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SPECTROPHOTOMETRIC DETERMINATION OF DISSOCIATION QUOTIENTS OF TRIAZENE – N^1 – OXIDES AND THE EFFECT OF SUBSTITUENTS ON pKa VALUES

ASHOK KUMAR AND GALAL M ZAIAD

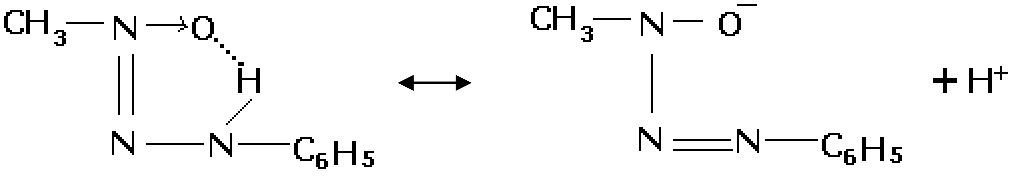
Department of Chemistry, Al-Mergheb University, Al-Khoms, LIBYA

Abstract- **Determination of dissociation quotients of thirty two substituted triazene-N^1-oxides has been done spectrophotometrically. The effect of different substituents present at both the ends of triazene-N^1-oxide moiety upon their pKa values has been studied and discussed. A comparision of pKa values of N^3- (aryl/ substituted aryl) – N^1- alkyl-triazene-N^1-oxides with N^3-(aryl/substituted aryl)-N^1-(aryl/substituted aryl)- triazene-N^1-oxides reveals that the presence of one more aromatic ring at N^1-end in the latter type of compounds decreases the pKa values due to the – I effect of the aryl ring.**

Index Terms—**Dissociation quotients, Triazene-N^1-oxides**

I. INTRODUCTION

Different workers[1-11] have reported different values of pKa, using the Robinson,s spectrophotometric method. Dissociation quotients for a large number of triazenes have reported and effect of substitution on pKa values discussed[1,6,7]. Triazene-N^1-oxides are very weak acids. The conventional and potentiometric methods can not be employed for determining their dissociation quotients. However, these compounds show a distinct colour change in acid and alkaline media. Ultraviolet absorption studies of these compounds have been made. The absorption maximum at 307 nm of N^3-phenyl-N^1-alkyl-triazene-N^1-oxides shifts to 337 nm in an alkaline solution. The following equilibrium possibly exists :



(absorption peak at 307 nm) (absorption peak at 337 nm)

This change in absorption maximum with pH has been used in determining the dissociation quotients of thirty two triazene- N^1 – oxides employing spectrophotometric methods.

<u>Outline of the method</u>: In acidic medium it is assumed that all triazene- N^1 – oxides are present in molecular form. With an increase of pH, it ionizes and finally at pH 14 it is completely in anion form. Hence it is reasonable to assume that the absorption peak at 307 nm is due to the unchanged molecule of N^3-phenyl- N^1- methyl – triazene – N^1- oxide and the peak at 337 nm is due to the anionic form (Table – 1).

The ideal analytical wave length for determining the dissociation quotients is that at which one species absorbs strongly and the other has no absorbance at all[12], but this condition is rarely met and hence wave length at which a big difference in optical density between the two species ‘ molecular and ionized’ of a compound is observed may be used for the determination of the dissociation quotients. The dissociation quotients of N^3-phenyl-N^1-methyl-triazene-N^1-oxide has been determined at 337 nm where the anion form shows a maximum and the molecular form also has appreciable absorption and also at 307 nm where the anion form has still appreciable absorption and the molecular form has negligible absorption . The values of dissociation quotients determined at the two wavelengths are particularly the same (Table 1) . Hence, the dissociation quotients of remaining compounds were determined at wave lengths at which the big difference in optical density between two species is obtained.

The pKa value, thus, calculated with the help of the following Stenstrom and Goldsmith[13] equation:

$$pKa = -\log (A - Aa / Ab - A)$$

Where, A is the absorbance in a buffer solution of intermediate pH at which the compound is present as anion, Aa is absorbance of the compound in acidic solution where all of it is present as molecular form, Ab is the absorbance in alkaline solution where all of it is present as anion form.

II. EXPERIMENTAL

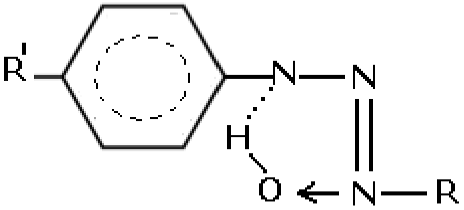
Absorbance measurements were made with a Beckmann Quartz Spectrophotometer model DU, using 1cm silica cells. All the triazene-N^1-oxides were prepared by the method given by Kumar et al[14]. Weighed amounts of these compounds were dissolved in dioxane to give 2 x 10^{-3}M solutions. Stock solution of 2 M $NaClO_4$ and 2 M NaOH were prepared and used for maintaining the constant ionic strength and for adjusting different pH values, respectively.

Procedure: A series of solutions containing varying amounts of sodium hydroxide and 2.5 ml of sodium per chlorate was prepared in 50 ml volumetric flasks so that pH of the final solution ranged from 5 to 14 and the ionic concentration was 0.1 M. They were suspended in thermostat kept at 25°C. In each of these solution 1ml of 2 x 10^{-3} M solution of triazene-N^1-oxide (freshly prepared in dioxane) was added with a pipette, the solution diluted to the mark and mixed. Absorbance was measured immediately after mixing at the wave length at which the big difference in optical density between molecular and ionized form of the compound is obtained.

The results, thus, obtained for different triazene-N^1-oxides are given in Table-2. The experimental error is ± 0.02.

III. DISCUSSION

Triazene-N^1-oxides are weak acids, although on general grounds they would be expected to be stronger acids than phenol. The dissociation of these compounds are depends upon the nature of the substituent present at the nitrogen 1 and 3. The suppression of acid character may be attributed to the intra molecular hydrogen bonded form (**I**) in which these compounds possibly exists.



(**I**)

Any substituent which has tendency to weaken the hydrogen bond increases its acid character.

An inspection of data presented in Table 2 shows that there is an increase in pKa value, when the aryl substituent at nitrogen-1 is replaced by alkyl groups ($-CH_3$, $-C_2H_5$, or n –) . This is due to +I effect (electron repelling) of the alkyl groups . In methyl substituted compounds hyper-conjugative effect would exert a similar effect . This is in the order, $n-C_3H_7 > -C_2H_5 > -CH_3$.

Substitution of alkoxy ($-OCH_3$ or $-OC_2H_5$) group in aryl nucleus attached to nitrogen-3 ($R^1 = -OCH_3$, $- OC_2H_5$) causes a corresponding increase in pKa values presumably due to the +M effect of the substituent, which is in the order $-OC_2H_5 > -OCH_3$. The chloro substituted compounds (R^1 = Cl or R = 4-$Cl.C_6H_4$) are more acidic than the corresponding parent compound.

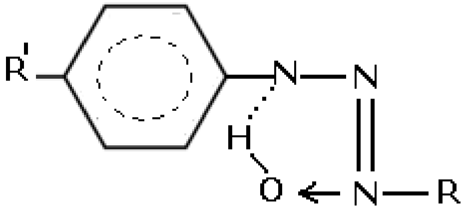
This shows that +M effect of chlorine is not in operation in these compounds. In that case acidity should have decreased. Thus, - I effect of chlorine effects the dissociation of these compounds increasing their acidic character. In the case of carboxy (-COOH) substituted compounds (R = 4- $COOH.C_6H_4$ or R^1 =-COOH) the pKa is low and has a strong acid character is due to the –M effect of this group. The high pka value in sulphonamido ($-SO_2NH_2$) substituted compounds is presumably due to the strong + I effect.

Table – 1: Dissociation quotients of N^3-phenyl- N^1-methyl-triazene-N^1-oxide.

Ionic strength : 0.1M (2M $NaClO_4$) ; Temperature : 25°C

Wave length 307 nm			Wave length 350 nm		
pH	**Absorbance**	**pKa**	**pH**	**Absorbance**	**pKa**
5.00	0.145(Aa)	--	5.00	0.020(Aa)	--
14.00	0.575(Ab)	--	14.00	0.225(Ab)	--
11.56	0.230	12.15	11.50	0.060	12.06
11.60	0.245	12.07	11.85	0.085	12.13
11.84	0.290	12.12	11.90	0.095	12.13
11.96	0.315	12.13	12.00	0.105	12.10
12.06	0.340	12.08	12.15	0.120	12.13
12.54	0.445	12.15	12.20	0.130	12.12
12.65	0.465	12.13	12.35	0.145	12.15
Average :		12.13	**Average** :		12.12

Table – 2 : Dissociation quotients of N^3-(aryl/ substituted aryl) –N^1- (alkyl/aryl/substituted aryl)- triazene-N^1-oxides.



Compound			Compound		
R	**R^1**	**pKa**	**R**	**R^1**	**pKa**
- CH_3	H	12.12	4-Cl.C_6H_4	- Cl	10.55
n-C_3H_7	H	12.39	4-CH_3.C_6H_4	-Cl	11.16
-C_6H_5	H	11.41	-CH_3	-SO_2NH_2	12.62
4-COOH.C_6H_4	H	10.61	-C_2H_5	-SO_2NH_2	12.82
-CH_3	-OC_2H_5	12.72	n-C_3H_7	-SO_2NH_2	13.01
-C_2H_5	-OC_2H_5	12.87	-C_6H_5	-SO_2NH_2	12.05
n-C_3H_7	-OC_2H_5	13.01	4-COOH.C_6H_5	-SO_2NH_2	11.25
-C_6H_5	-OC_2H_5	11.99	4-CH_3.C_6H_4	-SO_2NH_2	12.50
-CH_3	-NO_2	12.34	-CH_3	-$COOC_2H_5$	12.12
-C_2H_5	-NO_2	12.51	-C_2H_5	-$COOC_2H_5$	12.26
n-C_3H_7	-NO_2	12.63	n-C_3H_7	-$COOC_2H_5$	12.35
-C_6H_5	-NO_2	11.65	4-CH_3.C_6H_4	-$COOC_2H_5$	11.92
-CH_3	-Cl	11.52	-CH_3	-COOH	11.67
-C_2H_5	-Cl	11.65	-C_2H_5	-COOH	11.89
n-C_3H_7	-Cl	11.74	-CH_3	-CH_3	12.58
-C_6H_5	-Cl	10.72	-C_6H_5	-OCH_3	11.95

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