Temperature-jump Study of the Reversible Disproportionation of an Azaviolene Radical Ion

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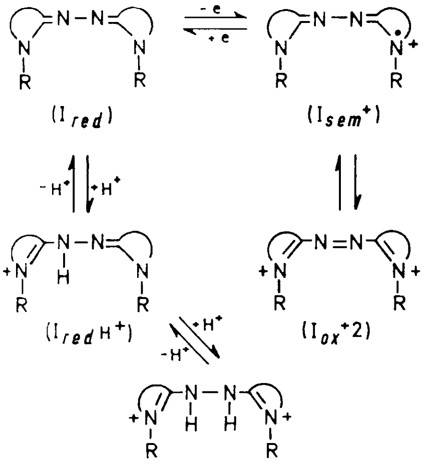
Summary Both the free base and its conjugate acid, of the reduced form of certain azaviolenes, react with the oxidized form to generate a stable radical ion, but the rate approaches the diffusion-controlled limit only with the free base.

POLAROGRAPHIC studies of a number of azaviolenes with the general structure (I) have shown that these compounds can be present in three forms, differing by their oxidation state, which can be converted reversibly into each other according to Scheme 1.[1,2] Since the reduced form is frequently appreciably basic, complications may arise through simple or even double protonation of (I_{red}). One can define a semiquinone formation constant K_1 by writing the redox equilibrium as in equation (1). K_1 Values and pK-values

$$I_{red} + I_{ox}{}^{+2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,I_{sem}{}^{+} \qquad (1)$$

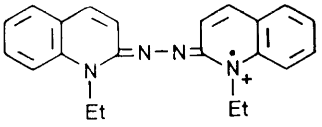
$$K_1 = \frac{k_1}{k_{-1}} = \frac{[sem]^2}{[ox^{+2}][red]} \qquad (2)$$

for (I_{red}) have been determined by polarography for several systems.[1]



SCHEME 1

Considerably more information about structure–reactivity relationships can be obtained from rate studies in these systems. We now report the results of a temperature-jump[3] study in methoxyethanol–water (1 : 1) at 25° on the system derived from 1-ethylquinolin-2-one azine (II).[†]



($II_{sem}{}^{+}$)

SCHEME 2

Scheme 2, in which a simplified symbolism is used is characterized by four relaxation times, three of which

$$\begin{tikzcd}[column sep=large]
red + ox^{+2} \arrow[r, rightleftharpoons, "k_1", "k_{-1}"'] \arrow[d, rightleftharpoons, "\mathrm{p}K_1^{\mathrm{R}}"', "\mathrm{H}^+"] & sem^+ + sem^+ \arrow[d, rightleftharpoons, "\mathrm{p}K_1^{\mathrm{S}}"', "\mathrm{H}^+"] \\
{}_{red}\mathrm{H}^+ + ox^{+2} \arrow[r, rightleftharpoons, "k_2", "k_{-2}"'] \arrow[d, rightleftharpoons, "\mathrm{p}K_2^{\mathrm{R}}"', "\mathrm{H}^+"] & sem^+ + sem\mathrm{H}^{+2} \\
{}_{red}\mathrm{H}_2{}^{+2} &
\end{tikzcd}$$

too fast to be measured with our method, are essentially associated with the vertical proton transfer equilibria.

[†] Two similar temperature-jump studies on somewhat related organic redox systems have been reported. H. Diebler, M. Eigen, and P. Matthies, *Z. Naturforsch.*, 1961, **16b**, 629; H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 396.

The fourth relaxation time (5—200 ms range) is associated with the two horizontal redox equilibria and is easily measured. From its dependence on substrate concentration and pH, combined with the literature data[1] on K_1 and pK_1^R, the following rate and equilibrium constants were determined by computer analysis: $k_1 = 1.22 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$, $k_{-1} = 5.7 \times 10^3\ \text{M}^{-1}\ \text{sec}^{-1}$, $K_1 = 2.14 \times 10^5$[1], $k_2 = 5.7 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$, $k_{-2} = 4.3 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$, $K_2 = k_2/k_{-2} = 1.3$, $pK_1^R = 6.5$[1], $pK_2^R = 1.0$, $pK_1^S = 1.3$. Note that the rate of reaction between *red* and ox^{+2} is close to the diffusion controlled limit,[4] but protonation of *red* reduces this rate about 2000 fold.

The finding that the redox reaction can also proceed through $_{red}H^+$ and $_{ox}H^+$, a pathway which becomes very significant below pH 3, is of considerable interest since this was not apparent from the equilibrium studies.[1] It demonstrates once more the power of this kinetic method.

Similar studies on a variety of violene and azaviolene systems are in progress.

This work was supported in part by a Frederick Gardner Cottrell grant from Research Corporation.

(*Received, September 1st, 1971; Com. 1530.*)

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[1] S. Hunig, H. Balli, H. Conrad, and A. Schott, *Annalen*, 1964, **676**, 52.

[2] S. Hunig, *Pure Appl. Chem.*, 1967, **15**, 109.

[3] M. Eigen and L. De Maeyer in 'Technique of Organic Chemistry', vol. 8, Part 2, Interscience, New York, 1963, p. 895.

[4] M. Eigen, *Angew. Chem., Internat. Ed.*, 1964, **3**, 1.