INTRAMOLECULAR HYDROGEN BONDING OF AZO DYES IN AQUEOUS SOLUTION*

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In 1963, Eigen and Kruse¹ used the Joule heating temperature-jump-relaxation method² to determine rate constants \( k_{23} \) for the reaction

\[
\begin{align*}
\text{N-O}_2^N &- R + \text{OH}^- \quad \rightarrow \quad \text{N-O}_2^N &- R + \text{H}_2\text{O} \\
\end{align*}
\]

in 0.1 \( M \) ionic strength aqueous solution at 12° for the following: 2,4-dihydroxy-4'-nitroazobenzene (I), 2,4-dihydroxy-4'-sulfonateazobenzene (II), and \( p \)-(2-hydroxy-1-naphthylazo)benzenesulfonic acid (III). The reported values of \( k_{23} \) were \( 4 \times 10^5 \), \( 3.6 \times 10^5 \), and \( 3.6 \times 10^6 \) M\(^{-1}\) sec\(^{-1} \). They attributed the much lower values of \( k_{23} \) for these acids than the value³ \( k_{23} \equiv 2 \times 10^9 \) M\(^{-1}\) sec\(^{-1} \) for the superficially similar reaction \( \text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O} \) to strong intramolecular hydrogen bonding in the protonated azo dyes that is absent in the hydrogen phosphate dianion. The greater electronegativity of the substituent \( -\text{NO}_2 \) in (I) than \( -\text{SO}_3 \) in (II) accounts qualitatively for a greater decrease in charge on the azo nitrogen of (I) with a necessarily weaker intramolecular hydrogen bond in (I) and consequent larger value of \( k_{23} \). These values of \( k_{23} \) for three azo dyes raise the question whether trends of \( pK_a M = -\log(a_{H^+}[A^{2-}]/[HA^-]) \) and \( k_{23} \) in a larger sample of azo dyes can be correlated with electrostatic effects of ring substituents on the electronegativity of the azo nitrogen atom that acts as a proton acceptor in the intramolecular hydrogen bond. Since resonance stabilization would promote a stable planar structure for the hydrogen bond about equally in all these azo dyes, this effect may be neglected.

Materials and Methods.—2,4-Dihydroxy-4'-nitroazobenzene (I), 2,4-dihydroxy-4'-sulfonateazobenzene (II), 4-(2-thiazolylazo)-resorcinol (IV), 6-methyl-4-(2-thiazolylazo)-resorcinol (V), and 4-(2-pyridylazo)-resorcinol (VI) were purchased from Aldrich Chemical Co., Inc., and 4-(m-nitrophenylazo)-resorcinol (VII) from Eastman Kodak Co. We
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synthesized 4-phenylazoresorcinol (VIII) from benzenediazonium chloride and resorcinol. The acids were recrystallized from water, and the mixed acid dissociation constants \( K_a^M \) of Table 1 were determined spectrophotometrically at 25º in 0.1 M ionic-strength aqueous solutions (adjusted with reagent grade KNO₃). The rate constants \( k_{3a'} \) in Table 1 were calculated from

\[
k_{3a'} = \frac{1}{\tau}([HA^-] + [OH^-] + \frac{K_w}{\gamma_H} K_a^M)^{-1}
\]

using experimental Joule heating temperature-jump relaxation times, \( \tau \), determined at 25º and 0.1 M ionic strength. The limits of experimental error in the values of \( k_{3a'} \) are of the order of ±20%. For instance, four independent rate measurements on compound VI yielded the following: total acid concentration \( c_0 = 1.0 \times 10^{-4} \) M, pH = 12.08, \( \tau = 39 \) μsec, \( k_{3a'} = 8.0 \times 10^6 \) M⁻¹ sec⁻¹; \( c_0 = 2.0 \times 10^{-4} \) M, pH = 12.21, \( \tau = 95 \) μsec, \( k_{3a'} = 6.9 \times 10^6 \) M⁻¹ sec⁻¹; and \( c_0 = 2.0 \times 10^{-4} \) M, pH = 10.73, \( \tau = 78 \) μsec, \( k_{3a'} = 7.1 \times 10^6 \)

**Table 1.** Spectrophotometric acid dissociation constants and temperature-jump relaxation-method rate constants for intramolecular hydrogen-bond breaking in a series of aqueous azo dyes.*

<table>
<thead>
<tr>
<th>Identifying no.</th>
<th>Formula of HA</th>
<th>( pK_a^M ) †</th>
<th>( k_{3a'} ) ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>O( ^{\cdot} )S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>9.67 ± 0.15</td>
<td>8.2 × 10⁶</td>
</tr>
<tr>
<td>V</td>
<td>S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>10.03 ± 0.10</td>
<td>2.0 × 10⁶</td>
</tr>
<tr>
<td>VII</td>
<td>S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>11.50 ± 0.04</td>
<td>2.6 × 10⁶</td>
</tr>
<tr>
<td>VIII</td>
<td>S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>11.67 ± 0.02</td>
<td>1.3 × 10⁷</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>( pK_a^M ) †</th>
<th>( k_{3a'} ) ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>11.95 ± 0.03</td>
<td>1.3 × 10⁶</td>
</tr>
<tr>
<td>VI</td>
<td>S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>12.01 ± 0.03</td>
<td>8.6 × 10⁶</td>
</tr>
<tr>
<td>VII</td>
<td>S( ^{\cdot} )N( ^{\cdot} )NO( ^{2-} )</td>
<td>12.16 ± 0.05</td>
<td>6.9 × 10⁶</td>
</tr>
</tbody>
</table>

* At 25ºC and 0.1 M ionic strength adjusted with KNO₃.
† \( pK_a^M = -\log_{10} K_a^M = -\log_{10} (a_H^+ [A^{2-}] /[HA^-]) \) determined spectrophotometrically.
‡ Rate constant for the reaction \( HA^{n-} + OH^- \rightarrow A^{(n+1)-} + H_2O \) calculated from equation (2) of the text and temperature-jump relaxation times.
$M^{-1}$ sec$^{-1}$. The average value of $k_{23}'$ for this acid is $6.9 \times 10^8 M^{-1}$ sec$^{-1}$ with standard deviation calculated from the range of $1.13 \times 10^8 M^{-1}$ sec$^{-1}$. [HA$^-$] represents the molar concentration of the protonated form of the azo dye, $K_w = 10^{-14.00}$, and $\gamma_{H^+} = 0.83$ is the Debye-Huckel activity coefficient of hydrogen ion under these conditions.

We verified relaxation times for compound I falling in the 20-100-μsec range with a solid-state, pulsed-laser temperature-jump apparatus. In this technique, a roughly 3° rise in temperature in a 10-3 ml volume of sample solution is achieved by focusing the 1.06-μ wavelength, 1-joule laser pulse from a neodymium-doped glass rod (Eastman Kodak) Q-switched with a rotating prism (Beckman and Whitley) into the center of a 1-cm path-length Pyrex sample cuvette. The small portion of the incident energy absorbed by the vibrational band of the solvent water is sufficient to give temperature-jump relaxations observed spectrophotometrically with a visible, monochromatic beam of light directed through the sample cell at 90° to the laser beam. This laser temperature-jump experiment will not capitalize on the far more rapid heating of the sample liquid, i.e. 0.02 μsec with a Q-switched laser pulse compared with the shortest (1.0 μsec by Joule heating), until either a substantially more sensitive, rapid detector than our RCA 1P21 photomultiplier is utilized or larger Q-switched laser pulses (~10 joules or more) are dissipated in comparable sample volumes. In the meantime, the most promising means of detecting temperature-jump relaxation initiated by 1-joule, Q-switch laser pulses is a conductivity technique pioneered by Hoffmann et al.$^8$

**Results and Discussion.**—As in our previous kinetic studies of deprotonation of intramolecularly hydrogen-bonded acids by hydroxide ion,$^9$ we see in Table 1 that, with one exception, as the $pK_a$ increases the rate constant $k_{23}'$ for deprotonation decreases. In other words, the stronger the intramolecular hydrogen bond becomes, the slower the deprotonation by hydroxide ion proceeds.

The relative strengths of the intramolecular hydrogen bonds as measured would have been difficult to predict *a priori* on the single basis of electrostatic effects of the ring substituents. For instance, it is difficult to explain why the para nitro group of I is less effective than the meta nitro group of VII in drawing charge away from the azo nitrogen proton acceptor or why the absence of a substituent in the ring of VIII does not give rise to an intramolecular hydrogen-bond strength in VIII that exceeds that of II.

We conclude that the electrostatic effects of substituents in these O-H...N intramolecularly hydrogen-bonded azo dyes are just one of possibly many important factors, such as solvation, that determine relative strengths of the intramolecular hydrogen bonds.

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