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Reactions of polyhomofunctional organic compounds: 5: Kinetics of N-oxide-N-hydroxide tautomerism in a novel class of triazine-1-oxides

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Triazine-1-oxides are one among the well known classes of fungicides. Abundant reports are available on the functionality of these compounds. These compounds are feared because of their certain impact as they are among the most potent carcinogens in existence. The coordination chemistry of triazine-1-oxides has been well reported. It has been well argued that the monofunctional analogues of the triazine-1-oxides engage in tautomerism. The metabolic conversion of these compounds into safe products assume greater importance from agricultural and medicinal points of view and hence the hydrolysis of these compounds is of still greater importance. Herein, is reported the kinetics of hydrolysis of two isochemical triazine-1-oxide sites of a series of 3,3'-disubstituted 4,4'-bis(3-alkyltriazine-3-oxide)biphenyls (**1**) abbreviated as R-triaz-bp-X investigated at different concentrations of acids and at different temperatures. The studies reveal that the two triazine-1-oxide sites undergo N-oxide-N-hydroxyde tautomerism which is first order in [R-triaz-bp-X] and no dissociation at any of the reaction sites has been identified. Linear regression best fits of the kinetic plots are used to determine the rate constants of the reactions. The activation energy values and other thermodynamic parameters of the hydrolysis of R-triaz-bp-X have been evaluated by Arrhenius plots and Eyring equation.

Keywords: Triazine-1-oxides, Fungicides, Hydrolysis, Tautomerism, Isosbesticity, Thermodynamic parameters

Triazine-1-oxides are known to be important class of fungicides[1-3]. As per reports, these are feared as potential carcinogens. Because of its carcinogenic impact, studies of their stability and structural identity in aqueous medium and the metabolic conversion in to safe products assume greater importance from agricultural and medicinal points of view. Sufficient reports on the hydrolytic fragmentation of mono functional or bi functional triazine-1-oxide organic compounds are not available and hence there is no well suggested mechanisms so far for their hydrolytic path ways. However, the coordination chemistry of triazine-1-oxides has been well reported and the mono functional analogues of certain triazine-1-oxides were earlier debated to be engaged in a tautomerism[7,8]. We, as a part of our kinetic studies of polyhomofunctional organic compounds, chose to study the kinetics of hydrolysis / structural reorganisation of a series 3,3′-disubstituted 4,4′-bis(3-alkyltriazine-3-oxide)-biphenyl (**1**) which contains two triazine-1-oxide moieties at the 4,4′ positions of a biphenyl. These compounds are here after denoted as R-triaz-bp-X. By appropriately altering R and X, a good number of members of R-traiz-bp-X could be realised. The coordination chemistry of these compounds reveal that even though there is a large separation between the two Cu (II) sites in the Cu_2L_2 complexes of these ligands (where LH_2 is R-triaz-bp-X), they involve in a weak anti-ferromagnetic interaction through the σ bond chain. The intramolecular interaction through the more labile π- bonds was ruled out on the basis of large dihedral angle between the benzene rings of R-traiz-bp-X[9]. The chloroform and acetone solutions of R-traiz-bp-X are very stable as evident from the UV-Vis electronic spectral integrity over a standing period of more than one month. However, an addition of even a minute quantity of mineral acid induces structural reorganisation of the molecules of R-traiz-bp-X. Further, it is found that the structural reorganisation of the molecules of R-traiz-bp-X is not in the same lines as in the case of it's mono analogous. On these considerations, it can be expected that the rate constants of processes occurring at two or more any iso functional sites might also be disproportionated with respect to those of their mono functional analogue[10-12]. We report herein the

results of kinetics of electronic conversion of a series 3,3′-disubstituted 4,4′-bis(3-alkyltriazine-3-oxide)biphenyl (**1**).

Experimental Section

Materials and Methods

The biphenyl bridged triazine-1-oxides were synthesized on the basis of detailed procedures available in the literature[7]. The procedure for the synthesis of a typical biphenyl bridged triazine-1-oxide is given here. O-dianisidine (AR grade) was recrystallised from methanol. 10 m moles of recrystallised O-dianisidine were taken in a 100 mL beaker and was made into paste by wetting with water. 2.2 mL of con. HCl were added to this. Further, addition of 25 mL of water rendered with diamine-dihydrochloride result in a homogeneous, brownish solution. The contents were cooled and to this was added 20 mL of cold solution containing 20 m moles sodium nitrite solution in two or three portions while maintaining temperature in the range of 5 – 10°C. Then 20 m moles of N-methylhydroxylamine hydrocloride in 25 mL of water was added drop wise. The contents were immediately buffered by 30 mL of 0.1 M sodium acetate. A brown coloured precipitate separated out slowly was filtered, dried and recrystallised from acetone. The same procedure was followed for the other triazine-1-oxides by taking other biphenyl bridged primary amine and N-alkyl hydroxyl amine. The obtained trizine-1-oxides were recrystallised in acetone- water mixture (70:30 v/v). The determined melting point was in agreement with the data available in the literature[5,7].

All the buffers and other solutions were prepared by standard methods using AR grade reagents[13]. Orion Research Expandable Ion Analyser Model EA 940 was used for measuring the *p*H of the buffers and the reaction mixtures whereas a Shimadzu Model UV 160A Spectrophotometer possessing a wavelength range of 1100 – 200 nm was used for spectral monitoring and kinetic studies. An INSREF model cryostatic circulating water-bath of Instrumentation & Refrigeration of India, Madras with a proportional temperature control device (± 1.0°C) was used to thermostat the double – walled cuvette holder of the spectrophotometer. Computer graphics software were extensively used for calculations, curve fitting and development of three dimensional structures.

The reaction mixtures were prepared every time by a quick mixing of 1 mL of the thermostatted acetone solution of **1** with 9 mL of the thermostatted HCl in different concentrations. An aliquot of this mixture was immediately transferred into the cuvette and the absorbance of the solution was monitored at 355 nm (λ_{max}) while employing the "Photomeric Mode" of the spectrophotometer at regular time intervals. The reagent blank was used as the reference during the studies. The time *vs*. absorbance data output were corrected for the delay in the mixing and measurement before the kinetic calculations.

Results and Discussion

Resonance Isomerisation in triazine-1-oxides

The structure of 3,3'-disubstituted 4,4'-bis(3-alkyltriazine-3-oxide)biphenyls (**1**) abbreviated as R-triaz-bp-X is shown in structure 1 (Fig. 1).

The conformational analysis of triazine-1-oxides have been developed by energy minimisation through Serina Software PCMODEL for Windows. The data reveal that dihedral angle between the two benzene rings is dependent on the substituent, X and also on the nature of R[9].

The chloroform and acetone solutions of R-traiz-bp-X are very stable as evident from the UV-Vis electronic spectral integrity over a standing period of more than one month. However, the addition of even a minute quantity of mineral acid induces structural reorganisation of the molecules of R-traiz-bp-X. The successive spectra of an acetone solution of CH_3-traiz-bp-OCH_3, as a representative case at room temperature when mixed to an aqueous HCl solution is shown in Fig. 2. From this figure, it is clear that the intensity of the spectral band at ~355 nm gradually falls whereas that of a new one at ~ 425 nm increases. The gradual red shift of the electronic spectral transition continues till reaching an equilibrium. The

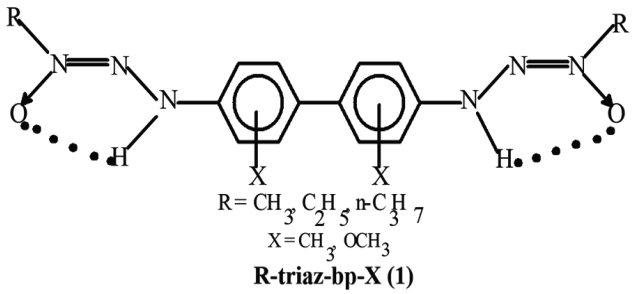


Fig. 1 — Structure of 3,3'-disubstituted 4,4'-bis(3-alkyltriazine-3-oxide)biphenyls (**1**)

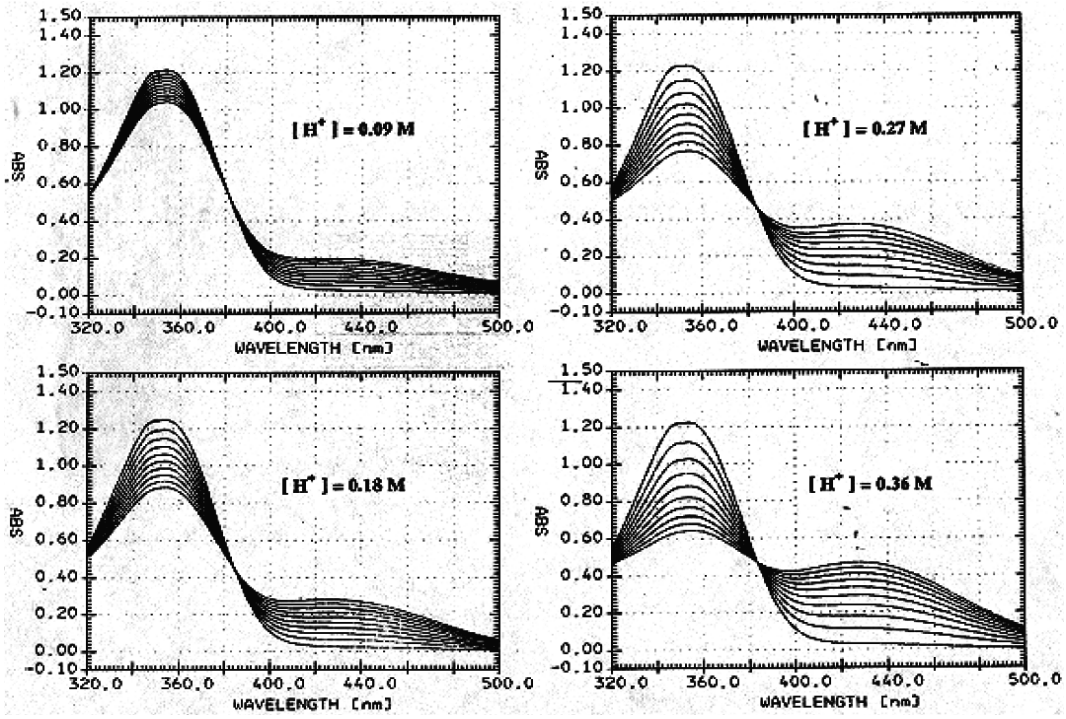


Fig. 2 — Successive spectral profiles of CH_3-triaz-bp-OCH_3 at 30°C (Time interval 2 min)

original λ_{max} along with the red - shifted ones are presented in Table 1 from which it is clear that the λ_{max} of various R-traiz-bp-X are vary with R and X. Table 1 also reflects the corresponding and respective differences of original and kinetically red - shifted λ_{max}. The $\Delta\lambda$ and the $\Delta\nu$ values are nearly uniform. This feature is also shown through a 3-d graphical representation in Fig. 3. These observations suggest that the R-triaz-bp-X might not be undergoing any drastic structural cleavage but only a minor structural reorganisation away from any major influence of R and X. Interestingly, the red shift is reversed upon addition of a base to the reaction mixture after equilibrium. This is an additional indication that the molecular skeleton is intact through the course of the reaction.

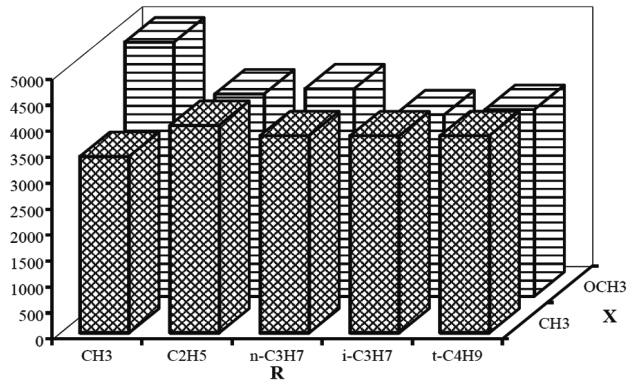


Fig. 3 — 3-d representation of R an X effects on the spectral variation of R-triaz-bp-X

Kinetics of Resonance Isomerisation in triazine-1-oxides

The kinetics of the resonance isomerisation of R-triaz-bp-X have been carried out in different concentrations of HCl. Interestingly, intensity of the spectral band at ~355 nm gradually falls whereas that of a new one at ~ 425 nm increases. Typically, the absorbance (A_t) *vs*. time plots for CH_3-traiz-bp-OCH_3 (as a representative case) at the two wavelengths in the presence of a 0.18 N HCl are shown in

Table 1 — The Spectral variations R-triaz-bp-X upon HCl addition

R-triaz-bp-X	λ_{max} [nm ($_v$ cm^{-1})] (reactant peak)	λ_{max} [nm ($_v$ cm^{-1})] (product peak)	$\Delta\lambda$ (nm) ($\Delta\nu$ cm^{-1})
CH_3-triaz-bp-OCH_3	355 (28200)	430 (23300)	75 (4900)
CH_3-triaz-bp-CH_3	363 (28200)	415 (23300)	52 (4150)
C_2H_5-triaz-bp-OCH_3	373 (27000)	433 (23100)	60 (3900)
C_2H_5-triaz-bp-CH_3	365 (27400)	428 (23400)	63 (4000)
C_3H_7-triaz-bp-OCH_3	372 (27000)	435 (23000)	53 (4000)
C_3H_7-triaz-bp-CH_3	375 (26600)	438 (22800)	63 (3800)
C_3H_7-triaz-bp-OCH_3	375 (26600)	433 (23100)	58 (3500)
C_3H_7-triaz-bp-CH_3	374 (26700)	434 (23000)	60 (3700)
C_4H_9-triaz-bp-OCH_3	371(26900)	430 (23300)	59 (3600)
C_4H_9-triaz-bp-CH_3	373 (26800)	434 (23000)	61(3800)

Fig. 4. It is clear from this figure that the two profiles are nearly mirror images to each other. It suggests an equimolar stoichiometry for the reactant and the reaction product, with comparable molar extinction coefficients. Further, there is a well defined isosbestic point in the repetitive spectral profiles of the compound supporting the equimolar stoichiometry and presence of only two absorbing species in the solution throughout the course of the reaction. The log (A_t - A_{inf}) or log (A_{inf} - A_t) *vs*. time plots for the absorbances at both 355 nm and 425 nm are shown in Fig. 5 for CH_3-traiz-bp-OCH_3. The data were taken till the absorbance at 355 nm fell to less than 25% of the initial absorbance. The data of Fig. 5 indicate a straight line with a linear regression coefficient of 0.987. These results suggest that R-traiz-bp-X undergo a pseudo first-order chemical transformation. This fact is in alliance with the above assumption that the reaction is a simple electronic isomerisation but does not involve any fragmentation. This fact is in alliance with the above assumption that the reaction is a simple electronic isomerisation but does not involve any fragmentation.

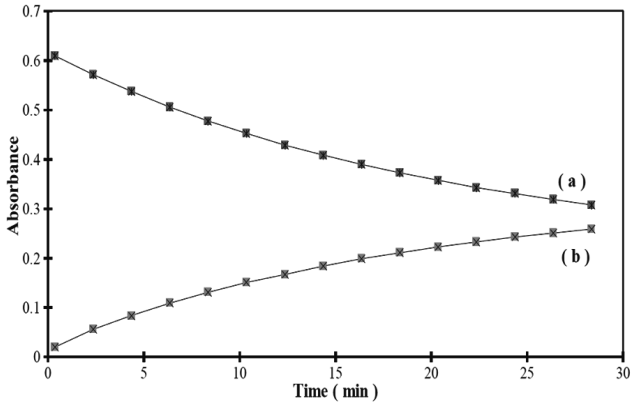


Fig. 4 — Absorbance change of CH_3-triaz-bp-OCH_3 at 30°C in 0.18 N HCl solution with time: (a) at 355 nm, (b) 425 nm

From the studies, it is clear that the triazine-1-oxide site alone is vulnerable for chemical changes in the mild reaction conditions. If the molecule

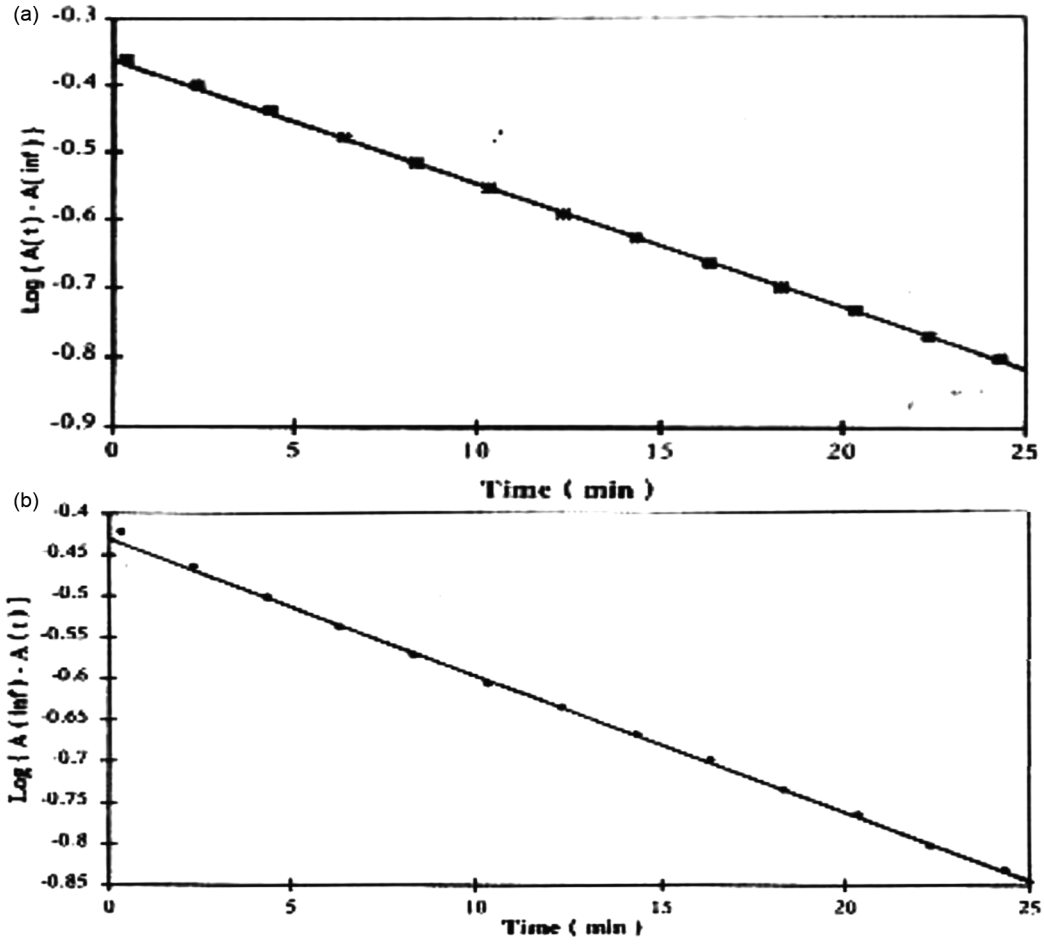
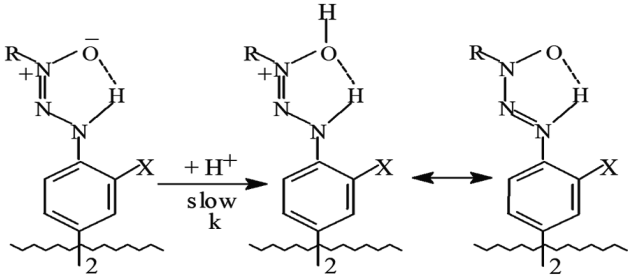


Fig. 5 — Hydrolysis of CH_3-triaz-bp-OCH_3 $C_0 = 1.8\times10^{-5}$ M in 0.18 N HCl solution at 30°C: (a) at 355 nm, (b) at 425 nm: Data fitting to pseudo-first order kinetics

undergoes hydrolysis as do the amides and Schiff bases reports submitted earlier[11,12,14], the products might include a 3,3′-di (X) substituted-4,4′-diaminobiphenyl and a nitro alkane besides nitrogen. Usually, dissociation of triazines is irreversible due to the formation of one or more gaseous products. However, the present studies indicate a very good reversibility upon addition of the base. Further, the event involves a red shift. We tentatively suggest that R-traiz-bp-X undergo a slow isomerization resulting in the red shift of electronic transition, instead of molecular dissociation.

We suggest the development of extended conjugation beyond the benzene ring in R-traiz-bp-X molecules upon acidification is responsible for the red shift[15,16]. The tautomeric mechanism is schematically presented in Scheme 1. The oxygen of the N-oxide is more basic than any of the other three nitrogens in each triazine-1-oxide group because of the negative charge on the oxygen. Hence, acidification of R-traiz-bp-X, initially renders one of the two triazine-1-oxides protonated at the N-oxide site's oxygen. This would induce an electronic reorganisation resulting in an N-oxide to N-hydroxide kind of tautomerism which renders an extended conjugation. The 425 nm absorption band is due to this product. Further, support for this idea comes from the very synthetic details of R-taiz-bp-X. The tetrazotised 4,4′-diaminobiphenyl (*i.e*., any of *o*-Tolidine, *o*-Dianisidine) is condensed with N-alkyl-hydroxylamines (RNHOH) in the presence of sodium acetate buffers. The reactant RNHOH has N-hydroxyl chemistry while its initial condensation to the tetrazotised diaminobiphenyl, is through the very quick reaction shown in Scheme 2. The immediate product *i.e*., the N-hydroxyl compound existing in initial acid environment quickly undergoes tautomerism when buffered by sodium acetate due to elevation of *p*H, as shown in Scheme 3. The final product is devoid of extended conjugation whereas the initial N-hydroxyl product is featured with one.

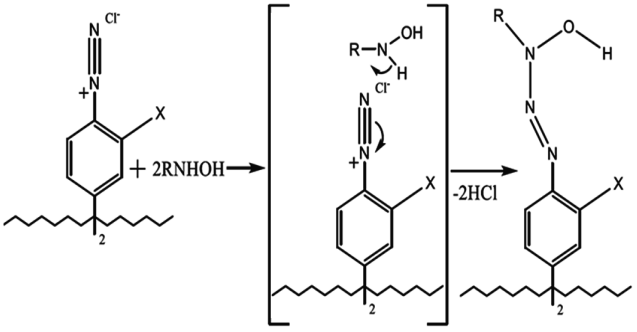


Scheme 1 — The N-oxide - N-hydroxyde tautomerism in R-triaz-bp-X

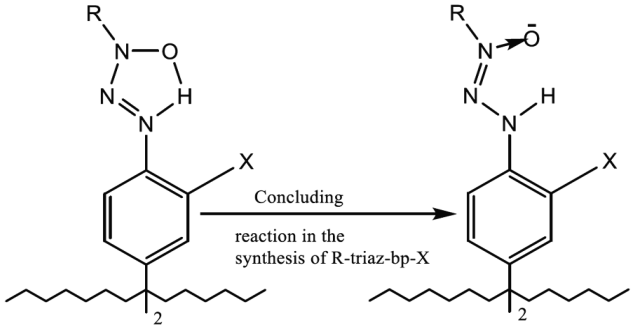
Incidentally, the reaction mixture before addition of sodium acetate buffer is deep red in colour which is due to the presence of large amounts of N-hydroxyl form of the product in that highly acidic environment. Hence, it can be viewed as if the R-triaz-bp-X exists in hydroxyl form in acid medium and that the present acid-catalysed reaction is a "home-coming for R-triaz-bp-X".

In order to know the order of the proton in this acid-catalysed tautomerism, we undertook the studies of this reaction at varied concentrations of H^+ ion. The rate constants obtained for the electronic isomerisation of CH_3-triaz-bp-OCH_3 are collected in Table 2. In Fig. 6, log k *vs*. [H^+] plot for a representative compound, CH_3-triaz-bp-OCH_3 where the slope is observed to be 2.1 with a regression coefficient of 0.987 is shown. Hence, the order with respect to the H^+ ion is 2 and this value is in agreement with the mechanism proposed in Scheme 2 and Scheme 3.

Further, the two traizine-1-oxide sites are chemically indistinguishable and since the two functional groups are largely separated with hardly and possibility of intramolecular interaction, the two sites undergo near simultaneous protan-catalysed tautomerism.



Scheme 2 — Mechanism of initial formation of N-hydroxyl compound



Scheme 3 — Final tautomeric conversion of N-hydroxyl compound to N-oxide

Table 2 — Pseudo-first order rate constant at 30°C

	K×103 s–1			
R-triaz-bp-X	[H+] = 0.09 M	[H+] = 0.18 M	[H+] = 0.27 M	[H+] = 0.36 M
CH3-triaz-bp-OCH3	3.01	6.99	11.00	21.59
CH3-triaz-bp-CH3	3.07	7.15	11.54	21.87
C2H5-triaz-bp-OCH3	3.15	7.23	11.45	22.02
C2H5-triaz-bp-CH3	3.23	7.34	11.65	22.11
n-C3H7-triaz-bp-OCH3	3.42	7.56	11.74	22.47
7.89 n-C3H7-triaz-bp-CH3	3.65	7.89	11.97	22.68
i-C3H7-triaz-bp-OCH3	3.78	8.02	12.23	22.97
i-C3H7-triaz-bp-CH3	4.21	8.78	12.99	23.56
t-C4H9-triaz-bp-OCH3	4.15	8.64	12.87	23.34
t-C4H9-triaz-bp-CH3	4.28	8.97	13.24	24.02

Table 3 — Thermodynamic data [p] of the hydrolysis of EDA-Sal

Acid Concentration	Ea	ΔH#	–ΔS# q	ΔG#
0.09	19.84	17.32	0.255	94.62
0.18	19.35	16.83	0.246	91.41
0.27	18.11	15.60	0.244	91.08

p, kJ mol–1, q, kJ mol–1K–1

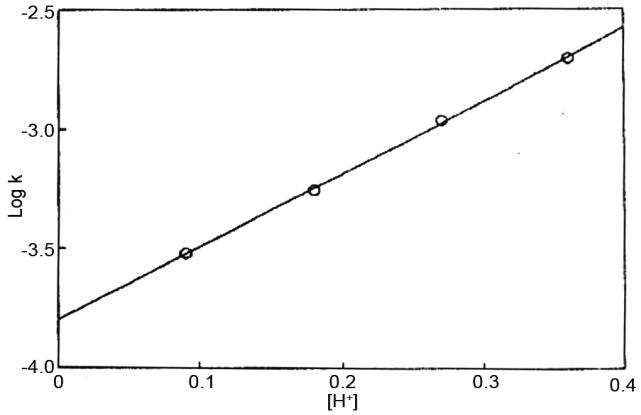


Fig. 6 — Effect of [H^+] on the pseudo-rate constant of the isomerisation of CH_3-triaz-bp-OCH_3 at 30°C

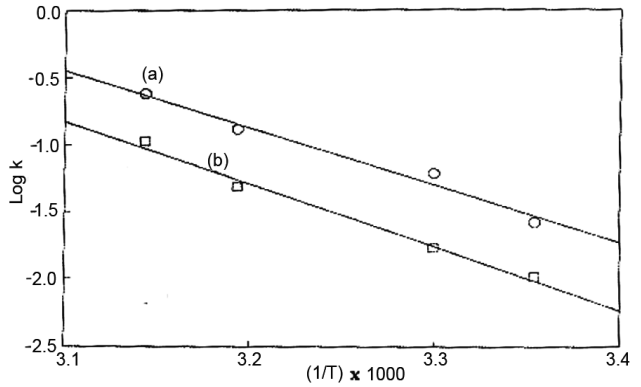


Fig. 7 — Arrhenius plots of the isomerisation of CH_3-triaz-bp-OCH_3 at 30°C: (a) [H^+] = 0.27 M, (b) [H^+] = 0.09 M

Effect of Temperature

The effect of temperature on the electronic summarization of R-triaz-bp-X have also been investigated[17,18]. These temperature dependent kinetic studies gave excellent straight line for log k *vs*. 1 / T plots as shown in Fig. 7, as a representative case for CH_3-triaz-bp-OCH_3. The activation energy values calculated from these graphs are presented in Table 3. These values are comparable to those of the energy barrier in the conformational analysis of rotational energy at 1,1′- position of a biphenyl. The other thermodynamic parameters such as $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ for CH_3-triaz-bp-OCH_3 have also been evaluated by means of Eyring equation and these are accompanied with the activation energy values in Table 3.

Conclusions

The present study involved the verification of kinetics of hydrolysis of two isochemical triazine-1-oxide sites of a series of 3,3'-disubstituted 4,4'-bis(3-alkyltriazine-3-oxide) biphenyls abbreviated as R-triaz-bp-X.

The invetigations carriedout at different concentrations of acids and at different temperatures to check their impact if any. The investigations indicated typical bathochromic shift of triazine-1-oxide chromophore.

The studies suggest that the reaction is not hydrolysis but an acid-catalysed tautomerism between N-oxide and N-hydroxide forms of triazine-1-oxide groups and it follows pseudo first- order chemical transformation

Valid reasons for variation in the rate of reactions were discussed which also includes the influence of *p*H. Temperature, *etc*. Most suitable mechanisms are suggested. Pseudo first order rate constants, activation

energy E_a and other thermodynamic parameters such as $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ were evaluated.

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