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Spectrophotometric Study of the Bleaching of Ferric Thioglycolate

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The autoöxidation–reduction reaction that produces the bleaching of ferric thioglycolate was investigated spectrophotometrically in air-free ammoniacal solutions buffered between *p*H 8.4 and 10.1. The reaction is second order with regard to the total concentration of ferric ion and can be explained by a reaction involving the formation of a hydroxyl-bridged dimer by a molecule of $FeOH(RS)_2^{=}$ with a molecule of either $FeOH(RS)_2^{=}$, $Fe(OH)_2RS^-$ or FeOHRS, where $RS^{=}$ refers to the divalent thioglycolate ion. Electron transfer occurs within the dimer which then breaks up into two molecules of ferrous iron and a molecule of the disulfide, $^-RSSR^-$. The rate of decrease in the concentration of $FeOH(RS)_2^{=}$ is given by the expression (5) where RSH^- refers to the uni-valent thioglycolate ion. In solutions at an ionic strength of 0.58 at 25° the value of the product k_1K_1 for the reactions $2Fe(OH)(RS)_2^{=} \overset{K_1}{\rightleftarrows} \text{dimer} \xrightarrow{k_1} \text{products}$ is $8.7 \pm 0.4 \times 10^{-2}$ mole^{-1} sec.$^{-1}$ with an over-all energy of activation equal to 20 ± 3 kcal., the value of the product $k_2K_2K_3$ for the reactions $FeOH(RS)_2^{=} + H_2O \overset{K_2}{\rightleftarrows} Fe(OH)_2RS^- + RSH^-$ and $FeOH(RS)_2^{=} + Fe(OH)_2RS^- \overset{K_3}{\rightleftarrows} \text{dimer} \xrightarrow{k_2} \text{products}$ is $1.5 \pm 0.1 \times 10^{-3}$ sec.$^{-1}$, and the value of product $k_3K_4K_5$ for the reactions $FeOH(RS)_2^{=} + H^+ \overset{K_4}{\rightleftarrows} FeOHRS + RSH^-$ and $FeOH(RS)_2^{=} + FeOHRS \overset{K_5}{\rightleftarrows} \text{dimer} \xrightarrow{k_3} \text{products}$ is $3.3 \pm 0.1 \times 10^{+6}$ mole^{-1} sec.$^{-1}$.

The intensely colored red-purple complex that is formed by the reaction of ferric iron with thioglycolate in alkaline solutions[2] recently has been found[3] to have the formula $FeOH(SCH_2CO_2)_2^{=}$. The complex is formed immediately upon mixing solutions of ferric iron with those of alkaline thioglycolate. On standing, the color slowly fades with the reduction of the iron from the complexed ferric state to the complexed ferrous and the oxidation of the thioglycolate to the disulfide, $^-O_2CCH_2SSCH_2CO_2^-$. In these alkaline solutions, complexed ferrous iron is very rapidly oxidized to the ferric state by oxygen. Through this cycle, iron catalyzes the air oxidation of thioglycolate.[4-8] It is the rapidity of the oxidation relative to the reduction that enables thioglycolate to be a useful reagent for the colorimetric determination of iron in air-saturated alkaline solutions.[9-11]

In acid solutions, ferric iron and thioglycolic acid react to form a blue complex. This complex undergoes a rapid oxidation–reduction reaction to form ferrous iron and the disulfide.[6]

Cannan and Richardson[6] have reported on a brief investigation of the iron(III)–thioglycolate reaction in alkaline solutions. In their experiments only a slight excess of thioglycolate over iron was employed. This makes an interpretation of the results difficult, because as is shown below, the rate of the reaction depends on the concentration of thioglycolate. Also, they state that their thioglycolate stock solutions were stored over mercury and quite possibly were contaminated.

In the present investigation the course of the reaction between iron(III) and thioglycolate in air-free ammonia buffers containing a large excess of thioglycolate was followed spectrophotometrically. The concentration of $FeOH(SCH_2CO_2)_2^{=}$ was followed as a function of time by means of its absorption maximum at 530 mμ.

Experimental

Pure thioglycolic acid was prepared as described elsewhere.[12]

The technique of preparing air-free buffered solutions of ferric thioglycolate and measuring their optical densities was essentially the same as that described in reference 3. In a typical experiment the desired amounts of 4 *M* ammonium nitrate, thioglycolic acid and sufficient water to bring the volume to 95 ml. were placed in a screw cap bottle equipped with a 1.00 cm. optical side-arm. The amounts used of the ammonia and ammonium nitrate solutions were adjusted to allow for the neutralization of one hydrogen ion from the thioglycolic acid. This was sufficient to maintain constant *p*H for a given series although the ionic strength did vary slightly. The bottle was stoppered with a flat self-sealing Firestone Buna N stopper which was held tightly in place by a metal screw-cap which had holes punched in the top. Access to the interior of the bottle was then had by hypodermic needles. The bottle was de-aerated with nitrogen and brought to temperature in a thermostated water-bath. To form the complex a 5.00-ml. volume of a de-aerated iron(III) solution which had also been brought to temperature was then injected into the sealed bottle by means of a syringe. The iron(III) solution was prepared by the appropriate dilution of a stock solution containing 0.102 *M* ferric ammonium sulfate and 0.1 *M* sulfuric acid. Periodically, the sealed bottle in which the complex had been formed was removed from the water-bath and the absorbance at 530 mμ measured using a Beckman Model B Spectrophotometer modified as described in reference 3. Distilled water was used as a blank in all experiments.

In some of the experiments the complete absorption spectrum between 340 and 700 mμ was obtained using the Beckman Recording Spectrophotometer, Model DK-1.

The spectra were recorded for solutions of the complex buffered at *p*H 8.4, 9.6 and 10.1 at periods of 3, 60 and 300 minutes after mixing. An interval of three minutes was required to scan the wave length range. The amount of error introduced by bleaching during this time was calcu-

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TABLE I

SPECTROPHOTOMETRIC RATE OF BLEACHING OF FERRIC THIOGLYCOLATE IN AIR-FREE AMMONIA BUFFERS AT 25°

$[\mathrm{Fe(III)}]$ initial = 2.04×10^{-4} *M*.

$[NH_4NO_3]$ initial (*M*)	$[NH_4OH]$ initial (*M*)	*p*H final	[TGA] (*M*)	*I*	A_0	$k \times 10^3$ (obsd.), A.$^{-1}$ min.$^{-1}$	$k \times 10^3$ (calcd.), A.$^{-1}$ min.$^{-1}$	$k'' \times 10^5$ (obsd.), MA.$^{-1}$ min.$^{-1}$
0.45	2.0	10.10	0.100	0.67	0.767	1.98	2.01	6.91
.50	2.0		.050	.61	.764	2.70	2.69	
.52	2.0		.030	.58	.747	3.50	3.60	
.53	2.0		.020	.57	.746	4.77	4.73	
.50	1.0	9.75	.050	.59	.755	2.32	2.40	4.95
.45	0.85	9.62	.100	.61	.786	1.91	1.86	5.02
.50	.80		.050	.59	.749	2.29	2.38	
.51	.79		.040	.58	.776	2.64	2.65	
.52	.78		.030	.57	.771	3.08	3.08	
.53	.77		.020	.56	.760	3.88	3.96	
.50	.60	9.45	.050	.59	.757	2.33	2.42	5.00
.45	.25	8.92	.100	.57	.763	2.23	2.24	9.23
.50	.20		.050	.56	.770	3.17	3.16	
.51	.19		.040	.56	.769	3.63	3.63	
.52	.18		.030	.55	.754	4.31	4.37	
.53	.17		.020	.55	.754	5.97	5.90	
.50	.10	8.40	.050	.55	.733	5.87	5.93	22.9
.52	.08		.030	.55	.743	9.07	9.00	
.53	.07		.020	.55	.674	12.6	12.8	
.18	.48	9.58	.100	.34		1.37	...	3.8
.23	.43		.050	.31		1.66	...	
.25	.41		.030	.30		2.18	...	
.26	.40		.020	.29		2.81	...	

lated to be less than 1% in the solution showing the maximum rate.

Although the absolute value of absorbance at any particular wave length decreased with time, the relative values throughout the investigated range were independent of both *p*H and time. Also, the relative values were identical to those obtained in air-saturated solutions. These results agree with those of the solubility studies[3] that only one ferric thioglycolate complex predominates in the solutions investigated in the present work.

The procedure was checked for the leakage of air by using ferrous iron in place of the ferric. No oxidation to the ferric complex occurred, indicating the rigorous exclusion of oxygen. However, it was observed that the air-free ferrous solutions were oxidized by irradiation with light of frequency in the near ultraviolet. Although the diffuse light of the laboratory had no effect on the solutions, as a precaution, the bottles were blackened except for the optical side-arms. The optical side-arms were covered with light-tight sleeves which were removed for making the optical measurements. The light that passed through the cells during the brief periods required for the measurements showed no effect.

At the completion of an experiment the *p*H of the solution was determined using a glass electrode with a Beckman Model G *p*H Meter. The *p*H meter was standardized with a Beckman Buffer, *p*H 10.00 ± 0.01 at 25°.

It was found for alkaline ferric solutions in which the concentration of thioglycolate is 0.01 *M* or greater that the absorbance *A*, at 530 mμ decreases according to a second-order rate law.

$$-\mathrm{d}A/\mathrm{d}t = kA^2 \qquad (1)$$

No evidence of a back reaction is given, although observations on some solutions had been made until the absorbances had decreased to about one-seventh the initial values. The rate constant, *k*, was found to be independent of the total concentration of iron over the range studied (1×10^{-4} to 4×10^{-4} *M*). However, the value of *k* is a function of the concentration of thioglycolate and the *p*H of the solution. The data and results are presented in Table I for solutions containing initially 2.04×10^{-4} *M* ferric iron at 25.0 ± 0.2°.

In Table I the values of A_0, the absorbance at zero time, were obtained by extrapolation. These values are noted to be less than the value 0.803 ± 0.005 which was obtained for all the solutions at the end of an experiment when air was admitted. The greatest deviations are observed in the experiments at *p*H 8.40. In repeating experiments the value of A_0 varied randomly but the rate constant, *k*, always remained the same within the experimental error.

The low values of A_0 are attributed to the rapid reduction of the ferric iron by a different mechanism that operates during the mixing of the solutions. On slowly adding a ferric solution dropwise to a thioglycolate solution at *p*H 8.4, a blue color is observed to be produced at the interface of the two solutions. This blue color rapidly fades and apparently is due to the formation of the same complex that has been reported previously[6] to exist transitorily in acid solutions.

Deviations from second-order behavior were noted for solutions in which the concentration of thioglycolate is less than 0.01 *M*. The rate of bleaching greatly increases and can be represented by an equation containing both first and second order terms with regard to the absorbance. The rate at the lower concentrations of thioglycolate also increases with the age after dilution of the iron stock solution. Apparently, this effect is associated with the degree of polymerization of the dilute hydrolyzed iron solution. The rate in solutions that are 0.01 *M* or greater in thioglycolate shows no dependency upon the age of the iron solution. The discussion below concerns only these latter solutions, where the results are not complicated by the age of the iron solution.

The variation of *k* in equation 1 with the total concentration of thioglycolate, [TGA], can be represented by the equation

$$k = k_1' + \frac{k''}{[\mathrm{TGA}]} \qquad (2)$$

The constant, k_1', is independent of *p*H while k'' is a function of *p*H. As the *p*H increases, k'' first decreases then increases. The increase on the more alkaline side follows the conversion of the predominant form of the thioglycolate in the solution from the uni-valent ion, $HSCH_2CO_2^-$, to the divalent ion, $^-SCH_2CO_2^-$. Henceforth, these species will be represented as RSH^- and $RS^=$.

The increase in k'' on the less alkaline side of the minimum follows the increase in the hydrogen ion concentration of the solution.

The dependency of *k* upon the concentration of hydrogen ion and thioglycolate can be represented by the equation

$$k = k_1' + (k_2' + k_3'[\mathrm{H}^+])/[\mathrm{RSH}^-] \qquad (3)$$

or, in terms of the total concentration of thioglycolate

$$k = k_1' + (k_2' + k_3'[\mathrm{H}^+])\left(\frac{[\mathrm{H}^+] + K_{2a}}{[\mathrm{H}^+]}\right)\Big/[\mathrm{TGA}] \quad (4)$$

where K_{2a} is the second dissociation constant of thioglycolic acid.

Values of K_{1a} and K_{2a} equal to 3.3×10^{-4} and 1.2×10^{-10} were determined by titrating at 25° a solution of 0.05 *M* thioglycolic acid in 0.5 *M* sodium nitrate with 0.728 *M* sodium hydroxide. This value of K_{2a} was used to calculate using the method of least squares values of k_1', k_2' and k_3' equal to $1.33 \pm 0.06 \times 10^{-3}$ A.$^{-1}$ min.$^{-1}$, $2.30 \pm 0.17 \times 10^{-5}$ MA.$^{-1}$ min.$^{-1}$, and $5.0 \pm 0.1 \times 10^4$ A.$^{-1}$ min.$^{-1}$ in solutions at an ionic strength, *I*, equal to 0.58 ± 0.03 and at 25°. Calculated values of *k* using these figures are presented in the next to the last column of Table I. The agreement with the observed values is quite good.

Effect of Ionic Strength and Temperature.—The last three experiments in Table I were carried out at 25° in solutions having an ionic strength of about 0.30 and *p*H 9.58. The results yield values of k_1' and k'' equal to 0.91×10^{-3} A.$^{-1}$ min.$^{-1}$ and 3.8×10^{-5} MA.$^{-1}$ min.$^{-1}$. Thus, both of these constants are seen to decrease with ionic strength. The decrease in k'' consists of a decrease in both K_{2a} and in the sum $k_2' + k_3'$ [H$^+$].

The data and results of experiments run at 15, 30, 35 and 40 ± 0.5° at an ionic strength of about 0.58 are presented in Table II.[13] As at 25° the rate of bleaching was found to be second order with regard to the absorbance with no indication of a back reaction over the period of observation (420 minutes). The data at 15°, yield a value of k_1' equal to $4 \pm 1 \times 10^{-4}$ A.$^{-1}$ min.$^{-1}$. Considering this value and comparing the values in Table II at 15°, with those obtained for the corresponding solutions at 25° in Table I it can be seen that k'' also decreases with temperature. The change in k'' is the summation of changes in k_2', k_3' and K_{2a}, in addition to the change in K_a for the ammonium ion.

The data at 35° shows that a plot of *k versus* the reciprocal of the thioglycolate concentration does not fit a simple linear equation. The value of *k* progressively increases with decreasing thioglycolate concentration. However, rough experiments at 30° indicate the same linear behavior as observed at 15 and 25°.

TABLE II

SPECTROPHOTOMETRIC RATE OF BLEACHING OF FERRIC THIOGLYCOLATE IN AIR-FREE AMMONIA BUFFERS AT 15, 30 35 AND 40°

[Fe(III)] initial = 2.04×10^{-4} *M*.

[NH$_4$NO$_3$] initial (*M*)	[NH$_4$OH] initial (*M*)	[TGA] (*M*)	*T*, °C.	A^0	*k*, A.$^{-1}$ min.$^{-1}$ × 10^3
0.45	0.85	0.100	15	0.780	0.69[a,b]
.50	.80	.050	15	.780	1.07
.52	.78	.030	15	.775	1.28
.53	.77	.020	15	.770	1.84
.50	.55	.050	15	.757	1.52[a,c]
.52	.53	.030	15	.787	1.86
.53	.52	.020	15	.770	2.9
.50	.80	.050	30	1.40	3.58
.50	2.0	.050	30	1.36	4.14
.45	0.85	.100	35	0.730	4.28
.50	.80	.050	35	.690	5.41
.52	.78	.030	35	.690	8.26
.53	.77	.020	35	.667	20.5
.50	.80	.050	40	1.39	9.17
.50	2.0	.050	40	1.39	9.78

[a] These data at 15° yield a value of k_1' equal to $4 \pm 1 \times 10^{-4}$ A.$^{-1}$ min.$^{-1}$. [b] These data obtained for solutions at 15° in which the ratio [NH$_3$]/[NH$_4^+$] at equilibrium was 1.36 yield a value of k'' equal to 2.7×10^{-5} MA.$^{-1}$ min.$^{-1}$. [c] These data obtained for solutions at 15° in which the ratio [NH$_3$]/[NH$_4^+$] at equilibrium was 0.91 yield a value of k'' equal to 4.4×10^{-5} MA.$^{-1}$ min.$^{-1}$.

Interpretation and Discussion

The data at 15 and 25° can be accounted for by assuming the following reactions

$$2\mathrm{FeOH(RS)_2}^{=} \underset{}{\overset{K_1}{\rightleftarrows}} \mathrm{Fe_2(OH)_2(RS)_4}^{-4}$$

$$\mathrm{Fe_2(OH)_2(RS)_4}^{-4} \xrightarrow{k_1} 2\mathrm{Fe(II)} + {}^{-}\mathrm{RSSR}^{-}$$

$$\mathrm{FeOH(RS)_2}^{=} + \mathrm{H_2O} \overset{K_2}{\rightleftarrows} \mathrm{Fe(OH)_2RS}^{-} + \mathrm{RSH}^{-}$$

$$\mathrm{FeOH(RS)_2}^{=} + \mathrm{Fe(OH)_2RS}^{-} \overset{K_3}{\rightleftarrows} \mathrm{Fe_2(OH)_3(RS)_3}^{-3}$$

$$\mathrm{Fe_2(OH)_3(RS)_3}^{-3} \xrightarrow{k_2} 2\mathrm{Fe(II)} + {}^{-}\mathrm{RSSR}^{-}$$

$$\mathrm{FeOH(RS)_2}^{=} + \mathrm{H}^+ \overset{K_4}{\rightleftarrows} \mathrm{FeOHRS} + \mathrm{RSH}^{-}$$

$$\mathrm{FeOH(RS)_2}^{=} + \mathrm{FeOHRS} \overset{K_5}{\rightleftarrows} \mathrm{Fe_2(OH)_2(RS)_3}^{-2}$$

$$\mathrm{Fe_2(OH)_2(RS)_3}^{-2} \xrightarrow{k_3} 2\mathrm{Fe(II)} + {}^{-}\mathrm{RSSR}^{-}$$

Because of the rapid rates of formation and discharge of the color[14] compared with the rate of bleaching, it is assumed that the various ferric thioglycolate complexes are in equilibrium. Presumably dimers formed by the reaction of molecules of Fe(OH)$_2$RS$^-$ and FeOHRS with themselves and each other also exist, but if the bleaching reaction were to take place at an observable rate through these, then a higher order dependency of *k* on the reciprocal of the thioglycolate concentration would be observed. This, indeed, may be the cause for the behavior observed at 35°.

Assuming the above reaction scheme, the rate of decrease in the concentration of FeOH(RS)$_2^=$ can be shown to be given by the expression

$$\frac{-\mathrm{d}[\mathrm{FeOH(RS)_2}^{=}]}{\mathrm{d}t} = \left\{k_1K_1 + \frac{k_2K_2K_3}{[\mathrm{RSH}^-]} + \frac{k_3K_4K_5[\mathrm{H}^+]}{[\mathrm{RSH}^-]}\right\}[\mathrm{FeOH(RS)_2}^{=}]^2 \quad (5)$$

The solubility[3] and spectrophotometric studies described above indicate that the absorbance

$$A = \epsilon l[\mathrm{Fe(III)}]_{\mathrm{total}} \sim \epsilon l[\mathrm{FeOH(RS)_2}^{=}] \quad (6)$$

Substituting equation 6 into equation 5, the rate of decrease of the absorbance can be shown to be given by the expression

$$\frac{-\mathrm{d}A}{\mathrm{d}t} = \frac{1}{\epsilon l}\left\{k_1K_1 + \frac{k_2K_2K_3}{[\mathrm{RSH}^-]} + \frac{k_3K_4K_5[\mathrm{H}^+]}{[\mathrm{RSH}^-]}\right\}A^2 \quad (7)$$

The value 3.93×10^3 M.$^{-1}$ cm.$^{-1}$ was obtained in air-saturated solutions for the extinction coefficient, ε, at 530 mμ. Using this value the products k_1K_1, $k_2K_2K_3$ and $k_3K_4K_5$ are calculated to be $8.7 \pm 0.4 \times 10^{-2}$ mole^{-1} sec.$^{-1}$, $1.5 \pm 0.1 \times 10^{-3}$ sec.$^{-1}$ and $3.3 \pm 0.1 \times 10^6$ mole^{-1} sec.$^{-1}$ from the experimentally determined values reported above for k_1', k_2' and k_3' in solutions at an ionic strength of 0.58 at 25°. Other values of the product k_1K_1 are calculated to be $2.6 \pm 0.6 \times 10^{-2}$ mole^{-1} sec.$^{-1}$ at an ionic strength of 0.58 at 15° and $5.9 \pm 0.4 \times 10^{-2}$ mole^{-1} sec.$^{-1}$ at an ionic strength of 0.30 at 25°.

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[13] The experiments at 15 and 35° were conducted by Mr. E. A. Heintz of these laboratories.

[14] When a solution of the red ferric complex is mixed with an excess of 0.1 *N* sodium hydroxide, the color is immediately discharged and ferric hydroxide precipitates.

Using the Brönsted equation[15]

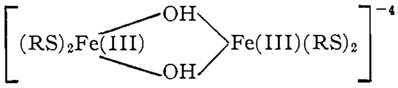
$$\log k = \log k_0 + \frac{2Z_AZ_B\alpha\sqrt{I}}{1 + \beta a\sqrt{I}}$$

it is calculated as an approximation that the value of k_1K_1 at zero ionic strength is 5.0×10^{-3} mole^{-1} sec.$^{-1}$ at 25° with the likely value of the mean effective ionic radius, a, equal to 6.0 Å. Here, both Z_A and Z_B are equal to minus two, α is equal to 0.509 and β is equal to 0.329.

The over-all energy of activation of k_1K_1 in solutions at an ionic strength of 0.58 is calculated to be about 20 ± 3 kcal.

The energy of activation of k in solutions which are 0.05 M in thioglycolate and at an ionic strength of 0.58 is found to be 16 kcal. both at pH 9.6 and 10.1.

Martell and Calvin[16] by analogy to the work of Michaelis and Schubert[17] on the Co(III)-thioglycolate complexes have postulated that a dimer of ferric thioglycolate can exist having the structure,



$$\left[(RS)_2Fe(III)\begin{matrix}OH\\ \\OH\end{matrix}Fe(III)(RS)_2\right]^{-4}$$

The dimers proposed in the above reaction scheme are probably of this same type, in which the iron atoms are connected by hydroxyl bridges.

Because of the low concentrations of $Fe(OH)_2$-RS^- and FeOHRS compared to that of FeOH-$(RS)_2^{=}$ the products k_2K_3 and k_3K_5 must be at least fifty to one hundred times as great as k_1K_1. This difference can be accounted for by the charge effect, the dimers of lower charge being more easily formed and less likely to dissociate. Quite possibly there also is a statistical effect due to the increase in the number of hydroxyl groups contributing to the increased reactivity of $Fe(OH)_2RS^-$. The larger number of hydroxyl groups would be expected to make collisions between molecules more fruitful toward dimer formation because of the increased possibility of bridge formation.

Orgel[18] has pointed out recently that the absorption spectrum of the ferric thioglycolate complex is due to charge transfer. Upon the absorption of energy, ferrous iron and a radical, RS^-, are formed within the hydration sheath of the original ferric thioglycolate molecule. The activated molecule can split apart, giving a first-order dependency of the rate of reaction upon the concentration of ferric thioglycolate. Evidently, because of the very rapid back reaction the first-order reaction is not observed in the diffuse light of the laboratory. It is interesting to note that each of the dimers that undergo the dark autoöxidation-reduction reaction contains a molecule of $FeOH(RS)_2^{=}$. In FeOH-$(RS)_2^{=}$ it is possible for two sulfur atoms to occupy adjoining positions on the central iron atom and in the dimer it is possible for both of these sulfur atoms to transfer simultaneously an electron to a ferric ion. The electron transfer to the far ferric ion can take place through the hydroxyl bridge according to the mechanism postulated by Taube and Myers.[19] Therefore, two $^-RS\cdot$ radicals can be formed in juxtaposition and these can react to form the disulfide $^-RSSR^-$, which then splits off.

At higher temperatures, because of the greater mobility, two radicals formed anywhere on the dimer may combine to form the disulfide.

Tanaka, Kolthoff and Stricks[20] have found for the ferric cysteinate complexes that under conditions similar to those used in the present work ferric iron is combined as $Fe(RS)_3^{-3}$ and $Fe(OH)(RS)_2^{-2}$, where $RS^{=}$ now refers to the cysteinate molecule. These authors report a value of 6.5×10^{-2} for the equilibrium constant, K_c, of the reaction

$$FeOH(RS)_2^{=} + RS^{=} \rightleftarrows Fe(RS)_3^{=} + OH^-$$

The rate of reduction of the ferric iron was found to be second order with regard to the total iron concentration with a rate constant, k, that is approximately inversely proportional to the reciprocal of the cysteinate concentration. Assuming that the autoöxidation-reduction reaction takes place through a dimer of $FeOH(RS)_2^{=}$, as with thioglycolate, and that $Fe(RS)_3^{=}$ does not react, the following rate equation can be derived.

$$\frac{-d[Fe]_t}{dt} = \frac{k_1K_1}{1 + \frac{K_c[RS^{=}]}{[OH^-]}}[Fe]_t^2 \qquad (8)$$

The constants, K_1 and k_1, are defined the same as with the analogous reactions described above for ferric thioglycolate.

The rate data of reference 20 for solutions at pH 10.30 to 10.35 and at an ionic strength of 0.13 to 0.14 M yield an average value of the product, k_1K_1, equal to 60 mole^{-1} sec.$^{-1}$ with less deviation than the average of the product, $k[RS^{=}]$, as reported by the previous authors.

The rate constant, k, is defined in reference 20 by the equation

$$\frac{-d[Fe(III)]}{dt} = k[Fe(III)]^2$$

Thus it appears that in alkaline solutions FeOH-$(RS)_2^{=}$ is the reactive species with ferric cysteinate as it is with ferric thioglycolate and that in both cases the oxidation-reduction reactions take place through a hydroxyl-bridged dimer.

The product k_1K_1 is about a thousand times greater for the ferric cysteinate system than for the ferric thioglycolate. The present data are too meager to elucidate this difference but it may be postulated that K_1 is greater for ferric cysteinate due to the possible reaction with hydrogen ion of the available basic group of the cysteinate molecule that is not used in chelate formation. This group may be either the $-CO_2^-$ or $-NH_2$ and reaction with hydrogen ion would result in a dimer of lower negative charge which would be expected to be more stable because of less electrostatic repulsion.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TURKU]

Low Valent Aluminum as a Product of Anodic Oxidation in Aqueous Solution

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In the electrolysis, between an aluminum anode and a platinum cathode, of various aqueous solutions, aluminum dissolves anodically with an initial mean valence number significantly lower than 3, and hydrogen is evolved at the anode. In solutions of oxidizing agents the valence number is lower than in halide solutions, and the amount of hydrogen given off is smaller. The lowest valence number observed, 1.67, was attained in the electrolysis of an aluminum chloride–aluminum nitrate mixture. Experiments with various oxidants in a divided cell revealed the presence in the anolyte of reduction products other than hydrogen. By means of a flowing electrolyte it was shown that in some instances the primary reducing agent can be transferred from one vessel to another. All of these facts may be interpreted in terms of primary anodic oxidation of aluminum partly to the unipositive state.

The anomalous behavior of an active aluminum anode was first observed almost a century ago by Wöhler and Buff,[2] who noted, during the electrolysis of an aqueous sodium chloride solution between aluminum electrodes of rather low purity, not only that hydrogen was evolved at the anode, but also that the dissolution of aluminum corresponded, on the assumption of oxidation to the tripositive ion, to a current efficiency of 130%. These authors specifically rejected the obvious explanation of a valence state of aluminum lower than 3. Turrentine,[3] in order to account for the evolution of hydrogen at an aluminum anode—termed by him an example of "reversed electrolysis"—postulated the existence of unipositive or dipositive aluminum, or both; he, however, made no direct determination of current efficiency. There appears to have been no systematic investigation of this apparent anomaly until Mazzitelli[4] repeated the experiments of Wöhler and Buff with an anode of pure aluminum, and obtained in one electrolysis an apparent valence number of 1.95. Meanwhile, other workers demonstrated the occurrence of parallel phenomena in acetone,[5] in liquid ammonia,[6,7] in anhydrous acetic acid[8,9] and in ethanol.[9] Indeed, the pattern of divergent behavior is so consistent that it is surprising to encounter the statement[10] that an aluminum anode in 15% aqueous sulfuric acid is so uniformly oxidized to a valence state of 3 that such a system may be used for coulometric measurements.

The present paper, which reports the results of a study of the electrochemical oxidation of an active aluminum anode in a number of different aqueous solutions under various conditions, definitely establishes, it is believed, the existence of an aluminum ion of low valence number. The fact that the mean valence numbers obtained are in many cases lower than 2, together with the electron structure of aluminum, make it almost certain that this ion is Al^+.

Experimental

The general method used in this investigation has been thoroughly described in a previous paper.[8] For most of the experiments, current was supplied through a simple undivided cell from a full-wave rectifier capable of furnishing up to 24 volts. The cathode consisted of a platinum foil. The aluminum rod used as anode, of 99.996% purity, was obtained from the Aluminum Company of America.[11] The electrolytes were of reagent quality, and were further purified by recrystallization when necessary. Except where otherwise noted, an inert atmosphere was maintained by the passage of nitrogen through the cell. The quantity of electricity passing through the circuit was determined by means of a silver coulometer.

In at least one electrolysis with each electrolyte, a second weighed piece of aluminum was immersed in the cell near the anode. In no case was there any appreciable decrease in weight of this test piece during the electrolysis. Hence there is no evidence of non-electrolytic corrosion of the aluminum.

In conformity with previous practice, the initial mean valence number V_i, of the aluminum ions resulting from anodic oxidation was determined by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 26.98}{107.88 \times \text{wt. of Al lost from anode}}$$

Results

Electrolysis in Halide Solutions.—A series of typical initial mean valence numbers obtained in an undivided cell with several halide electrolytes at varying concentrations and current densities is shown in Table I. In most instances, for a given set of conditions at least two (sometimes three)

TABLE I

ANODIC OXIDATION OF ALUMINUM IN AQUEOUS SOLUTIONS OF HALIDES

Electrolyte	Concn., moles/l.	Current density, amp./sq. cm.	Time, hr.	V_i
NaCl	0.05	0.0026	2.5	2.57
NaCl	.05	.0086	2.5	2.51
NaCl	.05	.0143	2.5	2.52
NaCl	.05	.0400	2.5	2.51
NaCl	.50	.0026	2.5	2.58
NaBr	.10	.0026	3	2.51
KI	.10	.0080	2	2.75

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