NOTES

Effect of Salt Concentration and Temperature on the Ultraviolet Absorption Spectra of Aqueous Thiosulfate and Sulfite

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Incidental to another investigation[1] we have observed that the molar extinction coefficients of thiosulfate in the range of 250 to 270 mμ: (1) are progressively decreased by increasing concentrations of lithium, sodium, potassium and magnesium salts; (2) are increased by increased temperature; (3) are independent of the ionic strength (in the range from 2 to 3) and of *p*H (in the range from 5 to 12). It seems probable that the spectra observed are electron transfer spectra,[2] and that the changes in extinction coefficients are due to changes in the concentration of the absorbing species (probably $S_2O_3^{=} \cdot xH_2O$) caused by shifting its equilibria with ion pairs[3] and other hydrated species. We are reporting our exploratory observations here because they seem to offer a new method for obtaining information about certain ionic interactions in aqueous solution.

Measurements were made with a Beckman DU spectrophotometer using a hydrogen discharge lamp and matched quartz cells with 1 cm. light paths. The reference cell solution was, in each case, identical in concentration of added salt and *p*H with the thiosulfate solution being measured. The thiosulfate concentration was determined iodometrically. All measurements except those designed to test temperature effects were made at room temperature.

Results

Effect of Normality of Sodium Salts.—Three solutions of identical thiosulfate concentration (0.0102 *M*), ionic strength (2.00) and *p*H (12.1) were prepared by making them 0.353 *M* in Na_3PO_4, 0.657 *M* in Na_2SO_4 and 1.97 *M* in NaCl, respectively. The molar extinction coefficients[4] of these solutions, plotted as curves III, IV and V of Fig. 1, decreased with increasing normality of salt at all wave lengths tested.

Other solutions (Fig. 1) with sodium salt concentrations which varied from 2×10^{-3} *N* to 10 *N* (while the ionic strength varied by a similar factor) always showed a decrease in molar extinction coefficient with increase in the normality of the added salt.

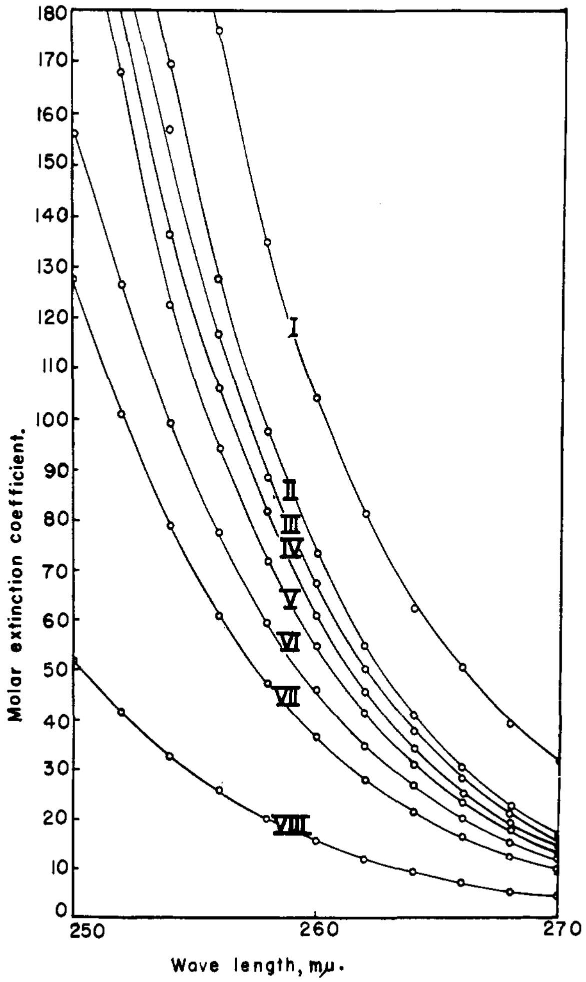

Fig. 1.—The effect of salt concentration on the molar extinction coefficients of thiosulfate solutions. The data opposite the roman numerals below give the conditions represented by the corresponding curves in the figure.

	Na^+ moles/l.	Ionic strength	*p*H	Anion	$S_2O_3^{=}$ mole/l.
I	0.002	0.003	9.4	$S_2O_3^{=}$	0.001
II	0.12	0.13	12.8	Cl^-	.0106
III	1.08	2.0	12.2	$PO_4^{\equiv}$	.0102
IV	1.33	2.0	12.1	$SO_4^{=}$	.0102
V	1.99	2.0	12.0	Cl^-	.0102
VI	3.77	5.6	12.3	$SO_4^{=}$	.0102
VII	5.48	5.5	12.0	Cl^-	.0104
VIII	10.0	10.0	12.0	ClO_4^-	.0100

Effect of Ionic Strength.—Two solutions of identical thiosulfate concentration (0.0106 *M*) and *p*H (12.8) were made up to have the same normality (1.91 *N*) by using sodium chloride in one case and sodium sulfate in the other. In the first

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(1) D. P. Ames and J. E. Willard, This Journal, **73**, 164 (1951).

(2) (a) E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942); (b) L. Farkas and F. S. Klein, *J. Chem. Phys.*, **16**, 886 (1948).

(3) Other types of observation which have been interpreted in terms of significant ion-pair formation in solutions of "strong" electrolytes include: (1) activity coefficient measurements, H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 423; (2) conductance measurements, I. L. Jenkins and C. B. Monk, This Journal, **72**, 2695 (1950); (3) the solubility of BaS_2O_3 in aqueous solutions of different chlorides, T. O. Denney and C. B. Monk, *Trans. Faraday Soc.*, **47**, 992 (1951); (4) rates of ionic reactions in aqueous solution, A. R. Olson and T. R. Simonsen, *J. Chem. Phys.*, **17**, 1167 (1949).

(4) Molar extinction coefficients of $S_2O_3^{=}$, at unspecified concentration have been reported by A. D. Awtrey and R. E. Connick, This Journal, **73**, 1842 (1951); L. Lorenz and R. Samuel, *Z. physik. Chem.*, **B14**, 219 (1931); H. Ley and E. Konig, *ibid.*, **B41**, 365 (1938).

case the ionic strength was 1.9 and in the second 2.9. The extinction coefficients were identical within 2% throughout the range from 250 to 270 mμ.

Effect of *p*H.—Two solutions of identical thiosulfate concentration (0.0106 *M*), sodium chloride concentration (2.0 *N*) and ionic strength (2.0) but with a *p*H of 4.6 in one case and 12.0 in the other were found to have identical molar extinction coefficients within 2% from 250 to 270 mμ.

Effect of Changing Cation Species.—A comparison of columns 2, 3 and 4 of Table I indicates that equal concentrations of lithium, sodium or potassium chloride have equal effect in reducing the thiosulfate extinction coefficient. Columns 5 and 6 show that magnesium sulfate exerts about the same effect (possibly slightly greater) as a solution of lithium chloride of the same normality. A similar result was obtained when a 1 *M* solution of magnesium sulfate was compared with a 2 *M* solution of sodium chloride.

TABLE I

EFFECT OF THE CATION SPECIES ON THE THIOSULFATE ABSORPTION SPECTRUM

	Molar extinction coefficients				
mμ	Li^{+a}	Na^{+b}	K^{+c}	Mg^{++d}	Li^{+e}
250		184.0	187.3	144.2	156.9
2	155.7	150.9	153.9	114.4	124.5
4	119.8	119.8	118.6	89.9	97.1
6	92.0	94.3	91.2	70.4	74.5
8	68.9	69.8	68.6	54.7	56.9
260	51.7	52.8	52.0	42.1	43.1
2	38.6	39.6	38.7	32.9	32.7
4	28.8	29.6	28.8	25.5	24.7
6	21.1	22.1	21.1	19.2	18.6
8	15.5	16.1	15.5	14.7	14.0
270	11.3	11.8	11.3	11.4	10.3

[a] $S_2O_3^=$ = 0.0106 *M*; LiCl = 1.91 *M*; *p*H = 12.5. [b] $S_2O_3^=$ = 0.0106 *M*; NaCl = 1.91 *M*; *p*H = 12.7. [c] $S_2O_3^=$ = 0.0102 *M*; KCl = 1.91 *M*; *p*H = 12.5. [d] $S_2O_3^=$ = 0.0104 *M*; $MgSO_4$ = 1.91 *M*. [e] $S_2O_3^=$ = 0.0102 *M*; LiCl = 3.82 *M*; *p*H = 12.5.

Effect of Sodium Salt Concentration on Sulfite Spectrum.—The molar extinction coefficient of sulfite is low in the wave length range above 260 mμ but rises rapidly below 250 mμ and depends on sodium salt concentration in a manner similar to that observed for thiosulfate. For example, a pure 0.010 *M* sulfite solution gave an extinction coefficient of 180 at 238 mμ. This was lowered to 110 when the solution was made 1 *M* in sodium chloride.

Effect of Temperature.—If the decrease in the extinction coefficients of thiosulfate and sulfite produced by increased salt concentration in solutions is due to ion pair formation, the coefficients might be expected to increase with increase in temperature. The effect of temperature has been tested qualitatively by determining the extinction coefficients of 0.010 *M* thiosulfite solutions in 2 *M* sodium chloride on a Cary recording spectrophotometer with the cell at room temperature and immediately after the cell was removed from a bath of boiling water. At 255 mμ the extinction coefficient increased from 111 to 145 and at 260 mμ from 54 to 76 at the elevated temperature. A spectrum taken after cooling was identical with that obtained before heating.

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The Rearrangement of 9α,11α-Oxido-$\Delta^{7,22}$-ergostadiene-3β-ol Acetate with Magnesium Bromide

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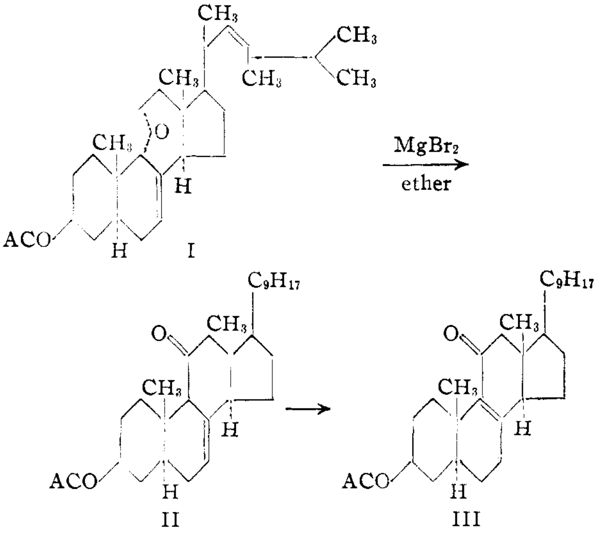
It has previously been reported that the monoepoxide derived from $\Delta^{7,9(11),22}$-ergostatriene-3β-ol acetate (ergosteryl D acetate) (I) may be rearranged to the corresponding α,β-unsaturated ketone III by the action of boron trifluoride etherate.[3] We have found that the rearrangement of I, as induced by magnesium bromide etherate, affords the non-conjugated ketone, $\Delta^{7,22}$-ergostadiene-3β-ol-11-one 3-acetate (II) in yields of 60–73%. On passing a benzene–petroleum ether solution of II over a column of activated alumina, the β,γ-unsaturated ketone II was isomerized to the known $\Delta^{8(9),22}$-ergostadiene-3β-ol-11-one acetate (III). In addition, it was found that the isomerization of the non-conjugated ketone II to the conjugated isomer III may be induced with a trace of hydrochloric acid in alcohol and it is possible to observe the transformation spectrophotometrically.



I

II

III

In the early stages of this investigation it became apparent that the methods available in the litera-

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[1] Deceased, March 22, 1951.

[2] Parke, Davis Postdoctoral Fellow, 1950–1951.

[3] H. Heusser, *et al.*, *Helv. Chim. Acta*, **34**, 2106 (1951).