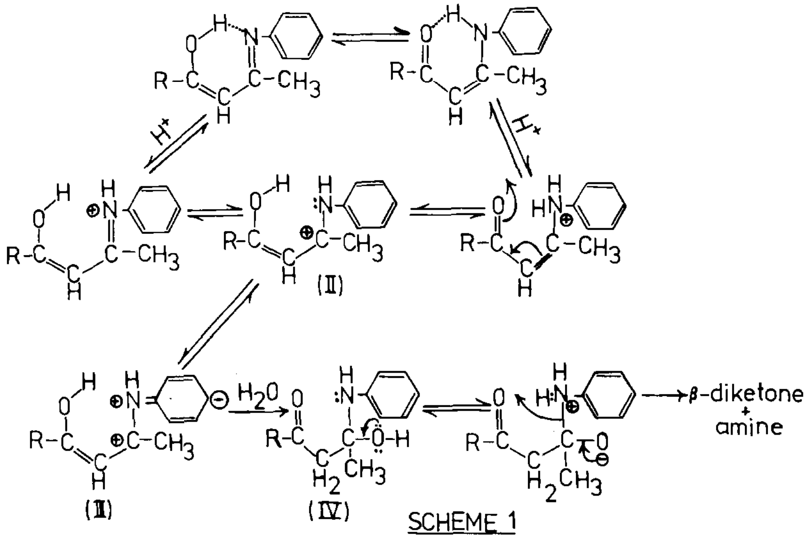
$k_{\mathrm{obsd.}}$ and the activation parameters of benzoylacetone Schiff bases, molecules Ih–k, in aqueous phosphate buffer at pH 3.4

Molecule	Analytical wavelength (nm)	Temp (K)	$k_{\mathrm{obs}} \times 10^3$ (sec^{-1})^a	ΔG^* (kJ mole^{-1})	ΔH^* (kJ mole^{-1})	ΔS^* (J mole^{-1})
Ih	338	294	0.36 ± 0.03	91.2	52.4	−132.1
		304	0.74 ± 0.02			
		312	1.17 ± 0.07			
Ii	361	294	6.30 ± 0.10	88.2	47.4	−125.4
		304	11.60 ± 0.60			
		312	23.60 ± 1.20			
Ij	362	294	6.90 ± 0.20	81.6	45.0	−124.4
		304	11.80 ± 0.40			
		312	20.10 ± 0.80			
Ik	370	294	5.40 ± 0.20	91.2	58.9	−109.6
		304	13.30 ± 0.50			
		312	22.50 ± 0.80			

[a] Each reading is the average of at least three measurements.

products according to the mechanism suggested previously [1,3,5,6,12].

Our suggestion concerning the formation of the intermediate (III) during the hydrolysis of our Schiff bases is confirmed by: (i) formation of the intermediate (III) depends on the increasing interaction of the nitrogen lone pair of electrons with the phenyl ring, therefore the presence of electron-withdrawing groups should enhance such interaction and lead to higher rates. This is probably why molecules If and Ig were hydrolyzed faster than



SCHEME 1

molecules Ic–e, molecules Ic–f slower than Ib, and molecules If–g faster than Ib (Table 1); (ii) values of k_{obs} for the hydrolysis of molecules Ib–g at 17 and 39°C were correlated to Hammett σ_p constants. The plots of $\log(k/k_0)$ vs. σ_p were linear, with slopes (ρ) equal to $+0.13$, $+0.12$, and $+0.155$, respectively. The positive values of ρ indicate that the hydrolysis is facilitated by electron-withdrawing groups substituted in the *para* position of the Ph_N ring. The activation energies of the hydrolyses were obtained from the slopes of Arrhenius plots which yield satisfactory straight lines. The activation parameters of the hydrolyses are summarized in Tables 1 and 2. The negative values of ΔS^* indicate that the hydrolyses involve attack of solvent on the protonated substrate [16,17]. The values of ΔG^* seem to be independent of the nature of polar substituents. On the other hand, values of ΔH^* and ΔS^* exhibit random variation with the nature of the polar substituent. The activation parameters are comparable in magnitude with those obtained by Willi and Robertson [11] for acid catalyzed hydrolysis of benzylideneanilines, by Geiseler et al. [14] for the hydrolysis of benzylideneaminooctanes in acidic aqueous dioxane solutions, and by Chaturvedi and Cordes [18] for acid catalyzed hydrolysis of benzylidene-1,1-dimethylethylamines, although uncertainties concerning the nature of the rate-determining step and random variation of the activation parameters with the substituent make comparison with results obtained in this study difficult.

REFERENCES

1 I.R. Bellobono and G. Favini, Tetrahedron, 25 (1969) 57.
2 J. Archila, H. Bull, C. Lagenaur and E.H. Cordes, J. Org. Chem., 36 (1971) 1345.
3 R.M. Pollack and M. Brault, J. Am. Chem. Soc., 98 (1976) 247; 99 (1977) 3379; 99 (1977) 8232.
4 A.A.H. Saeed and G.Y. Matti, Can. J. Spectrosc., 25 (1980) 29 and refs. cited therein.
5 A.A.H. Saeed, Indian J. Chem., 17B (1979) 462.
6 E.H. Cordes and W.P. Jencks, J. Am. Chem. Soc., 85 (1963) 2843. K. Koehler, W. Saudstrom and E.H. Cordes, J. Am. Chem. Soc., 86 (1964) 2413.
7 A.A.H. Saeed, M.N. Al-Zagoum and M.H. Watton, Can. J. Spectrosc., 25 (1980) 137 and refs. cited therein.
8 S. Dilli and P. Patsalides, Aust. J. Chem., 31 (1978) 765.
9 L.S. Chen and S.C. Cummings, Inorg. Chem., 17 (1978) 2358.
10 K.C. Moss and F.P. Robinson, Can. J. Chem., 51 (1973) 505.
11 A.V. Willi and R.E. Robertson, Can. J. Chem., 31 (1953) 361.
12 R.L. Reeves, J. Am. Chem. Soc., 84 (1962) 3332.
13 L.N. Ferguson, The Modern Structural Theory of Organic Chemistry, Prentice-Hall of India Private Ltd., New Delhi, 1973.
14 A. Geiseler, F. Asinger and G. Henning, Chem. Ber., 94 (1961) 1008.
15 A.A.H. Saeed, Iraqi J. Sci., 22 (1982) 85.
16 F.A. Long, J.G. Pritchard and F.E. Stafford, J. Am. Chem. Soc., 79 (1957) 2362.
17 L.L. Schaleger and F.A. Long, Adv. Phys. Org. Chem., 1 (1963) 1.
18 R.K. Chaturvedi and E.H. Cordes, J. Am. Chem. Soc., 89 (1967) 1230.