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KINETICS STUDIES OF THE DECOMPOSITION OF BENZYLIDENE ANILINE–$AlCl_3$ COMPLEXES

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ABSTRACT

The kinetics of the decomposition of Schiff base–aluminum chloride complexes have been investigated spectrophotometrically. The effects of substituent, temperature and solvent on the decomposition rates of these complexes were considered. Activation energy and other activation parameters such as $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were also determined. Hammett's equation has been used to correlate the rates of decomposition of the *para*-substituted Schiff base complexes and σ-values of the substituents.

INTRODUCTION

The study of Schiff base complexes is of interest because of their role in many biochemical reactions [1,2]. Eichhorn and Dawes [3] have indicated that the formation of metal–pyridoxal–amine pyruvic acid complexes or metal–pyridoxal–alanine complexes must be Schiff's base complexes. Snell and co-workers [4,5] studied the enzymatic reactions of pyridoxal which are catalyzed by metal ions. They postulated that pyridoxal, the amino acid and the metal ion all react initially to form a metal–Schiff base complex which undergoes a transamination reaction. The kinetics of hydrolysis of imines derived from aliphatic and aromatic amines have previously been studied extensively [6–8]. Many factors such as substituent, solvent polarity, and solvent acidity were found to play an important role in the hydrolysis. Other investigators considered the effect of metal ions on the hydrolysis of Schiff bases [9,10].

This investigation deals with the kinetics of the decomposition of Schiff base–aluminum chloride complexes; particular attention is paid to the effects of substituents, temperature, and solvents on the rate of decomposition.

EXPERIMENTAL

All Schiff bases used throughout this work were prepared and purified using procedures described in the literature [11]. Details of UV–VIS instrumentation and calculation of the rate constants have been described [12].

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TABLE 1

Physical properties of the Schiff's bases and their complexes

No.	Name	M.P. (°C)	UV in ethanol (nm)	UV maximum of complex	Stability period (min)	*k* of the decomposition ($s^{-1} \times 10^3$)
I	Benzylidene-*p*-hydroxy aniline	180 –182	337, 277	396	10.0	0.335
II	Benzylidene *p*-methoxy aniline	61 – 62.5	335, 275	395	5.0	1.519
III	Benzylidene-*p*-methyl aniline	30 – 31	322, 270	386	1.5	3.370
IV	*p*-Methoxy benzylidene aniline	59 – 61	317, 282	373	0.0	3.680
V	*p*-Hydroxy benzylidene aniline	190.5–192	318, 295	378	0.0	3.600
VI	*p*-Methylbenzylidene aniline	39 – 40	315, 277	356	0.0	6.500
VII	Benzylidene aniline	44 – 46	310, 260	360	0.0	10.604
VIII	*p*-Chlorobenzylidene aniline	57 – 59	309, 257	390	0.0	11.998
IX	Benzylidene-*p*-chloro aniline	54 – 56	308, 258	388	0.0	24.940
X	Benzylidene-*p*-bromo aniline	60 – 62	307, 256	385	0.0	26.380
XI	Benzylidene-*p*-fluoro aniline	53.5– 55	310, 260	380	0.0	23.904

The IR spectra were recorded using a Pye-Unicam Sp 200 infrared spectrophotometer. The temperature of the cell housing was maintained constant up to $\pm 0.2°C$ by circulating water from a constant temperature bath (HAAKB NK 22) through the cell housing. NMR spectra were recorded using a Varian A-60D NMR spectrophotometer.

The melting points and UV absorption maxima of the Schiff bases and their complexes together with stability periods and rate constants are shown in Table 1.

RESULTS AND DISCUSSION

It was observed [12] that the decomposition of the Schiff base–$AlCl_3$ complexes in absolute ethanol obeys first order kinetics. The data of Table 1 indicate that the rate constants of the decomposition of these complexes decrease with the increase of basicity of the nitrogen atom. The rate constant at a given temperature increases with decreasing electron-donating power of the substituent in the aniline moiety for compounds I, II, III, VII which follows the decreasing order $H > CH_3 > OCH_3 > OH$. Similar results were obtained for compounds IV–VIII in which the values of the rate constants show the following decreasing order: $Cl > H > CH_3 > OCH_3 > OH$. The data obtained for compounds VII, IX, X, XI indicate a decrease in the basicity of the nitrogen atom and consequently a decrease in the stability of the complexes.

The order of the values of the rate constants which are obtained for these compounds are as follows: Br > Cl > F > H. This indicates that the bromine atom affects the basicity of the nitrogen atom more than the other halogen atoms [13,14]. The Hammett equation [15] has been used to correlate the rates of decomposition of the *p*-substituted complexes with σ-values of the substituents. The more electron-attracting the substituents, by either resonance and/or inductive effect, the more positive its σ-value. This behavior was consistent with the data obtained, where a linear relationship is found when values of $\log(K/K_0)$ are plotted against σ^+ ($\sigma \pm$ values are for the resonance-electron donating *para*-substituent) for compounds having the substituent on the $\mathrm{Ph_C}$ part of the molecule. This may be due to the direct resonance interaction between the substituent group and the centre of the reaction. On the other hand, in compounds containing the substituent on the $\mathrm{Ph_N}$ part the $\log(K/K_0)$ values are found to be linearly proportional to the Hammett's σ-constants.

The observed rates of decomposition of these complexes were found to be temperature dependent, the reaction rates increasing with increasing temperature. The activation parameters were calculated using the following equation given by the transition state theory [18,19]

$$k = (kT/h)\mathrm{e}^{-\Delta G^*/RT}$$

Table 2 summarizes the rate constants and the activation parameters for the decomposition of the benzylidene aniline series at 287.15 K in n-butanol.

For compounds IV, V, VI, according to the electron-donating ability of the substituent, the following decreasing order in the enthalpy, activation energy, and free energy of activation was obtained: $\mathrm{OCH_3} > \mathrm{CH_3} > \mathrm{H}$. This indicates that complex IV is the most stable due to the presence of the methoxy group. On the other hand, results for compounds I, II, and VII are in the decreasing order $\mathrm{OH} > \mathrm{OCH_3} > \mathrm{H}$.

The effect of the position of the substituent on $\mathrm{Ph_N}$ or on $\mathrm{Ph_C}$ can be seen by comparing the rate constants of compounds II and IV. It is clear that at a given temperature, the value for compound IV which contain an

TABLE 2

Activation parameters and rate constants for the decomposition of the benzylideneaniline series at 287.16 K in n-butanol

Compound no.	$k \times 10^3$ ($\mathrm{s^{-1}}$)	Ea (kcal/mol^{-1})	ΔG^* (kcal/mol^{-1})	ΔH^*	ΔS^* (e.u.)	log A
I	0.518	13.728	21.103	13.157	27.670	7.1511
II	2.680	13.074	20.165	12.503	26.683	7.3385
IV	9.087	13.000	19.422	12.429	24.350	7.8901
VI	10.850	12.450	19.367	11.879	26.098	7.5310
VII	12.660	12.400	19.279	11.829	25.945	7.5349

TABLE 3

First order rate constants for the decomposition of benzylidene aniline complexes at 287.16 K in different solvents

Compound no.	$k \times 10^3$ (s^{-1})			
	Abs. ethanol	n-Butanol	*iso*-Butanol	*sec*-Butanol
I	0.335	0.518	0.844	1.250
II	1.519	2.680	3.358	4.890
IV	3.685	9.870	13.130	17.650
V	3.604	4.507	5.182	7.118
VI	10.600	12.660	16.580	21.490
XII	1.036	1.450	1.730	2.380
XIII	13.159	25.908	33.173	49.898
XIV	11.189	16.980	22.108	32.242

(OCH_3) group on Ph_C is larger than for the complex II. This may be attributed to the fact that the polar effect is transmitted to the nitrogen atom more readily when the group is on the aniline moiety.

The values of the decomposition rate constants of the complexes at 287.16 K in different alcoholic solvents, are outlined in Table 3. The following decreasing order is observed: *sec*-butanol > *iso*-butanol > n-butanol > absolute ethanol. These results indicated that the rate constant increased with increasing solvent basicity. Here it is clear that the solvent molecule plays an important role in the rate of decomposition of the resulting complex by attaching the carbonium ion produced in the transition state.

A mechanism similar to that proposed by Eichhorn and Bailar [20] can be suggested for this system.

The complexes of $AlCl_3$ with Schiff bases are formed instantaneously. The resulting metal-to-nitrogen bond causes a distortion of the nitrogen cloud in the direction of the Lewis acid away from the carbon. This may cause weakening of the carbon–nitrogen double bond and thus rendering it more susceptible to solvolytic attack.

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