

between the manifold of spin levels $S' = 0$ and 1 with the singlet level lying lowest could account for the decrease in μ_{eff} with decreasing temperature.¹⁶ Thus, the proposed dimeric structure is consistent with the spectral and magnetic properties of the carbonyl fluoride.

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Electrolytic Preparation of Nitrosodisulfonate Radical Anion

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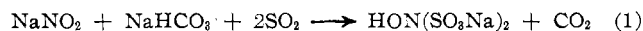
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Teuber, *et al.*,¹ have found that potassium nitrosodisulfonate is an extremely useful reagent for introducing an oxygen function into an aromatic nucleus, for example, the conversion of a variety of phenols and anilines to quinones.

The reagent itself, despite its potential utility in organic chemistry, has not become industrially important because its preparation has been tedious and expensive. The classical preparation^{1–3} of Frémy's salt involves the oxidation of a solution of hydroxylamine-disulfonate with inorganic oxidizing agents such as lead dioxide or potassium permanganate. This procedure necessitates the removal of the reduced metal oxides very carefully prior to the isolation of the Frémy salt.

We now wish to report a different, facile process by which the nitrosodisulfonate radical is formed in high yield. The disadvantages, already mentioned, which are inherent in the classical approach are completely eliminated by this procedure.

Hydroxylaminodisulfonate, conveniently prepared from sodium nitrite, sulfur dioxide, and sodium bicarbonate (eq 1), can be oxidized electrolytically to the Frémy radical in high yield (eq 2). It is necessary, however, to work in a solution buffered at approximately pH 9–11 since the nitrosodisulfonate radical is unstable under acidic conditions.

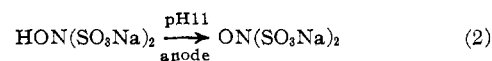


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The electrolytic oxidation is carried out in a conventional electrolytic cell, utilizing stainless steel anodes and cathodes. The cathode is separated from the anolite by a semiporous porcelain thimble. With continuous cooling a current of approximately 6 mA/cm² is maintained throughout the reaction at a potential of ca. 7–12 V. The appearance of a deep purple color indicates the formation of the Frémy radical which shows a characteristic absorption in the visible region at 540 m μ (1 N KOH, ϵ for the radical anion is 14.5). This band serves as an excellent quantitative tool for concentration measurements.

Isolation of the potassium salt can easily be achieved by addition of a saturated solution of KCl (eq 3). We



recommend, however, that the electrolytically prepared solution of the disodium salt be used as is, since two small samples of isolated Frémy's salt decomposed spontaneously at room temperature. At this point it is interesting to note the conflicting data in the literature concerning the stability of Frémy's salt. Raschig² stated that dried samples of potassium nitrosodisulfonate may *sometimes* be kept in a desiccator for 24 hr without decomposition. Harvey, *et al.*,³ stated that dry crystalline Frémy's salt is very stable. Teuber, *et al.*,¹ claimed that pure samples are stable indefinitely if stored in evacuated clean glass containers. These published statements appear to support our recommendation that the nitrosodisulfonate radical should be handled only in solution. This can be done conveniently since the half-life of a buffered solution (Na₂CO₃, pH 10) is approximately 2 weeks.

The Raman spectrum of a solution of Frémy's salt (ca. 5% in 10% Na₂CO₃ solution) shows the following nine absorption lines: 290, 450, 665, 930, 990, 1025, 1075, 1350, and 1420 cm⁻¹. The band at 1075 cm⁻¹ is due to the CO₃²⁻ ion. There are no differences in the Raman spectrum of authentic⁴ and that of electrolytically prepared Frémy's salt.

Experimental Section

Apparatus.—An NJE power supply (NJE Corp., Kenilworth, N. J.), Model RVC-36-25, 0–36 V dc, 0–25 A, was used. The anode was stainless steel mesh (ca. 16 mesh/cm²). The cathode was a stainless steel coil (1.5-mm wire diameter) which was set into a porous porcelain thimble filled to the level of the anolite with 10% sodium carbonate solution.

Procedure.—In a 1-l. resin jar, equipped with a mechanical stirrer, thermometer, gas-inlet tube, and ice cooling bath, were placed 15.0 g (0.217 mol) of sodium nitrite, 16.8 g (0.200 mol) of sodium bicarbonate, and 400 g of ice. With stirring, 25.6 g (0.40 mol) of SO₂ was bubbled into the initially heterogeneous mixture *via* the inlet tube which was placed approximately 2.5 cm from the bottom of the jar. The addition time was ca. 20 min. Near the end of the SO₂ absorption the light brown color faded almost completely. The SO₂ cylinder was mounted on a balance in order to have continuous control over the amount of sulfur dioxide added. The resulting solution of hydroxylaminodisulfonate had a pH of about 4. This clear and almost color-

(4) Obtained from Alfa Inorganics, Inc., Beverly, Mass. 01915.

less solution was stirred for ca. 10 min and 59.5 g (0.48 mol) of sodium carbonate monohydrate was added. The solution, pH 11, was ready for electrolytic oxidation which was carried out at 7–12 V and a current density of between 2 and 6 mA/cm² at ca. 12° (ice bath cooling). The formation of the nitrosodisulfonate radical was evidenced by the appearance of a deep purple color, absorbing at 540 m μ . After about 4.5 hr (depending on the current density) a quantitative absorption measurement [ϵ 14.5 for the radical anion $\cdot\text{ON}(\text{SO}_3)_2^{2-}$] indicated a 94% yield of the Frémy radical in the reaction mixture. It is recommended that this solution⁵ be used as is, although the potassium salt of the radical can be isolated as follows.

To the above cold purple solution was added dropwise, with stirring, a solution of 37.3 g (0.5 mol) of KCl in 100 ml of water. The orange-yellow potassium nitrosodisulfonate crystals precipitated readily. After refrigeration overnight the crystals were filtered by suction and washed with 100 ml of 1 N aqueous KOH. The damp crystals weighed 55 g.

A 1-g aliquot of the wet material, dried⁶ at room temperature in a desiccator over Drierite, gave 0.76 g of orange crystals. This corresponds to a 72% yield, based on sodium nitrite.

(5) Such a solution has a half-life of 2 weeks at 0°.

(6) On two occasions small samples of dried material decomposed spontaneously. It is suggested that the electrolyzed solution be used directly or that the isolated Frémy's salt be stored as a slurry in 1 N K₂CO₃ at 0°. If stored as a slurry in the indicated manner, 100-g lots have been stable for at least 4 months.

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Electron Paramagnetic Resonance Spectra of Some Low-Coordination Amido Compounds of Titanium and Chromium

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Electron paramagnetic resonance (epr) of transition metal ions is often difficult to detect at elevated temperatures by reason of low-lying excited states which facilitate rapid spin-lattice relaxations. Often times, liquid helium temperature has to be used to detect these resonances. However, if the compound has a ligand-field component of low symmetry, the energy separation between the ground state and the first excited state can be increased, and epr can be detected even at room temperature. Recently, Bradley, *et al.*,² reported the synthesis of tris(diisopropylamino)chromium(III). The compound is remarkable in that even with its unusually low coordination number it is monomeric in solution and in solid state. Paramagnetic compounds of this type should exhibit room-temperature epr spectra and large zero-field splitting when the spin multiplicity exceeds 2. We report here the epr spectra of amido compounds of Ti(III) and Cr(III).

The amido compounds of Ti(III) and Cr(III) were prepared from the respective chlorides and the appro-

priate secondary amine according to the procedure of Bradley and Thomas.³ The solvents were purified by vacuum distillation into a tube containing solid potassium and benzophenone to form a solution of K⁺(benzophenone)⁻. The solvent was subsequently distilled out of this solution into an epr sample tube containing the appropriate amido compound. Cr(*i*-C₃H₇)₂N)₃ was transferred by sublimation into the sample tube. The amido compounds of titanium cannot be sublimed. These were transferred into sample tubes under an inert atmosphere. The epr spectra were obtained with a Varian X-band spectrometer.

A dilute solution ($\sim 10^{-4}$ M) of Ti(*i*-C₃H₇)₂N)₃ in toluene, heptane, or tetrahydrofuran exhibits a single symmetric epr spectrum at temperatures between -85 and +25°. The *g* value is 1.987 and the line width is 20.9 G. Both these spectral parameters are insensitive to temperature variations. The powder spectrum obtained at -145° has an asymmetric line shape and a line width of 20 G indicating $g_{\parallel} \approx g_{\perp}$. No hyperfine interaction with ⁴⁷Ti, ⁴⁹Ti, or ¹⁴N could be resolved under these conditions. Substantially the same spectra were obtained for solutions of Ti[(C₆H₅)₂N]₃.

The epr spectra described above are similar to that given earlier for (π -C₅H₅)₂Ti(C₂H₅)₂.⁴ If we assume both Ti(*i*-C₃H₇)₂N)₃ and Ti[(C₆H₅)₂N]₃ to be monomeric like Cr(*i*-C₃H₇)₂N)₃, then all of the environment of the Ti(III) atom in these compounds must be nearly trigonal. According to the theory of Ti(III) in a trigonal field,⁵ the above epr results indicate the ground state to be ²A₁ and this ²A₁ state is separated from the excited ²E state by an energy of about 3000 cm⁻¹. A similar separation of 2000–4000 cm⁻¹ was found for Ti(acac)₃⁶ in which complex the cubic field contains a strong trigonal distortion.

At room temperature, solutions of Cr(*i*-C₃H₇)₂N)₃ exhibit single asymmetric epr spectra (*g* = 1.975 and line width is 10.8 G). At -195° the signal at normal field shows definite *g* anisotropy. The principal values are $g_{\perp} = 1.982$ and $g_{\parallel} = 1.966$. The g_{av} agrees with the experimentally determined value at 25°. At liquid nitrogen temperature there was found an intense signal at 1650 G having a line width of 63 G. No resonance was detected above the midfield signal up to 10,000 G.

The epr spectra of all Cr(III) compounds obtained so far can be fitted to the spin Hamiltonian⁷

$$\mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + D[S_z^2 - 5/4] + E(S_x^2 - S_y^2)$$

When the zero-field splitting is small compared to the microwave frequency, three resonance lines can be observed corresponding to transitions (³/₂ \leftrightarrow ¹/₂), (-¹/₂ \leftrightarrow ¹/₂), and (-¹/₂ \leftrightarrow ³/₂). The absence of a high-field line indicates that the low-field line does not arise from the (³/₂ \leftrightarrow ¹/₂) transition. Two alternative assignments are possible. In the first one, the zero-field splitting is assumed to be very large and the low-field

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