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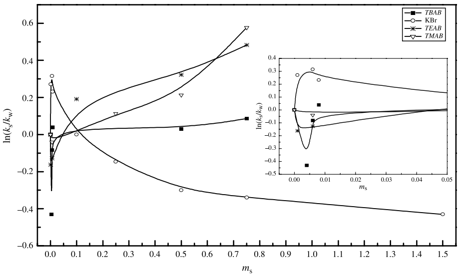
Graphical Abstract



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Salt Effects on Reactivity of Some Fe(II)-Azo Complexes Catalyzing Disproportionation of Hydrogen Peroxide

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Summary. Salt effects on kinetics of oxidation and decomposition of novel low-spin Fe(II) complexes of azo amino acids with hydrogen peroxide have been investigated in aqueous medium. The ligands are derived from amino acids (*DL*-phenylalanine, *DL*-tryptophane, histidine, and alanine) and *p*-nitroso aromatic substituted amines (*N*,*N*-dimethyl-4-nitrosoaniline and *N*,*N*-diethyl-4-nitrosoaniline). Hydrophobic salts of alkali metal and tetraalkylammonium halides, *e.g.*, KBr, tetrabutylammonium bromide (*TBAB*), tetraethylammonium bromide (*TEAB*), and tetramethylammonium bromide (*TMAB*) have been used.

Dilute salt solutions exhibit little effects on the reactivities of oxidation and decomposition of the title compounds. This behaviour would be ascribed to a decrease in the activity coefficients of the reacting species in these solutions. Moreover, these effects support the reported pathway in these reactions occurring *via* the association of dicationic complexes and undissociated H_2O_2. On the other hand, higher salt concentration shows considerable effects on the reactivities. This behaviour is explained in terms of hydrophilicity of the complexes, ion pair formation, salting out, and substituent effects. Hyrophilic nature of the recent complexes enhances reactivity with increasing [KBr] due to salting out effects in the aqueous medium. Increasing [*TBAB*] retards reactivity *via* ion pair formation with the reactants. In the presence of R_4N^+ ions, the reactivity increases with changing R in the following order; $R = C_4H_9 < C_2H_5 < CH_3$. The bulky R groups in the added tetraalkylammonium salts, exert medium steric hindrance against the approach of reactants.

Keywords. Salt effects; Iron(II); Azo amino acids; Hydrogen peroxide.

Introduction

Bronsted and *Bjerrum* rationalized salt effects on reactivity in terms of activity coefficients of initial and transition states. Furthermore, *Bronsted* and *Livingston* collected ionic strength effects on reactivities of inorganic complexes in the form of diagrams

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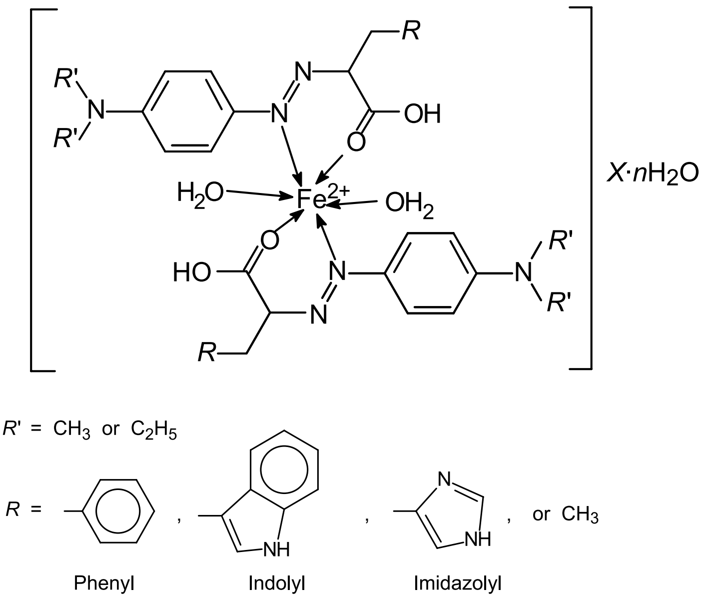
bearing the latter name [1]. As salt concentration increases, there would be deviation from the ideal behaviour observed in dilute salt solutions, and differences between cations arise. In high salt concentrations, specific ion–ion interactions should be considered. The effects of hydrophobic cations, particularly tetraalkylammonium cations, are often strikingly different from those of the simple aqua-cations. As the hydrophobicity of the ligands and thus of the complex increases, the difference in reactivity in the presence of alkylammonium halides and of alkali metal halides decreases [2].

The effects of the reaction medium on the reactivity have been established and discussed for a variety of reactions involving inorganic complexes in aqueous salt solutions [3–5]. To the best of our knowledge there is no information in the literature regarding the kinetics of the reaction of azo chelates with transition metals towards



Group Ligand	Abbr.	*R*	*R*′	*X*	*n*
[diaqua di(2-{[4-(dimethylamino)phenyl]azo}-3-phenylpropanoic acid)ferrous]sulphate	*MphA*	phenyl	CH_3	SO_4	2
[diaqua di(2-{[4-(diethylamino)phenyl]azo}-3-phenylpropanoic acid)ferrous]sulphate	*EphA*	phenyl	C_2H_5	SO_4	3
[diaqua di(2-{[4-(dimethylamino)phenyl]azo}-3-indol-3-ylpropanoic acid)ferrous]sulphate	*MinA*	indolyl	CH_3	SO_4	3
[diaqua di(2-{[4-(diethylamino)phenyl]azo}-3-indol-3-ylpropanoic acid)ferrous]sulphate	*EinA*	indolyl	C_2H_5	SO_4	2
[diaqua di(2-{[4-(dimethylamino)phenyl]azo}-3-imidazol-3-ylpropanoic acid)ferrous]sulphate	*MimA*	imidazolyl	CH_3	SO_4	3
[diaqua di(2-{[4-(diethylamino)phenyl]azo}-3-imidazol-3-ylpropanoic acid)ferrous]chloride	*EimA*	imidazolyl	C_2H_5	2Cl	5
[diaqua di(2-{[4-(diethylamino)phenyl] azo}propanoic acid)ferrous]chloride	*EprA*	methyl	C_2H_5	2Cl	4

Scheme 1

peroxo reagents generally and hydrogen peroxide specifically. Thus we determined to investigate medium effects on reactivity of a new series of Fe(II) chelates of azo amino acids against H_2O_2 in order to confirm the mechanism suggested in these reactions and the nature of the investigated complexes, as well as, to advance some novel insight concerning these effects. These complexes, *cf.* Scheme 1, have interesting structural features [6], reactivity [7], unusual spectroscopic properties [8], biological importance, as well as applications in the manufacture of polymers for optics [9, 10]. The title ligands bind strongly to Fe(II) to force pairing of all d^6 electrons and provide t_2g^6 configuration, thus kinetically inert octahedral Fe(II) complexes.

Results and Discussion

The plots of k_{obs} against hydrogen peroxide concentration exhibited linear relation consistent with our previous work [13]. The general rate law in wide ranges of hydrogen peroxide concentrations, is written as Eqs. (1) and (2).

$$-\mathrm{d}[\mathrm{complex}]/\mathrm{d}t = k_{obs}[\mathrm{complex}] \tag{1}$$

$$k_{obs} = k_1 + k_2[\mathrm{H_2O_2}] \tag{2}$$

The reaction exhibits a mechanism in which a composite rate-limiting step is assumed as substitution and oxidation, in the presence of relatively low concentrations of H_2O_2 reagent. The repeated spectral scans obtained in different molar ratios of the complex to hydrogen peroxide support the proposed mechanism. The following scheme presents the possible pathways for the reaction (Eqs. (3)–(7)).

$$\underset{\mathrm{A}}{[\mathrm{Fe(II)}L_2(\mathrm{H_2O})_2]} + 2\mathrm{H^+} \overset{K_1}{\rightleftharpoons} \underset{\mathrm{A^{2+}}}{[\mathrm{Fe(II)}(\mathrm{H}L)_2(\mathrm{H_2O})_2]^{2+}} \tag{3}$$

$$\mathrm{H_2O_2} \overset{K_2}{\rightleftharpoons} \mathrm{HOO^-} + \mathrm{H^+} \qquad K_2 = 5.59\times10^{-12}\,\mathrm{mol\,dm^{-3}} \tag{4}$$

$$\underset{\mathrm{A^{2+}}}{[\mathrm{Fe(II)}(\mathrm{H}L)_2(\mathrm{H_2O})_2]^{2+}} + \mathrm{H_2O_2} \xrightarrow[\mathrm{slow}]{k_3} \underset{\mathrm{B^+}}{[\mathrm{Fe(II)}(\mathrm{H}L)_2(\mathrm{H_2O})(\mathrm{HOO})]^+}\mathrm{H_2O} + \mathrm{H^+} \tag{5}$$

$$\overset{e^-}{\curvearrowright}$$

$$\underset{\mathrm{B^+}}{[\mathrm{Fe(II)}(\mathrm{H}L)_2(\mathrm{H_2O})(\mathrm{HOO})]^+} \xrightarrow[\mathrm{slow}]{k_4} \underset{\mathrm{C^+}}{[\mathrm{Fe(III)}(\mathrm{H}L)_2(\mathrm{H_2O})(\mathrm{O})]^+} + \mathrm{HO^{\bullet}} \tag{6}$$

$$\begin{aligned}&\underset{\mathrm{C^+}}{[\mathrm{Fe(III)}(\mathrm{H}L)_2(\mathrm{H_2O})(\mathrm{O})]^+} + 2\mathrm{HO^{\bullet}} + 2\mathrm{H_2O_2} + 4\mathrm{H^+} \xrightarrow[\mathrm{fast}]{k_5}\\ &\quad \mathrm{Fe^{3+}} + 2(R')_2\mathrm{N^+H{-}ph{-}NO_2} + 2R\mathrm{{-}CH_2CH(NH_2){-}COOH} + 4\mathrm{H_2O}\end{aligned} \tag{7}$$

$$\mathrm{H}L = (R')_2\mathrm{{-}N^+H{-}}ph\mathrm{{-}N{=}N{-}CH(CO_2H)CH_2{-}R}$$

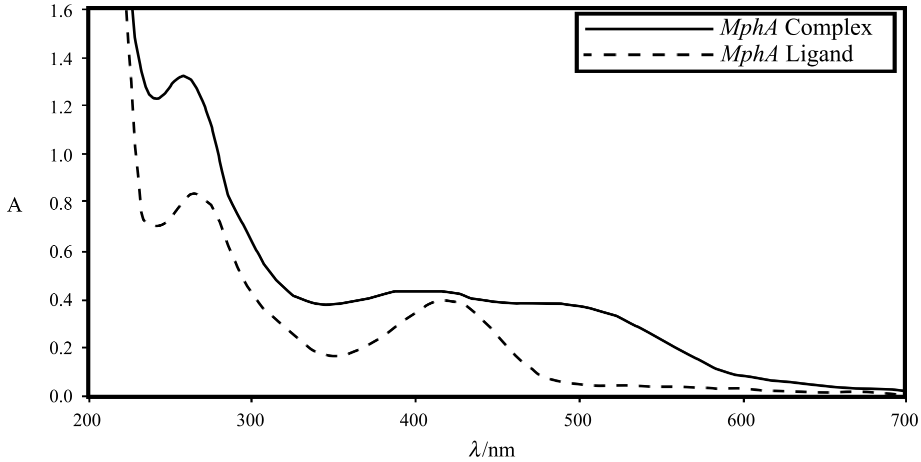


Fig. 1. Molecular electronic spectra of *MphA* and its corresponding ligand in aqueous media at [complex] and [ligand] ≈ 1×10^{-4} mol dm^{-3} and 298 K

K_1 is the protonation constant value of the complexes and log K_1 values range from 3.12 to 5.25 [11].

The spectra of the iron(II) azo amino acid complexes trace an absorption shoulder in the region of 480–500 nm (Fig. 1) [11]. The reaction of H_2O_2 with the complex solution enhances the molar absorptivity of the complex to a maximum value then decays due to the formation and decomposition of the peroxo intermediate complexes, respectively (Eqs. (5)–(7)). The rate and the extent of the enhancement depends on the [complex]:[H_2O_2] mixing ratio. In equimolar ratio, the rate of growth is very slow, therefore the complexes have not decomposed

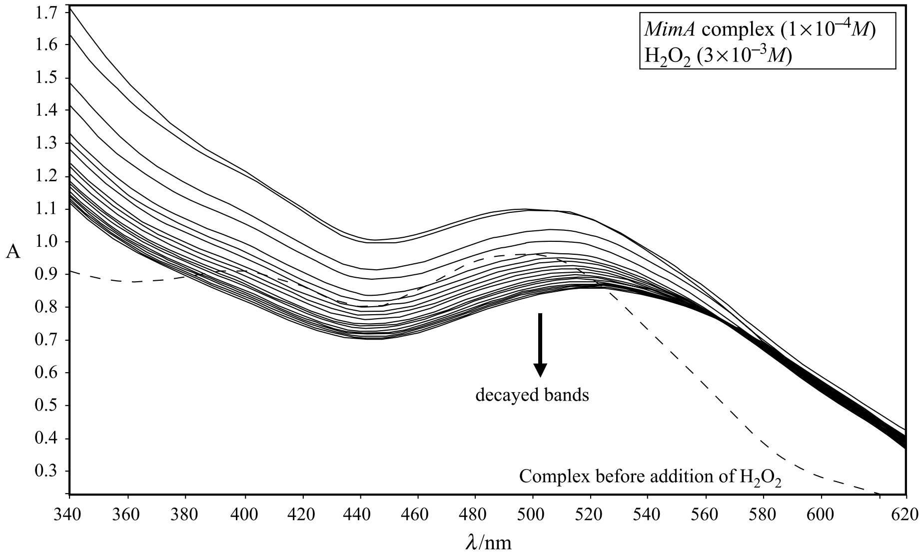


Fig. 2. Repeated spectral scans of *MimA* complex after the addition of H_2O_2 in aqueous media (for 1:30 molar ratio of complex to H_2O_2) with interval time 20 min (for ≈4 h) at [KNO_3] = 0.10 *M*, *pH* ≈ 2, and 298 K (for the rate of decomposition of *MimA* complex)

within 24 h. In the presence of 1:30 molar ratio of [complex]:[H_2O_2] the growth rate is faster, *cf.* Fig. 2. Upon mixing very large excess of H_2O_2, *i.e.*, in 1:3000 molar ratio, the rate of the band growth renders too rapid to be followed by conventionally available spectrophotometric tools. The enhancement of the complex band at 480–500 nm is explained [9, 14] as being due to the formation of the intraperoxo-intermediate by the substitution of one or two coordinated water molecules by hydrogen peroxide molecules and/or peroxo anions (HOO^-), as shown in the above mechanism (B^+), then the decay in the same band after a period of time corresponds to the rate of oxidation and decomposition of the peroxo-intermediate complexes C^+ [13]. It is assumed that decomposition of the intermediate complex C^+ is fast (Eq. (7)) but controlled by the slow preoxidation (Eq. (6)) and the release of $OH^{\bullet}$ free radical which destroys the azo chromophore as previously reported [15]. The present azo complexes are low spin as evidenced from the evaluated extremely low values of the rate constants, *cf.* Table 1, and of the magnetic

Table 1. The observed first-order rate constant ($10^4\ k_{obs}$, s^{-1}) values for the reaction of the Fe(II) complexes of azo amino acids at different [salt] in aqueous media at [complex] $\approx 1\times10^{-4}$ mol dm^{-3} [H_2O_2] = 0.300 mol dm^{-3}, [KNO_3] = 0.10 mol dm^{-3}, *pH* $\approx$ 2, and 298 K

		$10^4\ k_{obs}$, s^{-1}										
		Low concentrations					High concentrations					
Complex	Salt	0.00	0.001	0.004	0.006	0.008	0.10	0.25	0.50	0.75	1.00	1.50
MphA	*TBAB*	1.49	1.39		1.19		1.10		1.07	0.96		
	KBr	1.49			1.46	1.36	2.40			2.88	3.14	
	TEAB	1.49		1.04		0.79	0.96	1.11	1.33			
	TMAB	1.49		1.54		1.70	1.08	0.95				
EphA	*TBAB*	1.00		0.65	0.92	1.04			1.03	1.09		
	KBr	1.00	1.31	1.32	1.37	1.26	1.00	0.93	0.74	0.73		0.65
	TEAB	1.00	0.85		0.88	0.92	1.21		1.38	1.62		
	TMAB	1.00		0.93	0.96			1.12	1.19	1.78		
MinA	*TBAB*	0.93	0.24	0.41	0.47			0.66	0.98			
	KBr	0.93	0.77		0.47	0.54		1.47	1.34		1.33	
	TEAB	0.93		0.38		0.42	0.53	0.61	0.66	0.46		
	TMAB	0.93		0.35		0.36	1.35		1.63	2.40		
EinA	*TBAB*	0.97	1.07	1.21		1.35	0.98	0.97	1.00	1.01		
	KBr	0.97	0.66	0.73	0.76	0.88			0.96	1.03		1.22
	TEAB	0.97	0.91	0.79	0.73	0.72	0.90	1.13				
	TMAB	0.97	0.61	0.62	0.64		1.17	1.04		1.27		
MimA	*TBAB*	1.77	0.75	0.80	0.81		0.71			0.44		
	KBr	1.77	1.55	1.44	1.25		1.06			1.30		
	TEAB	1.77	0.81		0.95	1.22	1.18					
	TMAB	1.77	1.07		1.42	1.61						
EprA	*TBAB*	0.96	0.81		0.70	0.66	0.67	0.96	1.04			
	KBr	0.96	0.89	0.85		0.75	0.80	0.98		1.56		1.93
	TEAB	0.96	0.70	0.76	1.03	0.91	0.84	1.17				
	TMAB	0.96	1.27	1.09	1.04	1.34	1.37					

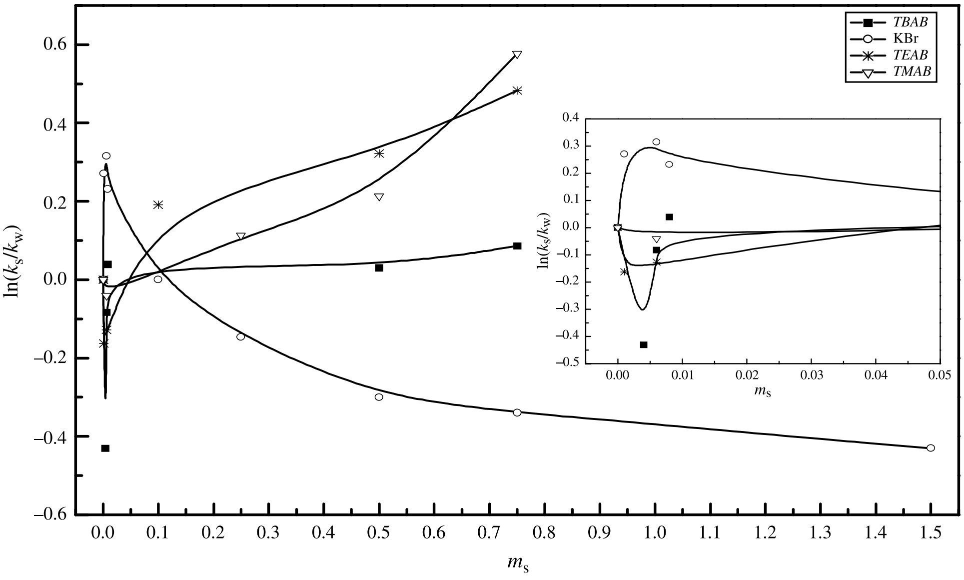


Fig. 3. Plot of ln(k_s/k_w) *versus* the molality of salts for the reaction of *EphA* complex with H_2O_2 in aqueous media at [complex] = 1×10^{-4} *M*, [H_2O_2] = 0.30 *M*, [KNO_3] = 0.1 *M*, *pH* ≈ 2, and 298 K (k_s/k_w) is the relative rate constant in the presence and absence of salt in the aqueous solution

moments, thus they exhibit high stability and hydrophilic character [16]. These characteristics are expected to result in interesting and surprising different reactivity trends in the presence of different salts and co-organic solvents.

The salt effect patterns in Figs. 3–5 show little effects in dilute salt solutions. This behaviour assists the suggested scheme for the tested reaction, that the tran-

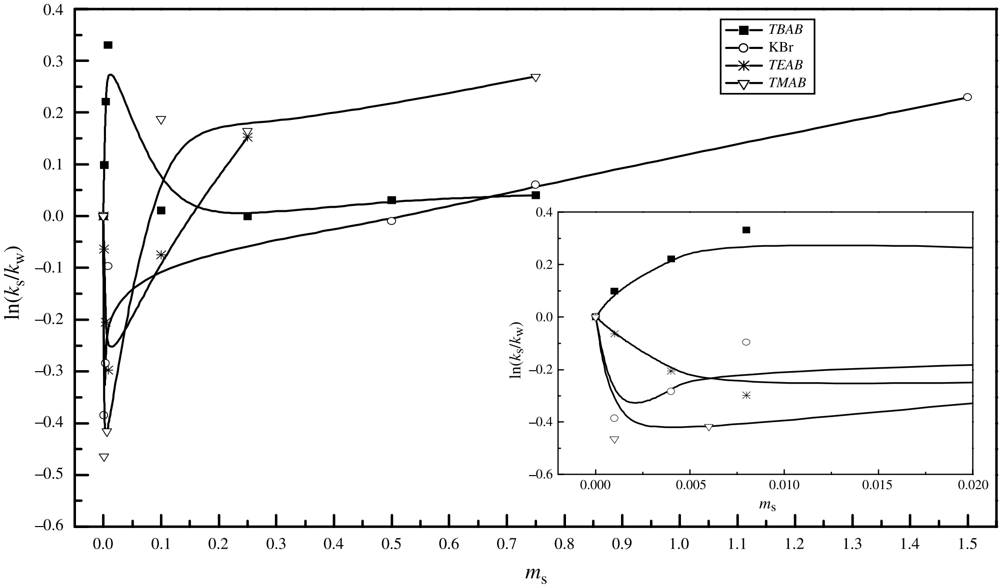


Fig. 4. Plot of ln(k_s/k_w) *versus* the molality of salts for the reaction of *EinA* complex with H_2O_2 in aqueous media at [complex] = 1×10^{-4} *M*, [H_2O_2] = 0.30 *M*, [KNO_3] = 0.1 *M*, *pH* ≈ 2, and 298 K

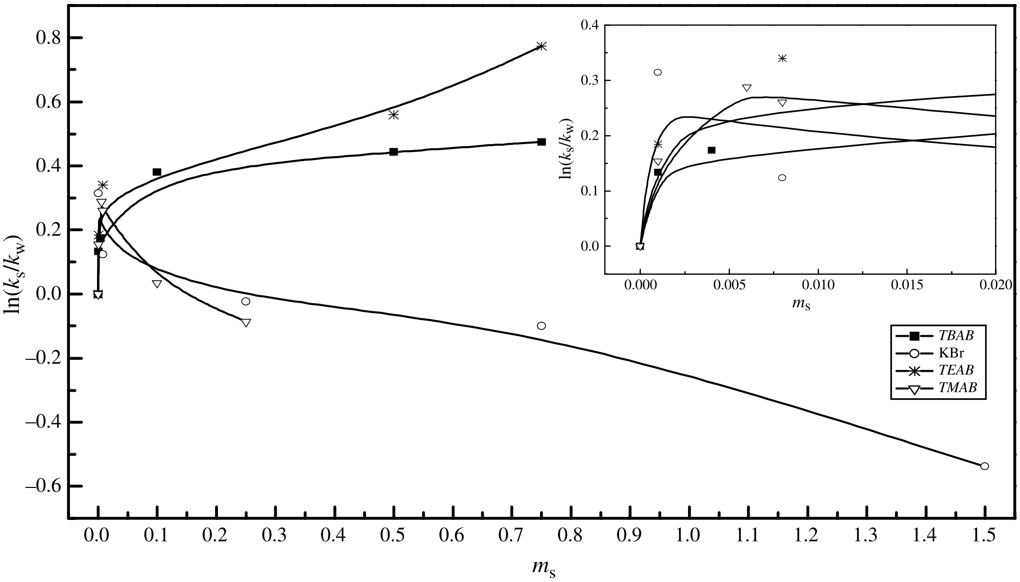


Fig. 5. Plot of $\ln(k_s/k_w)$ *versus* the molality of salts for the reaction of *EimA* complex with H_2O_2 in aqueous media at $[\text{complex}] = 1\times10^{-4}\,M$, $[H_2O_2] = 0.30\,M$, $[KNO_3] = 0.1\,M$, $pH \approx 2$, and 298 K

sient species compromise association of dicationic complexes and undissociated H_2O_2 species [17]. At higher salt concentrations, the salt effects appear to be more pronounced. In these solutions, increasing [KBr] generally enhances the reactivity, but decreases with increasing [*TBAB*]. This trend differs from that observed for previously reported hydrophobic Fe(II) amino acid schiff base complexes [2, 16]. The recent azo complexes are mainly hydrophilic in character, in particular, the transient species, *cf.* the mechanism proposal.

Moreover, as hydrophobicity of the ligands and thus of the complexes increases, the difference between reactivity in *TBAB* and in KBr containing solutions, decreases. The hydrophilicity of the studied azo complexes decreases in the following series: *EprA* > *MimA* > *EimA* > *MphA* > *EphA* > *MinA* > *EinA*. This order is deduced based on the structures, as well as, on the evaluated transfer chemical potentials for water into 10%, 30%, and 50% methanol [11], with little deviations due to the expected error limits in solubility measurements. The positive values obtained for the transfer chemical potential indicate hydrophilic character of the tested complexes. Hydrophilicity increases as transfer chemical potential increases.

Accordingly, from Fig. 4 and Table 1 it is observed that the less hydrophilic *EinA* complex exhibits the least difference between the reactivity in KBr and in *TBAB* solutions. The observed high reactivity in the presence of KBr relative to that in the presence of tetraalkylammonium bromide salts, would be explained as due to that large size cations of the latter salts form ion pairs *via* electrostatic interactions with peroxo anions and delay their attack on the cationic complex species leading to less reactivities. The formation of these ion pairs appears in reducing conductance of the reaction mixture solution compared with the corresponding conductance values in the individual component solutions. Salting out effects of KBr [18] on hydrophilic complex transient species and H_2O_2, enhance their combination to form the preoxo-intermediate complex. The opposite reactivity trends are shown by *EphA* and *EimA* (Figs. 3 and 5), that there are higher reactivities with *TBAB* than with KBr. This could be interpreted on the basis that these two complexes are relatively more hydrophobic, thus of lower activity coefficients in aqueous solutions due to their aggregation. The relatively less decrease in solubility on going from aqueous to binary aqueous solutions, accordingly their smaller transfer chemical potentials, would support the relatively higher hydrophobicity of these two complexes. It is assumed that hydration characteristics of *TBAB* prevail in determining reactivity trends of these two particular complexes [16].

The generally observed decrease in the reactivity in lower concentrations of the added salts would be ascribed to the decreasing activity coefficients of the reacting species according to *Debye-Huckel* theory [17]. The observed reversed trend in the case of *EinA* and *EimA*, that reactivity increases in low salt concentrations, may be assumed as being due to the more hydrophobic of these complexes, this leads to their decreased activity coefficients in aqueous solutions. Thus this effect in combination with the released peroxo species from their aqua cage (*via* hydrophobic hydration of *TBAB* cations), would result in enhancing reactivity due to the increase in transfer chemical potential of the free peroxo attacking nucleophiles. The observed decrease in conductance upon adding salt to the solution containing the complex and the peroxide reactants, would help in understanding this argument.

As salt concentration in the reaction medium increases, reactivity is enhanced. At high concentrations of *TBAB*, the large size cation of this salt would expand the cavities in hydrogen bonded aqua net and cave both reactants in, leading to their closer approach and facility of interaction between them to afford the reactive intermediate species and thus this would enhance reactivity of the reaction. This reactivity trend towards tetraalkylammonium bromide salts appears to be more detectable in hydrophilic chelates, as in the case of the present complexes, than in hydrophobic cases (Table 1 and Figs. 3–5). The hydrophilic complexes are usually encapsulated in aqua cages and need to destroy their walls to come together with the nucleophile to react.

The reactivity increases in the presence of R_4N^+ with changing R in the following series: $R = C_4H_9 < C_2H_5 < CH_3$.

It seems that steric hindrance of the large size groups attached to the added salt cations would exert a medium barrier against the reactants to come in contact and react. Moreover, it is reasonable that, as R changes from CH_3 to C_2H_5 to C_4H_9 the basicity of tetraalkylammonium increases in the same direction. This effect results in decreasing the coulombic electrostatic field of R_4N^+ cations and so their ability to bind to aqua net cage surrounding the reacting species, hence keeping the reactants inside to react.

The lowest reactivities observed for *EphA*, *EimA*, *EinA*, and *EprA* in the presence of KBr can be attributed to the high electrostatic force, generally characteristic of alkali metal cations, thus to their exclusive greater ability to form ion pairs with peroxo ions and then delay their attack on the complex to form the transient species leading to the products.

EimA exhibited an opposite reactivity trend against salts of tetraalkylammonium bromide. The reactivity towards H_2O_2 increases with changing R in the tetraalkylammonium salts in the following order: $CH_3 < C_2H_5 < C_4H_9$.

This behaviour can be interpreted on the basis that *EimA* contains both donor ethyl groups on one side and the imidazole moiety on the other side of the complex, *i.e.*, this complex exhibits relatively high basicity. The basic nature of this complex retards the attack of H_2O_2, thus the addition of tetraalkylammonium

Table 2. UV-vis. spectral data[a] with λ_{max} (nm) and ε_{max} ($mol^{-1}\,cm^2$) values for the complexes in aqueous medium at [complex] $\approx 1\times10^{-4}\,mol\,dm^{-3}$ and 298 K

	Electronic spectra		
Complex	λ_{max}/nm	$\varepsilon_{max}/mol^{-1}\,cm^2$	Assignment
MphA	497 (b)	1680.72	d–d band
	410 (b)	2425.63	LMCT band
	264	6785.33	π–π^* band
Ligand of *MphA*	251	1183.57	π–π^* band
	426	5091.63	Intermolecular CT band
EphA	489 (b)	2376.48	d–d band
	360 (b)	2115.92	LMCT band
	278	4490.08	π–π^* band
Ligand of *EphA*	252	4790.21	π–π^* band
	465	5495.07	Intermolecular CT band
MinA	498 (b)	1928.66	d–d band
	373 (b)	2710.98	LMCT band
Ligand of *MinA*	253	1422.69	π–π^* band
	422	6453.78	Intermolecular CT band
EinA	481 (b)	1616.22	d–d band
	385 (b)	1652.47	LMCT band
	270	6125.64	π–π^* band
Ligand of *EinA*	251	1219.18	π–π^* band
	430	6118.67	Intermolecular CT band
MimA	500 (b)	1466.73	d–d band
	390 (b)	1589.28	LMCT band
	270	6944.11	π–π^* band
Ligand of *MimA*	225	1904.74	π–π^* band
	468	3940.57	Intermolecular CT band
EimA	488 (b)	1853.24	d–d band
	372 (b)	1902.77	LMCT band
	275	4689.52	π–π^* band
Ligand of *EimA*	228	1912.49	π–π^* band
	465	4028.44	Intermolecular CT band
EprA	485 (b)	1512.34	d–d band
	368 (b)	1664.32	LMCT band
	273	4587.65	π–π^* band
Ligand of *EprA*	270	7321.25	π–π^* band
	429	2229.61	Intermolecular CT band

[a] *b* Broad band

cations would enhance nucleophilicity of H_2O_2 *via* hydrogen bonding with R_4N^+. Therefore, the ability for this hydrogen bonding increases with R_4N^+ in the following series: $R = CH_3 < C_2H_5 < C_4H_9$ and the reactivity against H_2O_2 increases in the same direction. The highest stability and lowest conductance values of the complex *EimA* support our assumption (Table 1).

Experimental

All chemicals used in the preparation of the novel complexes and in the kinetic studies such as hydrogen peroxide, potassium bromide (KBr), tetrabutylammonium bromide (*TBAB*), tetraethylammonium bromide (*TEAB*), tetramethylammonium bromide (*TMAB*), and potassium nitrate are all of analytical grade AnalaR reagent (BDH and Aldrich) products.

The complexes were synthesized and characterized by different physical tools by *Shaker et al.* [11]. Equimolar ethanolic solutions of *N*,*N*-dialkyl-4-nitrosoaniline were mixed with an aqueous solution of each amino acid used in slightly basic media. The resulting solutions were treated with an aqueous solution of the stoichiometric amount of ferrous ammonium sulphate containing glacial acetic acid to avoid the oxidation of Fe(II) and the formation of $Fe(OH)_3$ [12]. The *pH* of the final solutions was maintained at ≈1 by adding HCl. These solutions were stirred for two hours and kept for about four days in a vacuum desiccator when the intensely violet complexes precipitated. The separated compounds were dried, washed with diethyl ether, and crystallized from bidistilled water. Kinetically tested solutions were kept under N_2 and checked for Fe(II) oxidation state from time to time by treating the solutions with peroxodisulphate and hydroxylamine hydrochloride to ensure that they were oxidizable and not reducible, respectively. The composition of the complexes was characterized by CHN microanalyses, IR and UV-visible spectra, thermal analyses, and magnetic and conductance measurements. The UV and visible spectra's and all kinetic runs' data are summarized in Table 1 and were recorded on a Cecil CE 599 automatic scanning spectrophotometer connected with a CE 836 cell and wavelength program control using 1 cm matched stoppered silica cells. Infrared spectra of all complexes and their corresponding ligands were monitored on a Shimadzu FTIR-8101 Fourier Transform Infrared spectrophotometer. Conductance measurements were carried out by using a Pye conductance bridge at different temperatures using a Haak F3 ultrathermostate for temperature control within ±0.2°C. All complexes gave satisfactory CHN microanalyses which were in agreement with the presence of two coordination and crystal water molecules, confirmed by thermal analysis [11]. The authenticity of the complexes was checked spectrophotometrically, *cf.* Table 2, by confirming that the kinetics were exactly first order up to 90% of the complete reaction, and that the obtained rate constants agreed well with the reported values in parallel reactions.

The kinetic measurements were executed under pseudo-first order conditions in [complex] in the presence of large excess of H_2O_2, by following the decay with time (t) in absorbance (A) at λ_{max}, the absorption maximum of each complex, and there was no interference from any other reagents at this wavelength (Fig. 1). Total ionic strength was maintained at $0.1\,\mathrm{mol\,dm^{-3}}$ with inert KNO_3, *pH* of the medium kept by using *Britton* universal Buffer (within the stability range of the investigated complexes (≈1.5–3). The different hydrophobic salts, KBr, *TBAB*, *TEAB*, and *TMAB* have been used in different concentrations.

The pseudo-first order rate constants were computed by means of a least-mean squares program from the slopes of the first order $\ln A/t$ plots and reported in Table 1.

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