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Rate and Equilibrium of the Hydration of 1,3-Benzodithiolylium Ion

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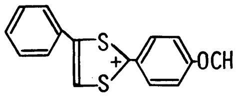
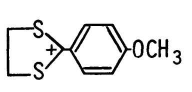
Rates and the equilibrium constant of hydration of 1,3-benzodithiolylium ion were spectrophotometrically measured at 30 °C in aqueous acidic solutions. The hydrate was stable below pH 5 and $pK_{R^+}=-0.40$. The cation does not seem to be very stable as compared with the corresponding dithiolanylium ion.

Considerable attention has recently been focused on the chemistry of 1,3-dithiolylium ions[1–3] because of their potential aromaticity and their use in the synthesis of tetrathiafulvalene derivatives. The CMR chemical shifts of the cations were considered to be evidence for the aromaticity by some authors[4,5] while the opposite conclusion was reached from similar results by others.[6] Equilibrium constants of the hydration of some 1,3-dithiolylium ions were measured in 50% ethanol: pK_{R^+} of 2-(*p*-methoxyphenyl)-4-phenyl-1,3-dithiolylium ion **1** was found to be 4.11.[7] The saturated dithiolanylium ion **2** has a similar pK_{R^+} value (4.1).[8] That is, the π-electonic sextet of the former cation contributes little to its equilibrium stability.

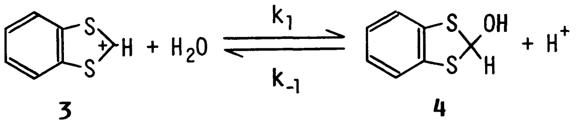


1, $pK_{R^+} = 4.11$



2, $pK_{R^+} = 4.1$

In the present study, we have measured pK_{R^+} and rates of hydration of an easily available cation, 1,3-benzodithiolylium ion **3**, in order to compare its stability with the dithiolanylium analogue.



(1)

Results

The cation **3** is stable in strong acid, having UV absorption maxima at 238 (log ε 3.65), 253.2 (3.85), 257.5 (3.81), and 308.5 (3.62) nm. On dilution of acid, the absorption at longer wavelength diminishes with formation of a strong absorption at 226.5 nm (log ε 4.49). The spectrum was stable at least for several days in acid solutions and even in unbuffered water (pH≈5). The spectrum at low acidities closely resembles that of 2-isopentyloxy-1,3-benzodithiole which has absorption maximum at 226 nm with log ε 4.42 in aqueous solution. On acidifying strongly the unbuffered solution of **3**, the absorption at 226.5 nm immediately disappears with simultaneous regeneration of the absorption due to the original cation **3**; *i.e.*, the spectrum change is rapid and reversible. The change must be due to the equilibrium between the cation **3** and its hydrate **4** (Eq. 1). The hydrate **4** must be responsible for the absorption at 226.5 nm.

Absorbance changes at 226 and 330 nm (shoulder of the spectrum of **3**) were measured at 30 °C with changing acidity in hydrochloric and perchloric acid solutions. The absorbance changes are plotted against the acidity function H_R[9,10] in Fig. 1, plots following sigmoid curves with $pK_{R^+}= -0.40$.

Rates of the absorbance decrease at 226 nm were measured at 30 °C on a stopped-flow spectrophotometer by mixing a stock solution of **4** obtained by dissolving **3** in unbuffered water and an aqueous perchloric acid solution of an appropriate concentration. Results are given in Table 1. Observed pseudo-first-order rate

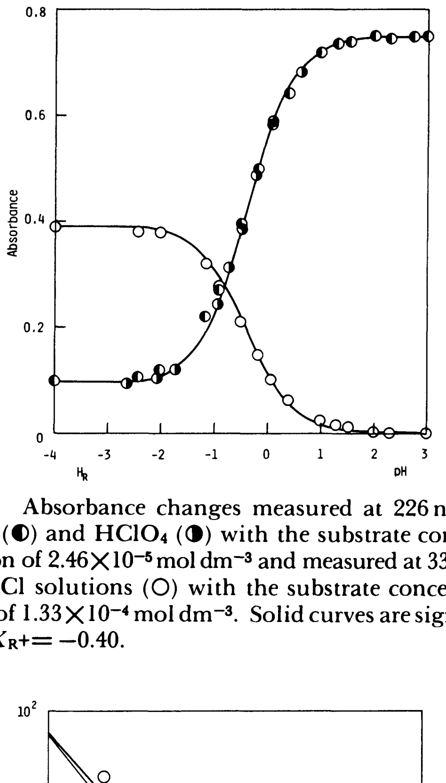


Fig. 1. Absorbance changes measured at 226 nm in HCl (◐) and $HClO_4$ (◑) with the substrate concentration of 2.46×10^{-5} mol dm^{-3} and measured at 330 nm in HCl solutions (○) with the substrate concentration of 1.33×10^{-4} mol dm^{-3}. Solid curves are sigmoid of $pK_{R^+}= -0.40$.

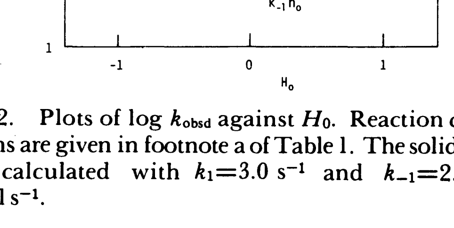


Fig. 2. Plots of log k_{obsd} against H_0. Reaction conditions are given in footnote a of Table 1. The solid curve is calculated with $k_1=3.0$ s^{-1} and $k_{-1}=2.9$ dm^3 mol s^{-1}.

TABLE 1. RATE CONSTANTS FOR REACTION 1 AT 30 °C

$[HClO_4]$/mol dm^{-3} a)	k_{obsd}/s^{-1}	[HCl]/mol dm^{-3} b)	$k_{obsd/s}$$^{-1}$
0.391	4.75	1.0×10^{-4}	9.13
0.587	5.20	5.0×10^{-4}	8.75
0.978	7.52	2.5×10^{-3}	9.05
1.174	8.86	5.0×10^{-3}	9.50
1.468	12.8	5.0×10^{-2}	9.18
1.761 c)	19.2	0.25	9.28
1.957 c)	23.5		
2.348 c)	40.0		
2.935 d)	101.9		

a) Rates were measured by the absorbance decrease at 226 nm in aqueous solutions containing 1 vol% of CH_3CN. The initial concentration of the substrate (**4**) was 2.46×10^{-5} mol dm^{-3}. b) Rates were measured by the absorbance decrease at 308 nm in 1 : 1 (v/v) CH_3CN-H_2O of μ=0.25. The initial concentration of the substrate (**3**) was about 1.3×10^{-4} mol dm^{-3}. c) Temperature may slightly higher than 30 °C because of heat of mixing. d) Temperature was about 33 °C owing to heat of mixing.

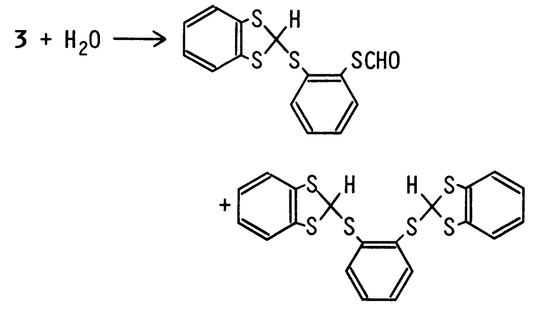
constants k_{obsd} are plotted logarithmically against the acidity function H_0 9,10) Fig. 2.

Disappearance of **3** was also followed at 308 nm by a stopped-flow mixing of a stock solution of **3** in dry acetonitrile and an aqueous hydrochloric acid solution of the ionic strength of 0.50 maintained with KCl, the resultant reaction solution being 1 : 1 (v/v) CH_3CN-H_2O of μ=0.25. The rate constant was nearly independent of acid concentration [HCl] over the range 1.0×10^{-4}—0.25 mol dm^{-3} as listed in Table 1.

In alkaline solutions, reactions seemed to be somewhat more complicated. When 30 μl of the stock solution of **3** in acetonitrile (2×10^{-3} mol dm^{-3}) was added to 3 ml of a borate buffer (pH=9.1) or aqueous NaOH (0.01 mol dm^{-3}), the solution became usually turbid. However, a clear solution of the same composition was always obtained when the aqueous solution (unbuffered) of **3** containing 2 vol% CH_3CN was mixed with an appropriate alkaline solution. The latter solutions in dilute NaOH (0.01—0.1 mol dm^{-3}) showed an absorption maximum at 243 nm, which disappeared in a few hours. The clear borate buffer solution of **3** had the absorption of 226 nm which gradually changed to the absorption of $\lambda_{max}\approx240$ nm and then disappeared, the final spectrum showing no maximum absorption above 220 nm. These spectral changes did not have any clear isosbestic point.

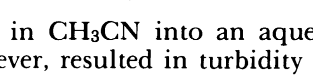
Discussion

Reaction of the cation **3** with water was previously studied and was found to give dimeric and trimeric products as shown in Eq. 2.11,12) The reaction was undertaken in relatively high concentration of **3** and a small amount of water, resulting in polymeric products.



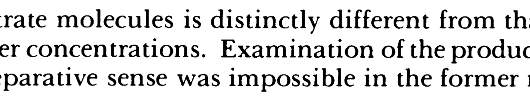
(2)

The reaction carried out in very dilute solutions at acidic pH is obviously simple and UV spectral and kinetic behavior conforms with the equilibrium hydration (Eq. 1). Ring-opening reaction of the hydrate **4** must be reversible, if occur, and the equilibrium favors the cyclic structure (**4**).



(3)

The reaction seems to proceed further in alkaline solutions, probably to give the ring-open product followed by the hydrolysis of a resultant thioformic acid *S*-ester (Eq. 4). Direct dissolution of a stock solution of **3** in CH_3CN into an aqueous alkaline solution, however, resulted in turbidity probably owing to the polymeric products (Eq. 2). Because of very rapid reaction, the local concentration of **3** may be high in this case. Thus, the reaction in always dilute solution which avoids bimolecular reactions between two substrate molecules is distinctly different from that in higher concentrations. Examination of the products in a preparative sense was impossible in the former mild reaction.



(4)

The pK_{R^+} value of **3** (−0.40) is smaller than that of 4-phenyl-1,3-dithiolylium ion (*ca.* 2)7,13) but seems to be close to that of dithiolanylium ion.14) The pK_{R^+} values of 2-(*p*-methoxyphenyl) derivatives of the unsaturated and saturated cations (**1** and **2**) are also similar to each other7,8) as mentioned above. Equilibrium stabilities of 1,3-dithiolylium and 1,3-benzodithiolylium ions (relative to their hydrates) are not much greater than the corresponding saturated systems (dithiolanylium ions). The π-electronic sextet of the former cations does not seem to be effective in their stabilization in the above sense.

The rate of disappearance of the cation **3** (9.13 s^{-1} in 1 : 1 (v/v) CH_3CN-H_2O at 30 °C) is about 1/10 of that of 2-methyl-1,3-dithiolanylium ion (88 s^{-1}). That is, the rate of decay of **3** is smaller but that of formation of **3** (from the hydrate) is greater than that of a similar saturated analogue (since the equilibrium constants are similar).

Kinetic measurements were also carried out in essentially aqueous solutions (containing 1 vol% of CH_3CN) at 30 °C with use of a stock solution of the hydrate **4** in water by following its disappearance to form **3** in acidic solutions. The rate constant k_{obsd} for the reversible reaction (Eq. 1) is the sum of the rate constants for the forward and reverse reactions.

$$k_{obsd} = k_1 a_w + k_{-1} h_0 , \qquad (5)$$

where a_w and h_0 stand for the activity of water and the acidity function (10^{-H_0}),[9,10] respectively. The value h_0 corresponds to $[H^+]$ in dilute acid. The value a_w diminishes with acidity but it is not smaller than 0.9 in the present acidity range ($H_0 > -1$); the effect of a_w is small. Thus, rate constants k_{obsd} are logarithmically plotted against H_0[10] in Fig. 2. In the acidity scale of H_0, $H_R = -0.40$ (pK_{R^+}) corresponds to -0.02,[10] where $k_1 a_w = k_{-1} h_0$. The theoretical curve calculated with $k_1 = 3.0\,s^{-1}$ and $k_{-1} = 2.9\,dm^3\,mol^{-1}s^{-1}$ according to Eq. 5 is shown in Fig. 2. The range of acidity examined was necessarily narrow because of no equilibrium formation of **3** at low acidities and of heat of mixing at high acidities. Upward deviations of the observed points at high acidities may in part be due to the temperature rise on mixing.[16]

The rate of decomposition of **3** (k_1) is 1/3 of that observed in 1 : 1 CH_3CN-H_2O. The enhanced rate in the aqueous organic medium may be ascribed to instability of the cation in the less polar solvent.

Experimental

Materials. 2-Isopentyloxy-1,3-benzodithiole and 1,3-benzodithiolylium (**3**) perchlorate were prepared according to the method of Nakayama.[12] Acetonitrile was distilled from P_2O_5. Glass-distilled water was used throughout the work.

Equilibrium Measurements. Hydrochloric and perchloric acid solutions were prepared from concentrated HCl and 70% $HClO_4$, respectively, and concentrations were determined by titration. A stock solution of **3** was obtained by dissolving a weighed amount of the perchlorate in dry CH_3CN, concentration being usually $2.5 \times 10^{-3}\,mol\,dm^{-3}$. Into 3.0 ml of acid in a quartz cuvette equilibrated at 30 ± 0.1 °C was introduced 30 μl of the stock solution of **3** from a microsyringe and the absorbance was measured on a Shimadzu UV 200 spectrophotometer. Measurements were made in triplicate under the same conditions and averages are plotted in Fig. 1. Other spectral measurements were carried out in a similar way.

Kinetic Measurements. Rates were measured on a Union RS 1100 stopped-flow spectrophotometer at 30 ± 0.2 °C by mixing the acid solution with a dilute stock solution of **3** in CH_3CN or in aqueous solution (as a form of **4**). The aqueous stock solution was prepared by dissolving 1.0 ml of the stock solution of **3** in CH_3CN into water in a 50 ml volumetric flask. Good pseudo-first-order kinetics were observed over 3 halflives. Averages of 4 or 5 measurements are summarized in Table 1.

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14) Our unpublished results show that 2-methyl-1,3-dithiolanylium ion has $pK_{R^+} = 0.27$.

15) T. Okuyama, unpublished results.

16) Mixing of 6 mol dm^{-3} $HClO_4$ with water resulted in a temperature rise of 30 to 33 °C. Mixing of 4.7 mol dm^{-3} $HClO_4$ with water, which gives a resultant solution of $H_0 = -1.0$, gave rise to only about 0.5 °C temperature rise.