Spectrophotometric Determination of Ionisation Quotients of Hydroxytriazenes and the Effect of Substituents on $p K_a$ Values

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Hydroxytriazenes are very weak acids. The conventional potentiometric and conductometric method cannot be employed for determining their ionisation constants. However, these compounds show a distinct colour change in acid and alkaline media. Ultra-violet absorption studies of these compounds have been made. The absorption maximum at 305 m$\mu$ of 3-hydroxy-3-methyl-1 phenyltriazene shifts to 335 m$\mu$ in an alkaline solution. The following equilibrium possibly exists:

\[
\begin{align*}
\text{CH}_3\text{N}^-\text{O}^- \text{CH}_3 \quad & \text{CH}_3\text{N}^-\text{O}^- \text{CH}_3 \\
\text{(molecular form, absorption)} & \text{(anion form, absorption)} \\
\text{peak at 305 m} & \mu \quad \text{peak at 335 m} \\
\end{align*}
\]

This change in absorption maximum with $pH$ has been used in determining the ionisation constants of fourteen hydroxytriazenes employing Robinson's spectrophotometric method.

Recently the ionisation constants of fourteen different hydroxytriazenes with different groups at different positions of the aryl nuclei of 3-hydroxy-1,3-di-phenyltriazenes have been reported from this laboratory. This work has been extended and the effect of replacing the phenyl group at position 3 in the above compound with a methyl, ethyl or propyl group and the effect of substituting -CH$_3$, -OCH$_3$, and -Cl group in the phenyl group at position 1 upon the ionisation constants of the resulting hydroxytriazenes have been studied.

**Outline of the Method:** In an acid medium, it is assumed that the hydroxytriazene is all present in the molecular form and that at $pH$ 14 it is all in the ionic form. The absorbance measurements are usually made at a wave length where the anion form exhibits its maximum absorption. 3-Hydroxy-3-methyl-1-phenyltriazene has its maximum in alkaline media at 335 m$\mu$, where the molecular form also has an appreciable absorbance. However, at 370 m$\mu$ the molecular form has negligible absorbance but the anion form still has appreciable absorbance (see Fig. 1). Hence 370 m$\mu$ was considered a suitable wave length. The ionisation constant of the above compound was determined from the ab-

1 S. M. Dugar, Ph. D. Thesis, University of Rajasthan, Jaipur (India), 1964.
Wave length 335 mμ Wave length 370 mμ

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<td>(Ab)</td>
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<tr>
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<td>Average: 12.11</td>
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</table>

Table 1. Ionisation quotient of 3-hydroxy-3-methyl-1-phenyltriazene. Ionic strength 0.1 M KCl, Temperature 25°.

all present in anion form, and A is the absorbance in a buffer solution of intermediate pH, where a fraction of the triazene is present as anion.

Experimental

Solutions: Hydroxytriazenes are prepared by the method given by GUPTA and SOGANI. Weighed amounts of these compounds were dissolved in dioxan to give 2·10⁻³ M solutions; 1 M potassium chloride and 2 N sodium hydroxide were used for maintaining ionic concentration and for adjusting different pH values, respectively.

Apparatus: Absorbance measurements were made with a Beckmann Quartz Spectrophotometer, model DU, and 1 cm Quartz cells. pH measurements were done with a Cambridge bench type pH meter.

R-N=O

Comparison of pKa values of 3-hydroxy-1,3-diphenyltriazenes and -3-hydroxy-3-alkyl-1-phenyltriazene

Purohit and Soganı reported the pKa value of 3-hydroxy-1,3-diphenyltriazene as 11.41 and that of 3-hydroxy-3-methyl-1-phenyltriazene as 12.11. This increase in the pKa value of the latter compound is possibly due to the change from the -I effect of the aryl group in the former compound, to the +I effect of the methyl group. The pKa values of 3-hydroxy-3-methyl-1-phenyltriazene, 3-hydroxy-3-ethyl-1-phenyltriazene, and 3-hydroxy-3-propyl-1-phenyltriazene are 12.11, 12.28, and 12.39 respectively. This corresponds to the increasing +I effect, which is in the order: methyl < ethyl < propyl.

Effect of Substitution on pKa values

Hydroxytriazenes have been assigned intramolecular hydrogen bonded structure and any substituent which has a tendency to weaken the hydrogen bonding will increase its acid character. Thus, nature and position of the substituent in the benzene ring of hydroxytriazene molecule (I) greatly influences the ionisation of these compounds.
A comparison of the $pK_a$ values of the methyl substituted hydroxytriazenes (Table 2) with the corresponding parent compounds reveals that a methyl group in *para* position in the benzene ring increases the $pK_a$ value ($I$, $R=R'=\text{CH}_3$, and $R''=\text{H}$, $\Delta pK_a=0.41$; $I$, $R=C_2\text{H}_5$, $R'=\text{CH}_3$, and $R''=\text{H}$, $\Delta pK_a=0.39$; and $I$, $R=C_3\text{H}_7$, $R'=\text{CH}_3$, and $R''=\text{H}$, $\Delta pK_a=0.40$). This is due to the $+1$ effect of the methyl group. A hyperconjugative effect from the methyl group would have a similar influence. The methyl group substituted in *ortho* position in the benzene ring ($I$, $R=R''=\text{CH}_3$, and $R'=\text{H}$, $\Delta pK_a=0.19$) should further decrease the acid character, due to the nearness of the $+1$ effect. However, the contrary is the case. The greater acidity of the *ortho* isomer, than the *para*-isomer, is due to the *ortho*-effect of the methyl group.

The suppression of acidic character due to the substitution of methoxy group in *para* position ($I$, $R=\text{CH}_3$, $R'=\text{OCH}_3$ and $R''=\text{H}$, $\Delta pK_a=0.58$; $I$, $R=C_2\text{H}_5$, $R'=\text{OCH}_3$, and $R''=\text{H}$, $\Delta pK_a=0.57$) is attributed to the $+M$ effect of the methoxy group.

The chloro substituted hydroxytriazenes are more acidic than the corresponding parent compounds. It appears, therefore, that the $+M$ effect of chlorine is not operative owing to the strong $+M$ effect of the $-\text{N}=$ group and it is only the $-I$ effect of the chlorine which affects the ionisation in hydroxytriazenes. The compounds with chlorosubstitution at *para* position of the benzene ring are less acidic than the compound with chloro substitution at *ortho* position ($I$, $R=\text{CH}_3$, $R'=\text{Cl}$, and $R''=\text{H}$, $pK_a=11.52$; $I$, $R=\text{CH}_3$, $R'=\text{H}$, and $R''=\text{Cl}$; $pK_a=11.31$; $I$, $R=C_2\text{H}_5$, $R'=\text{Cl}$, $R''=\text{H}$, $pK_a=11.65$; $I$, $R=C_2\text{H}_5$, $R'=\text{H}$, and $R''=\text{Cl}$, $pK_a=11.41$). The greater acidity of the *ortho* substituted chloro compounds, compared with the *para* substituted chloro compounds is due to the nearness of the $-I$ effect and also due to the inhibition of hydrogen bonding by virtue of the *ortho*-effect of the chlorine atom.

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