ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 1, pp. 168–172. © Pleiades Publishing, Ltd., 2015.

Kinetic Study of the Base-Catalyzed Hydrolysis of Novel High-Spin Hydrophobic Fe(II)–Azomethine Amino Acid Chelates: Salt and Structure Effects on the Reactivity[1]

Laila H. Abdel-Rahman, Rafat M. El-Khatib, Lobna A. E. Nassr, and Ahmed M. Abu-Dief

Chemistry Department, Faculty of Science, Sohag University, Sohag, 82534 Egypt
e-mail: ahmed_benzoic@yahoo.com

Received August 30, 2014

Abstract—The effect of salts on reactivity of basic hydrolysis of Fe(II) chelates bis(naphthylidenealanate) (nali), bis(naphthylidenephenylalanate) (nphali), bis(naphthylideneaspartate) (nasi), (naphthylidene histidinate) (nhi), bis(naphthylidene arginate) (nari) has been studied in aqueous media containing alkali metal halides, LiBr, NaCl, KBr, tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), and tetrabutylammonium bromide (TBAB). The suggested mechanism of the base hydrolysis involves the parallel attack of OH^- ions on Fe^{2+} central atom attached to a singly bonded OH^- ligand and dissociation of the first ligand as rate-determining step. Generally, presence of a salt markedly enhances the rate of the reaction compared to that without a salt. Such tendency is in accord of anionic nature of the transient species. Upon gradual addition of NaCl and NaBr the rate of the reaction decreases. On the contrary, addition of TMAB, TEAB and TBAB salts results in the initial rate increase followed by decrease when their concentration increases further.

Keywords: salt, hydrophobic, hydrophilic, kinetics, reactivity, reaction mechanism
DOI: 10.1134/S1070363215010296

INTRODUCTION

Salt effects on reactivity in solutions have been of considerable interest since studies of so called "cation catalysis" of reactions of organic substrates with nucleophiles such as hydroxide and thiocyanate. Brønsted rationalized salt effects on reactivity in terms of activity coefficients (Debye-Huckel) of initial and transition states. Brønsted and Livingston subsequently collated ionic strength effects on reactivity of inorganic complexes in the form of diagrams that bear the latter's name.

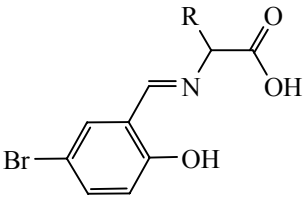
Effects of reaction media on reactivity have been established and discussed for a variety of reactions of inorganic complexes in aqueous salt solutions [1]. Various solutes and/or co-solvents can increase or decrease the distribution of hydrogen bond in water. Presence of salts in a reaction medium influences the rate of a reaction and modifies solubility of reactants. Therefore, we carried out an extensive study of the salt effect which, in turn, may provide valuable information on base hydrolysis of the title compounds pathways and the hydrophobic character of the ligands/complexes. The prepared Schiff base amino acid complexes can be characterized as efficient chelating agents [2] that demonstrate biological [3, 4] and cytotoxic [5] activity. Schiff base amino acids complexes are considered to constitute new kinds of potential antibacterial and anticancer reagents [6]. The new series of important Fe(II) chelates of Schiff bases are derived from 2-hydroxy-1-naphthaldehyde (HN) and amino acids including L-alanine (nali), L-phenylalanine (nphali), L-aspartic acid (nasi), L-histidine (nahi), and L-arginine (nari) (Scheme 1). Thus this study aims to elucidate the details of the salt effect on the base hydrolysis rate of the above complexes, exhibited by alkali metal cations, on one hand, and hydrophobic tetraalkylammonium cations, on the other [7].

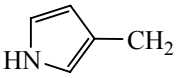
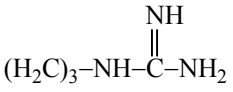
EXPERIMENTAL

Iron(II) complexes were prepared by the known method [2, 3]. An aqueous solution of an α-amino acid

[1] The text was submitted by the authors in English.

Scheme 1. Structures and abbreviations of the Schiff base ligands and abbreviations of their corresponding complexes



Ligand	Complex	R
bsal	bsali	CH_3
bsphal	bsphali	$CH_2C_6H_5$
bsas	bsasi	CH_2COOH
bsh	bshi	
bsar	bsari	

was mixed with hot ethanolic solution of the aldehyde in the stoichiometric ratio. The resulting amino acid Schiff base ligand was stabilized by chelation to Fe(II) upon adding an aqueous solution of ferrous ammonium sulfate in the equivalent ratio. To avoid Fe(II) oxidation five to six drops of glacial acetic acid were added. The resulting solution was stirred magnetically for 14 h in atmosphere of nitrogen. The isolated complexes were recrystallized from water–ethanol solutions. Composition of the complexes was elucidated by CHN microanalysis, IR and UV–Vis spectrophotometry as presented in our previous publication [3]. Purity of the complexes was tested spectrophotometrically [2, 3, 8, 9]. The solutions were tested for at least one month for the stability of Fe(II) cation by their resistance toward reduction with dithionite. Kinetic studies were carried out by monitoring the decrease in absorbance at λ_{max}, in a 1 cm thermostatted cell of a Jasco automatic scanning spectrophotometer and a wavelength programmer. There was no interference from any other reagents at this wavelength. The reactants, the complex and a hydroxide were mixed to allow the hydrolysis product precipitate as brown $Fe(OH)_3$ that resulted from oxidation by O_2.

The effect of salts on the rate of hydrolysis of the Schiff base amino acid Fe(II) complexes was studied in the presence of salts of different hydrophobicity: LiBr, NaCl, KBr, tetramethylammonium bromide, tetraethylammonium bromide, and tetrabutylammonium bromide in the solutions of various concentrations.

RESULTS AND DISCUSSION

Fading color of the solutions of Fe(II) amino acid Schiff base complexes indicates that the complete dissociation occurs. In presence of an excess of OH^- and O_2, the ultimate product, in addition to the ligand,

Scheme 2.

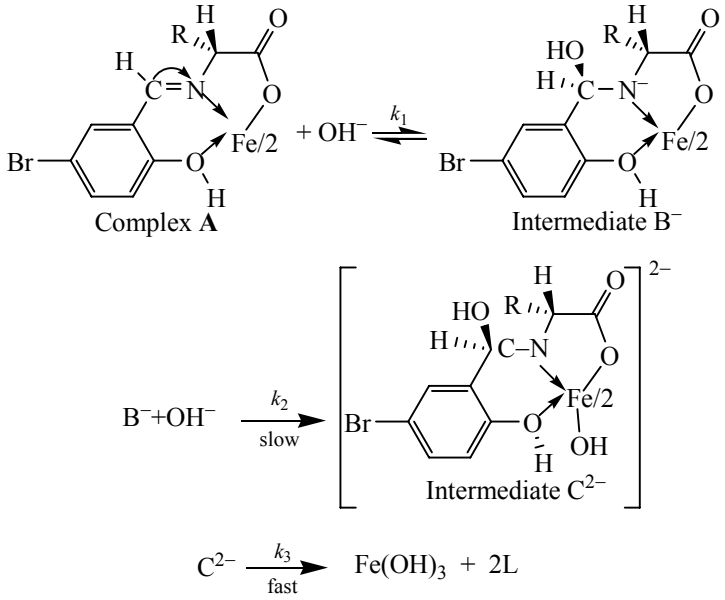


Table 1. Observed first order rate constant values ($k_{obs} \times 10^3$, s^{-1}) for the base hydrolysis of bsali complex with different molar concentrations of salts in aqueous medium at [bsali] = 1×10^{-4} mol/dm^3, [OH^-] = 5.83×10^{-3} mol/dm^3, T = 298 K[a]

Salt	Concentration, M										
	0.005	0.01	0.05	0.10	0.15	0.20	0.30	0.50	0.70	1.00	1.20
NaCl	–	–	–	11.39	11.27	11.19	11.02	10.76	10.49	10.03	9.72
KBr	–	–	–	11.27	11.18	11.03	10.82	10.47	10.13	9.67	9.26
LiBr	–	–	–	11.87	11.94	12.05	12.21	12.48	12.79	13.18	13.45
TMAB	10.81	11.95	11.35	11.17	10.67	–	–	–	–	–	–
TEAB	11.23	11.08	10.69	10.41	10.18	–	–	–	–	–	–
TBAB	11.17	11.29	11.85	11.62	11.35	–	–	–	–	–	–

[a] Maximum error is 2%.

Table 2. Observed first order rate constant values ($k_{obs} \times 10^3$, s^{-1}) for the base hydrolysis of bsphali complex with different molar concentrations of salts in aqueous medium at [bsphali] = 1×10^{-4} mol/dm^3, [OH^-] = 5.83×10^{-3} mol/dm^3, T = 298 K[a]

Salt	Concentration, M										
	0.005	0.01	0.05	0.10	0.15	0.20	0.30	0.50	0.70	1.00	1.20
NaCl	–	–	–	13.03	13.10	13.31	13.47	13.75	13.95	14.37	14.68
KBr	–	–	–	12.91	13.02	13.11	13.25	13.41	13.63	13.98	14.22
LiBr	–	–	–	13.29	13.41	13.56	13.81	14.34	14.79	15.13	15.49
TMAB	12.95	12.81	12.54	12.22	11.95	–	–	–	–	–	–
TEAB	12.71	12.85	13.21	13.49	13.78	–	–	–	–	–	–
TBAB	12.85	12.97	13.52	13.25	13.02	–	–	–	–	–	–

[a] Maximum error is 2%.

is $Fe(OH)_3$. The overall rate law for the reaction under the adopted conditions of pseudo first order kinetics is as follows:

$$\text{Rate} = k_{obs}[\text{complex}] = (k_1 + k_2[OH^-])[\text{complex}].$$

The k_1 term is assigned to the rate determining dissociation of the complexes and the k_2 term to the rate determining attack by OH^- at the compounds, where $k_{obs} = k_1 + k_2[OH^-]$ [9–14]. The first hydroxide ion adds to the electrophilic carbon atom of the polarized azomethine in the fast pre-equilibrium step (Scheme 2) [15–17]. The second hydroxide ion slowly attacks the central iron atom in the intermediate B^{2-} followed by degradation of the complex.

Pseudo-first order rate plots were obtained on the basis of the above mentioned conditions. The slopes of the plots were applied to calculations of the base hydrolysis rate constant values (k_{obs}) by least squares (Tables 1–5).

Data listed in Tables 1–5 demonstrate the sharp increase of the rate constant upon adding salts with low concentrations. This correlates well with the idea of Brønsted–Bjerrum and Livingston [18] and is also supported by the mechanism presented earlier [19] according to which the slow step involves formation of the negatively charged complex conjugate base. According to the publication [20] rates of bimolecular organic reactions in water are enhanced substantially by salting out reagents, including KBr, NaCl, and LiBr. Decrease in solubility of both reactants induced by the salts facilitates their tendency to form an activated complex and thus enhances reactivity [17, 20]. The observed decrease in reactivity of the base hydrolysis of the prepared bsali complex with increasing concentration of the hydrophilic salts agrees with anionic nature of the reactants in the rate determining step and supports the suggested mechanism.

Table 3. Observed first order rate constant values ($k_{obs} \times 10^3$, s^{-1}) for the base hydrolysis of bsasi complex with different molar concentrations of salts in aqueous medium at [bsasi] = 1×10^{-4} mol/dm^3, [OH^-] = 5.83×10^{-3} mol/dm^3, T = 298 K[a]

Salt	Concentration, M										
	0.005	0.01	0.05	0.10	0.15	0.20	0.30	0.50	0.70	1.00	1.20
NaCl	–	–	–	15.43	15.55	15.67	15.86	16.08	16.33	16.81	17.11
KBr	–	–	–	15.19	15.25	15.38	15.52	15.85	16.12	16.59	16.87
LiBr	–	–	–	15.59	15.72	15.85	16.07	16.51	16.73	17.22	17.48
TMAB	13.91	14.01	14.42	14.22	14.03	–	–	–	–	–	–
TEAB	14.03	14.15	14.57	14.33	14.12	–	–	–	–	–	–
TBAB	14.26	14.37	14.86	14.48	14.04	–	–	–	–	–	–

[a] Maximum error is 2%.

Table 4. Observed first order rate constant values ($k_{obs} \times 10^3$, s^{-1}) for the base hydrolysis of bsphali complex with different molar concentrations of salts in aqueous medium at [bshi] = 1×10^{-4} mol/dm^3, [OH^-] = 5.83×10^{-3} mol/dm^3, T = 298 K[a]

Salt	Concentration, M										
	0.005	0.01	0.05	0.10	0.15	0.20	0.30	0.50	0.70	1.00	1.20
NaCl	–	–	–	13.71	13.83	14.01	14.23	14.38	14.62	14.89	15.23
KBr	–	–	–	13.54	13.69	13.87	14.03	14.18	14.42	14.65	14.91
LiBr	–	–	–	13.82	13.95	14.25	14.46	14.83	15.01	15.32	15.56
TMAB	13.47	13.56	13.87	13.65	13.52	–	–	–	–	–	–
TEAB	13.52	13.65	14.18	13.91	13.75	–	–	–	–	–	–
TBAB	13.68	13.75	14.39	14.06	13.87	–	–	–	–	–	–

[a] Maximum error is 2%.

Table 5. Observed first order rate constant values ($k_{obs} \times 10^3$, s^{-1}) for the base hydrolysis of bsphali complex with different molar concentrations of salts in aqueous medium at [bsari] = 1×10^{-4} mol/dm^3, [OH^-] = 5.83×10^{-3} mol/dm^3, T = 298 K[a]

Salt	Concentration, M										
	0.005	0.01	0.05	0.10	0.15	0.20	0.30	0.50	0.70	1.00	1.20
NaCl	–	–	–	9.65	9.78	9.91	10.12	10.48	10.74	11.14	11.49
KBr	–	–	–	9.53	9.67	9.81	9.97	10.17	10.39	10.87	11.19
LiBr	–	–	–	9.78	9.93	10.05	10.34	10.76	11.07	11.56	11.87
TMAB	9.61	9.47	9.24	8.97	8.41	–	–	–	–	–	–
TEAB	9.53	9.39	9.09	8.76	8.23	–	–	–	–	–	–
TBAB	9.45	9.31	8.89	8.43	7.93	–	–	–	–	–	–

[a] Maximum error is 2%.

Under the action of a salt solubility of the activated hydrophilic complex in the rate determining step decreases.

The increase in the rate constant of base hydrolysis of the complexes at low concentrations of TMTB, TETB and TBAB is determined by anionic nature of the transition state step in the proposed reaction pathway. Subsequent decrease in reactivity under high concentrations of TMTB, TETB and TBAB is attributed to the dominating desolvation effect of the hydrophobic cations combined with the hydroxide anion.

CONCLUSIONS

Due to the salt effects on different substrates hydrophobicity of a complex or ligand increases and the relative influence of alkali metal and tetra alkly ammonium salt on the same decreases. High electrostriction of alkali metal halides (LiBr, KBr, NaCl) that act as salting out reagents results in more compact binding of the hydrophobic organic reactants with each other so that the activated complex is formed easily and, hence, the reactions proceed faster. On the other hand, tetra–*n*-butyl ammonium bromide as a salting in reagent enhances solvation of organic reactants highly so that they tend to exist separately and thus formation of the activated complex is retarded. But in our study the salting in effect of TBAB enhances the OH^- ion attack making formation of the activated complex more attainable and the reaction faster.

REFERENCES

1. Barrios, A., del Mar Graciani, M., Jiménez, R., Muñoz, E., Sánchez, F., Luisa Moyá, M., Alshehri, S., and Burgess, J., *Trans. Metal Chem*., 1992, vol. 17, p. 231.
2. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E., Abu-Dief, A.M, Ismail M., and Seleem, A.A., *Spectrochim. Acta*, 2014, vol. 117, p. 366.
3. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E., Abu-Dief, A.M., and Lashin, F.E., *Spectrochim. Acta*, 2013, vol. 111, p. 266.
4. El-Said, A.I., . Zidan, A.S.A., El-Meligy, M.S., Aly, A.A.M., and Mohammed, O.F., *Transit. Met. Chem*., 2001, vol. 26, p. 13.
5. Wang, Z.M., Lin, H.K., Zhu, S.R., Liu, T.F., and Chen, Y.T., *J. Inorg. Biochem.*, 2002, vol. 89, p. 97.
6. Prashanthi, Y., Kiranmai, K., Ira, S., kumar K., Chityala, V. K., and Shiyaraj, *Bioinorg. Chem. and Appl*., 2012, vol. 2012, p. 1.
7. Nilmoni, S., Kaustur, D., Debnarayan, N., and Kankan, B., *Chem Phys. Lett*., 1994, vol. 218, p. 492.
8. Patel, A.D., Prajapati, N.K., and Vora, J.J., *Der Pharmacia Sinica*, 2012, vol. 3, p. 93.
9. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E. and Abu-Dief, A.M., *Russ. J. Gen. Chem*., 2014, vol. 84, p. 1830.
10. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E. and Abu-Dief, A.M., *Russ. J. Gen. Chem*., 2014, no. 84, p. 578.
11. Abu-Gharib, E.A.,El-Khatib,R.M., Nassr, L.A.E., and Abu-Dief, A.M., *Kinet. Catal.*, no. 53, p. 182.
12. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E., and Abu-Dief, A.M., *Int. J. Chem. Kinet.,* 2014, no. 46, p. 543.
13. Abu-Gharib, E.A., El-Khatib, R.M., Nassr, L.A.E., and Abu-Dief, A.M., *J. Korean Chem. Soc.*, 2011, no. 55, p. 346.
14. Abu-Gharib, E.A., El-Khatib, R.M., Nassr, L.A.E., Abu-Dief, A.M., *Z. Physik. Chem*., 2011, no. 225, p. 235.
15. Mahmoud, M.R., El-Gyar, S.A., Moustafa, A.A., and Shaker, A.M., *Polyhedron*, 1987, vol. 6, p. 1017.
16. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E., and Abu-Dief, A.M., *J. Saudi Chem. Soc.*, accepted manuscript, 2013, *http://dx.doi.org/10.1016/j.jscs.2013.11.004.*
17. Abdel-Rahman, L.H., El-Khatib, R.M., Nassr, L.A.E. and Abu-Dief, A.M., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 12, p. 2510.
18. Alshehri, S. and Burgess, J., *Bioinorg. React. Mech*., 2003, vol. 5, p. 2191.
19. Shaker, A.M. and Nassr, L.A.E., *Int. J. Chem. Kinet*., 2002, vol. 34, p. 595.
20. Breslow, R., *Accounts Chem. Res*., 1991, vol. 24, p. 159.