tions of Griffith[13] for an axially elongated Cu^{2+} complex and the optical data, we calculate $g_{\parallel} = 2.30$ and $g_{\perp} = 2.09$ if we use Gerritsen's[14] value of -660 cm.$^{-1}$ for the spin–orbit coupling constant.

The e.s.r. spectrum shows no nitrogen ligand hyperfine interaction which means either that (a) the complex has weak Cu–N interaction, (b) the ligand orbitals admixed to the metal ligand orbitals have no nitrogen s-orbital character, or (c) the metal is complexed by the NO_2^- oxygens. Gillard and Wilkinson[8] rule (c) out on the basis of the infrared spectrum, although the reason given actually excludes only M–N–O–M bridging nitrites. The possibility that choice (b) is correct offers interesting implications about the geometry of the complex but we do not feel that the data available warrant these speculations. Choice (a) seems to be preferred on the basis of the $Cu-NO_2$ wagging bands at about 450 cm.$^{-1}$ observed by Gillard and Wilkinson.[8] Fujita, *et al.*,[11] measured the M–N wag for a number of nitrite complexes and concluded that there was good correlation between the position of this band and the strength of the M–N band. Consequently, it appears that this is a weakly complexed copper—an idea that seems to be supported by the instability of this complex, but not by the molecular parameters derived from the e.s.r. spectrum. In order to calculate molecular bonding parameters for $K_3Cu(NO_2)_5$ from e.s.r. data, one needs to know the energies of the $xy \rightarrow x^2–y^2$ and $z^2 \rightarrow x^2–y^2$ transitions. Our values are 9700 and 12,000 cm.$^{-1}$, respectively, which are similar to those in anhydrous $Cu(NO_3)_2$.[15] Using the equations of Neiman and Kivelson[10] and the anisotropic e.s.r. data one obtains $\alpha = 0.81$, $\beta_1^2 = 0.67$, and $\beta^2 = 0.51$; where α, β_1, and β are molecular parameters that characterize the in-plane σ-bonding, in-plane π-bonding, and out-of-plane π-bonding, respectively. For comparison, anhydrous $Cu(NO_3)_2$, also studied in a glass,[15] gives $\alpha^2 = 0.6$, $\beta_1^2 = 0.96$, and $\beta^2 = 0.88$. These results mean the σ-bonds in anhydrous $Cu(NO_3)_2$ are much stronger than in $K_3Cu(NO_2)_5$, while the opposite is true for the π-bonds. The value for β^2 is the least reliable of the parameters given, since it depends on two quantities, $g_{\perp}$ and ΔE_{xz}, known to be unreliable. The other two results are more trustworthy and similar to the relevant values in copper phthalocyanine.[10] This latter observation is worth contrasting with the foregoing results of Gillard and Wilkinson[8] based on the assignment of the $Cu-NO_2$ wagging modes.

Conclusions

(1) The absence of an infrared band at 1485 cm.$^{-1}$ suggests that this compound may be pentacoordinated. However, the validity of this criterion is not well established and its negative aspect is disturbing.

(2) Magnetic, optical, and e.s.r. data have been shown to be self-consistent and demonstrate only that the complex has to be axially elongated. No further data can be derived about the geometry from the results. It is unfortunate that the N ligand hyperfine splittings could not be observed to determine the number of nitrogen ligands. Further work using other glasses is in progress since it may be possible to achieve better resolution in other media.

(3) The absence of nitrogen ligand hyperfine splitting and the Cu–N wagging band at 450 cm.$^{-1}$ indicate that the NO_2^- groups act as weak ligands in this case. These results, however, are in contrast with the molecular parameters derived from the e.s.r. measurements and with the known ability of NO_2^- ligands to give low-spin Co^{2+} complexes.[16,17]

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Electron Spin Resonance Studies of Sodium Dithionite and Sodium Formaldehyde Sulfoxylate

BY R. G. RINKER, T. P. GORDON, AND W. H. CORCORAN

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To provide information on the structure of sodium formaldehyde sulfoxylate in aqueous solution with particular relation to sodium dithionite, studies were made which are reported here. E.s.r. spectra of an aqueous solution of sodium dithionite, of solid sodium dithionite, and of an acidified sodium formaldehyde sulfoxylate solution are compared and discussed.

Experimental

In the preparation of the sodium formaldehyde sulfoxylate, material from Eastman Kodak with a melting point of 65° was recrystallized at about 0° from a water–methanol solution and dried at 50° under vacuum. The dry powder was used to prepare saturated solutions at room temperature in pure water, 1 *M* NaOH, and 1 *M* HCl. Sample tubes of Pyrex were filled with each solution. Tubes of sodium dithionite in aqueous solution and in powder form were prepared as previously noted.[1]

A calibration tube was made using a 0.1 *M* solution of manganous chloride in order to compare the resonance signals of the prepared samples with known values of the splitting factor and the gauss separation between resonance peaks for the free

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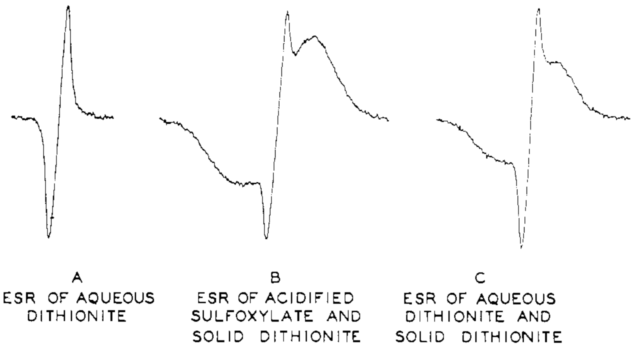

Fig. 1.—Electron spin resonance signals for various samples.

electron of the manganous ion. In the calibration runs the instrument settings for the sweep rate of the magnetic field were kept the same as those used in the examination of the experimental samples.

In the collection of the e.s.r. data an arbitrary signal voltage which was a first-derivative function of the phase-sensitive detection system of the e.s.r. apparatus was the ordinate in Fig. 1, and the abscissa was the magnetic field strength. Because the klystron frequency of the apparatus was held constant, the magnetic field strength was varied over the range in which resonance was expected to occur. The rate of magnetic scanning in relation to chart speed on the graphic recorder fixed the time constant from which the magnetic field strength at resonance and the resonance peak width were calculated. The scale factor for conversion of instrument readings to corresponding field-strength values was obtained from the calibration using the resonance peaks of manganous ions which have a peak-to-peak distance of 98 gauss.

Results

As reported,[1] sharp resonance for the oxygen-free, stabilized dithionite solution occurred at 3.365 kgauss with a fixed klystron frequency of 9.453×10^9 c.p.s. For the saturated dithionite solution, the width of the single resonance peak shown in Fig. 1A was approximately 1.3 gauss at half-peak height, and the spectroscopic splitting factor g was found to be 2.0051 based upon the comparison with the free-electron g value of 2.0023 for manganous ion[2] in aqueous solution.

Sodium formaldehyde sulfoxylate crystals did not exhibit paramagnetism. The saturated aqueous solutions in pure water or 1 M NaOH gave the same results. For the solution which was 1 M in HCl, however, there was a sharp resonance peak whose width and g value were indistinguishable from those obtained with the saturated dithionite solution. Figure 1B shows the resonance absorption obtained with the acidified sodium formaldehyde sulfoxylate solution and with the $Na_2S_2O_4$ powder[1,3] when both samples were placed in the cavity of the e.s.r. instrument. Two peaks superimposed upon one another can be distinguished. The inner peak corresponds to the liquid sample, and the outer peak shows the resonance absorption in the solid. Figure 1C shows the results obtained when both $Na_2S_2O_4$ powder and a saturated aqueous solution of sodium dithionite were in the cavity at the same time. Within the limits of experimental detection, the peaks shown in Fig. 1 are all for the same entity. There is reasonable evidence then to support the presence of SO_2^- ion in the acidified aqueous solution of sodium formaldehyde sulfoxylate.

The observed paramagnetism of the dried dithionite powder[1,4] is somewhat surprising since results in aqueous solution required interpretation that the undissociated dithionite dimer be diamagnetic. The work by Dunitz[4] indicates that the dithionite ion is not dissociated in the crystal. Although a completely unambiguous explanation of this phenomenon cannot be given at this time, it seems likely that extremely small amounts of SO_2^- or $NaSO_2$ are occluded or trapped in the crystals. Since an extremely small concentration of SO_2^-, that is about one part in one hundred thousand, would give the observed resonance, crystal-structure studies would not detect these occlusions.

The observed paramagnetism of acidic solutions of sodium formaldehyde sulfoxylate is also surprising since the unprotonated complex is diamagnetic in neutral and basic solutions. Evidently protonation of the ionized complex causes cleavage of the carbon–sulfur bond with liberation of the radical ion SO_2^- according to the expression

$$\mathrm{CH_2(OH)SO_2^-} \xrightarrow{\mathrm{H^+}} \mathrm{SO_2^-} + \mathrm{CH_2(OH)}\cdot \tag{1}$$

The $\mathrm{CH_2(OH)}\cdot$ subsequently reacts in this system to produce methyl alcohol, formaldehyde, formic acid, and various other carbon compounds. Additional support of the thesis that SO_2^- is obtained directly by acidification of sodium formaldehyde sulfoxylate is the fact that only sodium formaldehyde sulfoxylate and sulfite ion are formed from formaldehyde and dithionite in basic solution according to the over-all equation

$$\mathrm{S_2O_4^{2-}} + \mathrm{CH_2O} + \mathrm{OH^-} \longrightarrow \mathrm{CH_2(OH)SO_2^-} + \mathrm{SO_3^{2-}} \tag{2}$$

where it should be remembered that $S_2O_4^{2-}$ in solution is a source of SO_2^-. Heretofore three investigators[5–7] believed that acidification of the complex liberated the anion of sulfoxylic acid and regenerated formaldehyde as suggested in the equation

$$\mathrm{CH_2(OH)SO_2^-} \xrightarrow{\mathrm{H^+}} \mathrm{CH_2O} + \mathrm{SO_2^{2-}} + \mathrm{H^+} \tag{3}$$

Qualitative evidence for prevalence of eq. 1 over eq. 3 is found in the products observed in the decomposition of acidic solutions of sodium formaldehyde sulfoxylate, the nature of eq. 2, and finally in the fact that if eq. 2 is not of consequence the instability of pyridine nucleotide complexes,[7–10] which are similar to formaldehyde complexes, with dithionite and sulfoxylate in acidic media can be explained. Also explainable is the rapid decomposition of neutral and acidic solutions of formaldehyde sulfoxylate complexes in the

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presence of metal ions known to catalyze free-radical decompositions.[6]

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Kinetics of Aquation of *trans*-Dibromobis(ethylenediamine)chromium(III) Cation

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A considerable amount of kinetic data has been reported for the aquation of *cis*- and *trans*-dihalobis(ethylenediamine)cobalt(III) cations of the type $[Co(en)_2X_2]^+$ where X = F, Cl, or Br.[2] It has been of recent interest to compare these data with the aquation rates of corresponding chromium(III) complexes. To date the only three chromium analogs which have been studied are the *cis*-difluoro-,[3] *cis*-dichloro-,[4] and *trans*-dichlorobis(ethylenediamine)chromium(III)[5] cations. The paucity of kinetic data on chromium complexes of this type is undoubtedly related to the difficulties encountered in their preparation. In the present study we have attempted to extend knowledge in this area of coordination compounds by determining the pseudo-first-order rate constant and activation constants for the first step aquation of *trans*-dibromobis(ethylenediamine)chromium(III) cation, represented by the equation

$$trans\text{-}[Cr(en)_2Br_2]^+ + H_2O \longrightarrow [Cr(en)_2(H_2O)Br]^{+2} + Br^-$$

Experimental

trans-$[Cr(en)_2Br_2]_2S_2O_6$ was prepared according to the method of Pfeiffer.[6] The dithionate salt was converted to *trans*-$[Cr(en)_2Br_2]Br$ by triturating several times with concentrated HBr and drying overnight at 110°. The possibility of contamination of the bromide by dithionate was ruled out by observing the disappearance of the dithionate absorption band at 1250 cm.$^{-1}$ on a Beckman IR-5 spectrophotometer. Nitrogen was determined in this laboratory by Kjeldahl microanalysis. The remaining elements were also determined by microanalysis.[7] *Anal.* Calcd. for *trans*-$[Cr(en)_2Br_2]Br$: C, 11.67; H, 3.92; Cr, 12.63; Br, 58.25; N, 13.59. Found: C, 11.83; H, 3.68; Cr, 12.10; Br, 57.90; N, 13.46.

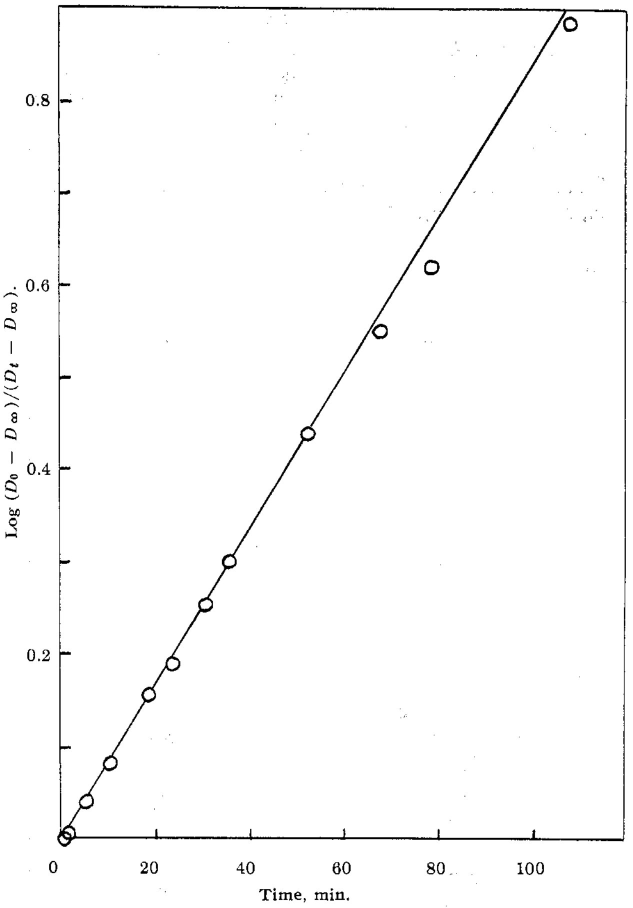

Fig. 1.—Data from a typical kinetic run at 25° in 0.1 *M* HNO_3.

Spectrophotometric data were obtained *in situ* using a Beckman DU spectrophotometer equipped with 1-cm. quartz cells. Temperature was maintained constant within ±0.04° by a thermostatically controlled constant temperature bath. A wave length of 610 mμ was selected for the spectrophotometric study since, at this wave length, there is a maximum difference in the molar absorbency indices of reactant (~34) and product (~9). A sufficient quantity of the salt for a 0.01 *M* solution was quickly dissolved in 0.1 *M* HNO_3, prewarmed to 25°. During the first 80 min., readings were taken at approximately 5-min. intervals and the final reading, D_∞, was recorded at a time corresponding to 10 half-lives. Samples were prepared for study at lower temperatures by quickly dissolving the salt in precooled 0.1 *M* HNO_3 and immediately filtering the solution. Readings were taken at constant intervals over 2–3 half-lives and the final reading again corresponded to the 10 half-life value.

Results and Discussion

Pseudo-first-order rate constants were obtained from the slope of plots, $kt = 2.303 \log (D_0 - D_\infty)/(D_t - D_\infty)$, as illustrated in Fig. 1. Rate plots were linear over 2 half-lives. In previous studies of this type, a positive deviation from linearity of the initial slope was observed after 1–2 half-lives due to interference of the second aquation step.[4,5b] No such deviation was observed in either the spectrophotometric or titration (*vide infra*) data obtained in this study. The value reported in Table I is an average of all runs at 25°.

The relative rates in Table I are in accord with the lower activation energy for the chromium complex. It was found that the rate constant for the aquation

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