^{31}P spectra and when taken into account leads to satisfactory calculated ^{19}F spectra.[9]

Experimental Section

Tetrafluorodiphosphine–Borane, $F_2PPF_2 \cdot BH_3$.—It was found that when $F_2PPF_2 \cdot BH_3$ was prepared by the method of Morse and Parry[1] using a twofold excess of B_2H_6, the product was always contaminated by a small amount of the bis adduct, $H_3B \cdot F_2PPF_2 \cdot BH_3$, recently characterized by Paine and Parry.[2] The bis adduct was not easily removed by fractional distillation, and appeared to facilitate decomposition of the $F_2PPF_2 \cdot BH_3$ in the liquid state. The best yields of the desired mono adduct were obtained when only a slight excess of B_2H_6 was used. In a typical run, 3.50 mmol of F_2PPF_2[10] and 1.88 mmol of B_2H_6 were condensed together at −196° in a 1000-ml reaction bulb, which was then allowed to warm slowly to 25°. After 12 hr the volatile products were collected at −196° and purified by passing through traps held at −97 and −196°. A 2.45 mmol sample of $F_2PPF_2 \cdot BH_3$ (70% yield based on F_2PPF_2) was recovered from the −97° trap. The −196° trap contained unreacted B_2H_6, PF_3, and $PF_3 \cdot BH_3$. The products were characterized by their infrared spectra. A small amount of unidentified, nonvolatile, pyrophoric yellow oil remained in the reaction bulb.

Spectra.—Known amounts of purified $CFCl_3$ and $F_2PPF_2 \cdot BH_3$ were measured out as gases, condensed into nmr tubes, and the samples then sealed off *in vacuo*. Spectra were obtained in the −100 to 0° temperature range on a Varian instrument operating at 100, 94.1, 40.4, and 32.1 MHz for ^1H, ^{19}F, ^{31}P, and ^{11}B, respectively. The ^{19}F spectra were run with $CFCl_3$ as an internal lock signal. Spectra for the other nuclei were calibrated with audio side bands of known frequency.

Acknowledgment.—Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are grateful to Mr. Frank Parker for help with the nmr spectra and to Professor Sheldon Shore, Ohio State University, for use of the freezing-point cell and cryostat.

(9) The main features of the spectra can be fit with the computer program LAOCN3 [No. 111, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.] if H–F and B–F coupling features are neglected so that the system reduces to six spins. A comprehensive investigation of the fluorine spectra, including simplification by spin-decoupling, temperature dependence, and concentration dependence, is under further investigation.

(10) L. C. Centofanti and R. W. Rudolph, *Inorg. Syn.*, **12**, 282 (1969).

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Formation of Chlorine Dioxide by the Electrolytic Oxidation of Perchlorate Anion[1,2]

BY GARY E. GLASS*[3] AND ROBERT WEST

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Early studies using the electrolytic technique to produce radical chemical species employed perchlorate salts as electrolytes.[4,5] Oxidative electrolysis of those solutions yielded transient esr signals which were assigned to the perchlorate radical.[4,5] In this note we report the identification of chlorine dioxide by low-temperature esr and uv spectra as the reaction product resulting from the electrolytic oxidation of perchlorate salts in ethereal solutions.

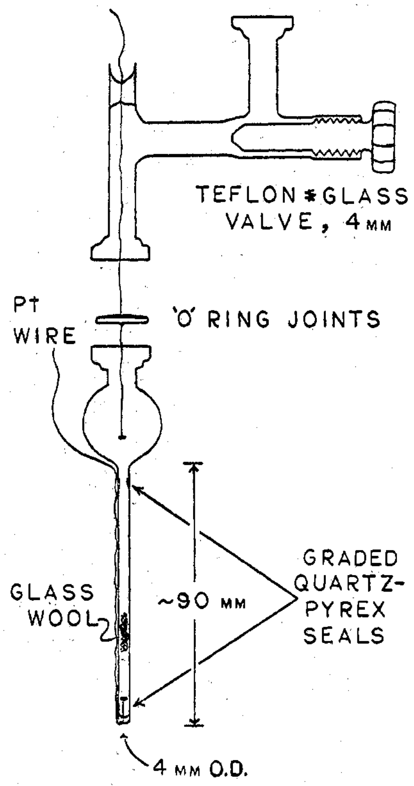

Figure 1.—Electrolytic cell for variable-temperature esr and electronic spectral measurements.

Experimental Section

Electrolysis Cell.—Electrolysis was carried out directly in the esr cavity or in the light path using the cell shown in Figure 1. The cell design allows both variable temperature esr and electronic spectral measurements to be made on either the anodic or cathodic compartments. Several milligrams of electrolyte, sodium perchlorate, or tetra-*n*-butylammonium perchlorate was placed in the mixing bulb and the cell assembled with a brass clamp. The electrolytic cell was then evacuated to $<10^{-4}$ Torr and solvent, tetrahydrofuran, dimethyl ether, or tetrahydrofuran–dimethoxyethane distilled into the mixing bulb. The glass wool plug separates the two electrolysis chambers and prevents connection. The cell was kept at constant temperature in a quartz dewar insert attached to a Varian V-4557 variable-temperature controller. The electrolysis cell is operated at a constant current, 0–40 μA, using a simple voltage divider, 300 V battery, and a microammeter.

Esr Spectra.—A Varian V-4502-13 spectrometer utilizing 100 kc modulation was used to observe the esr spectra. A dual cavity was used with a water solution of peroxylaminedisulfonate anion to record simultaneously spectral *g*-value calibrations. *g* values are believed accurate to ±0.00004 G. Coupling constants were determined on an X-Y recorder calibrated using tetracene radical cation and values reported by Carter and Vincow.[6] Line-sharpened spectra were obtained using the method according to Glarum[7] by adding partial third-derivative character to the first-derivative signal. This technique significantly decreased the amount of overlap in the recorded spectra and allowed more accurate determination of line positions.

Electronic Spectra.—A Cary 14 spectrometer was modified so that the quartz dewar insert attached to a Varian variable-temperature accessory could be inserted into the light path of the sample compartment.

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(3) Author to whom correspondence should be addressed at the National Water Quality Laboratory, Duluth, Minn. 55804.

(4) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959); *J. Amer. Chem. Soc.*, **82**, 2671 (1960).

(5) G. Cauquis and D. Serve, *C. R. Acad. Sci.*, **262**, 1516 (1966).

(6) M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 292 (1967).

(7) S. H. Glarum, *Rev. Sci. Instrum.*, **36**, 771 (1965).

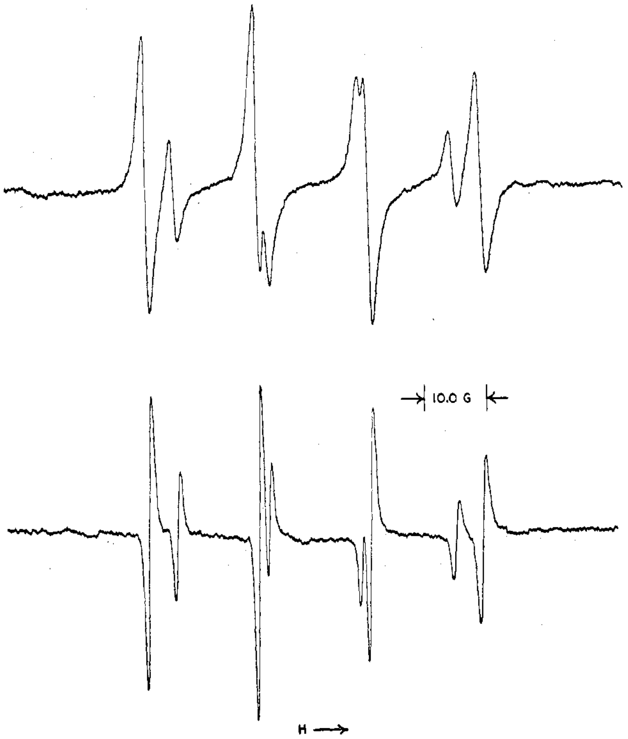

Figure 2.—Esr spectra of ClO_2 produced by oxidizing ClO_4^- in tetrahydrofuran solution at −110°: top, first-derivative spectrum; bottom, line-sharpened spectrum produced by adding third-derivative character.

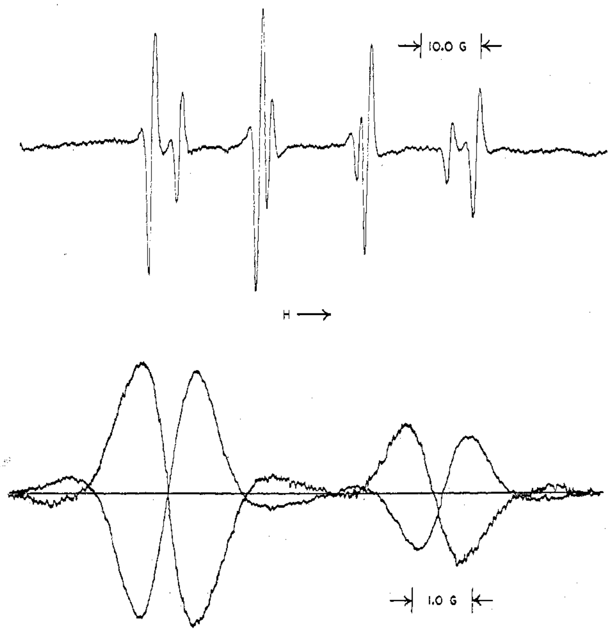

Figure 3.—Esr spectra of ClO_2 in solution: top, third derivative; bottom, superposition of outermost lines, expanded scale, showing nonexact symmetry.

Chlorine Dioxide.—ClO_2 was prepared by reacting potassium chlorate and oxalic acid in cold sulfuric acid.[8] The final product was resublimed into the mixing bulb of the cell under vacuum at Dry Ice temperature. Solvent, tetrahydrofuran, was then distilled in and the esr and uv spectra of the solution were recorded.

Results and Discussion

The esr and uv spectra of chemically prepared chlorine dioxide and the electrolytic oxidation product of perchlorate anion are identical. The spectra are shown in Figures 2–5. The hyperfine splittings (hfs) for the ^{35}Cl and ^{37}Cl isotopes were found to be 17.85 and 14.85 G, respectively. The ratio of the hfs for the isotopes, 1.2020, agrees well with the ratio of the nuclear magnetic moments, 1.2013. The g value was found to be 2.01016 for both isotopes with a difference of less than 0.00008 being undetectable. The esr spectra shown in Figure 2 are far better resolved than those reported previously for chlorine dioxide in a number of studies.[9–13] The peak-to-peak line width of the first-derivative signal decreased from 1.36 to 1.18 G for the extreme downfield line and from 1.61 to 1.48 G for the extreme upfield line as the temperature decreased from −115 to −130°. The line width dependence on temperature/viscosity has been discussed recently by McClung and Kivelson.[12]

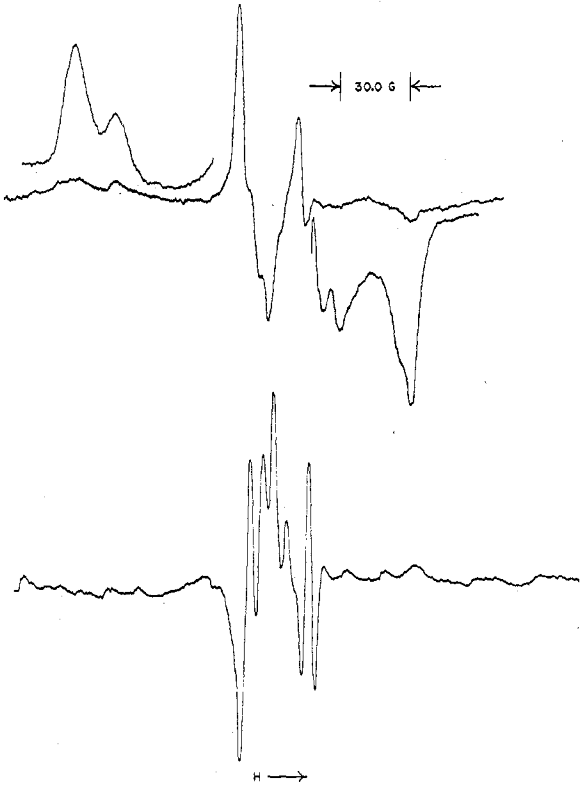

Figure 4.—Top: esr spectra of ClO_2 frozen in tetrahydrofuran, −180°. Bottom: third-derivative spectrum.

The sharp well-defined third-derivative signal is shown in Figure 3. The lower trace shows the resultant of folding the upper trace about its center and comparing the outermost lines. The nonexact symmetry of ^{37}Cl isotope lines is probably due to second-order differences in the isotropic hyperfine coupling constants.

Attempts to form and observe the esr spectrum of perchlorate radical[14–16] by electrolysis at −125° fol-

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[8] G. Brauer, "Handbook of Preparative Inorganic Chemistry," 2nd ed, Vol. I, Academic Press, New York, N. Y., 1963, p 301.

[9] P. W. Atkins, A. Horsfield, and M. C. R. Symons, *J. Chem. Soc.*, 5220 (1964).

[10] N. Vanderkooi and T. R. Poole, *Inorg. Chem.*, **5**, 1351 (1966).

[11] J. Q. Adams, *J. Chem. Phys.*, **45**, 4167 (1966).

[12] P. W. Atkins and D. Kivelson, *ibid.*, **44**, 169 (1966).

[13] R. E. D. McClung and D. Kivelson, *ibid.*, **49**, 3380 (1968).

lowed by quick freezing to −190° yielded only the spectrum of ClO_2 in a rigid lattice,[16,17] Figure 4.

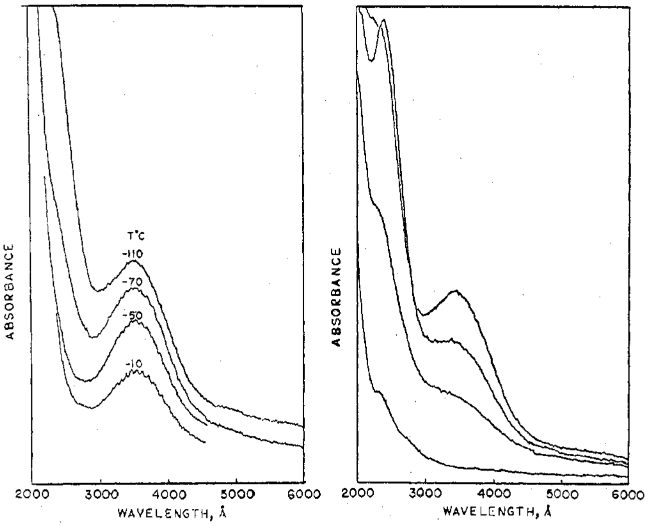

Figure 5.—Electronic spectra of ClO_2 in solution: right, increasing absorbance as electrolysis proceeds; left, decreasing absorbance with resolution of vibrational fine structure as the solution is warmed.

Ultraviolet spectra of a solution contained in the anode compartment of the cell are shown in Figure 5 (right). As electrolysis proceeds, the spectrum of chlorine dioxide increases in intensity as a function of time (30 min total at 30 μA). The absorbance maximum is at 355 nm and the spectrum is identical with that of chemically prepared ClO_2 dissolved in tetrahydrofuran. The absorbance decreases upon warming, Figure 5 (left), with increased resolution of vibrational fine structure being observed. The decrease in absorbance is due to reaction with the solvent, where in some cases the tetrahydrofuran polymerized in the cell at room temperature. The increased resolution of vibrational fine structure with increasing temperature is the reverse of what is observed for benzene in tetrahydrofuran. The uv spectrum of benzene in solution becomes extremely sharp and well defined as the temperature is lowered to −110°.

The electrolytic oxidation of perchlorate solutions yields, in addition to ClO_2, small bubbles of a colorless gas, oxygen. The oxidation of perchlorate ion proceeds according to the reaction

$$ClO_4^- \xrightarrow{-e} ClO_2 + O_2$$

with no evidence supporting the formation of the perchlorate radical from either esr or uv spectral measurements. The esr spectrum previously assigned[4,5] to the perchlorate radical was that of chlorine dioxide.

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Kinetics of the Reaction of Some First-Row Transition Metals with Protoporphyrin IX Dimethyl Ester

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Glacial acetic acid has been used as the solvent to study the kinetics of protoporphyrin dimethyl ester with some of the first-row transition metals, a continuation of earlier work in this medium.[1,2]

Experimental Section

Materials.—Metals were used as the divalent acetates. Manganese and zinc acetate were obtained from British Drug Houses Ltd., and cupric acetate was from Anachemia Chemicals Ltd. Glacial acetic acid was obtained from Allied Chemicals Ltd. and was found to contain less than 0.04% water as analyzed using the Karl Fischer reagent.

Protoporphyrin dimethyl ester was purchased from Sigma Chemicals Co., St. Louis, Mo. Its spectra in pyridine and chloroform were in good agreement with those published.[1,3]

Kinetic Measurements.—A Beckman DB-G recording spectrophotometer, with a thermostated cell compartment maintained to within ±0.1°, was used to follow the reaction.

Treatment of the Data.—An excess of metal was used. A graph was drawn of $-\log (A_\infty - A_t)$ against time, where A_∞ is the absorbance of the solution after all the porphyrin has been complexed, and A_t is the absorbance of the solution at any time t. If the reaction is first order in metal as well as in porphyrin, the rate constant is $k_1 = 2.303m/[M]$, where m is the slope of the graph and [M] is the average metal concentration for the points used in the graph. If the reaction is half order in metal, the rate constant is $k_{1/2} = 2.303m/[M]$. In most cases the excess of metal was >10, so that $[M] \simeq [M]_0$, the initial concentration of metal. However, for some runs, particularly those of zinc, the reaction was so fast that smaller excesses of metal had to be used. Even on these runs, although [M] might be as little as 3 times the initial porphyrin concentration $[P]_0$, more than half the porphyrin had complexed before the first readings were taken so that the graph was usually close to a straight line.

To check the validity of this procedure second-order plots were drawn for some of these runs with less than a tenfold excess of metal. It can be shown that

$$\log \frac{A_\infty - A_t + \dfrac{A_\infty - A_0}{[P]_0}([M]_0 - [P]_0)}{A_\infty - A_t} = \frac{([M]_0 - [P]_0)}{2.303}k_1t + \log \frac{[M]_0}{[P]_0}$$

In every case the value of k_1 obtained by using this equation graphically agreed very well with that obtained from the pseudo-first-order plot using an estimated value of [M].

Results

Table I gives data for the spectra of the metal complexes of protoporphyrin dimethyl ester in glacial acetic acid.

Isosbestic points were found for all the complexation reactions except that between cobalt and protoporphyrin dimethyl ester, where conversion of the Co^{2+} complex to the Co^{3+} complex produced a third absorbing species.

Figure 1 shows successive spectra of a solution of

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(14) T. Cole, *Proc. Nat. Acad. Sci. U. S.*, **46**, 506 (1960).

(15) J. R. Morton, *J. Chem. Phys.*, **45**, 1800 (1966).

(16) J. R. Byberg, S. J. K. Jensen and L. T. Muus, *ibid.*, **46**, 131 (1967).

(17) P. W. Atkins, J. A. Brivati, N. Keen, M. C. R. Symons, and P. A. Trevalion, *J. Chem. Soc.*, 4785 (1962).

(1) D. A. Brisbin and R. J. Balahura, *Can. J. Chem.*, **46**, 3431 (1968).

(2) D. J. Kingham and D. A. Brisbin, *Inorg. Chem.*, **9**, 2034 (1970).

(3) S. Granick, *J. Biol. Chem.*, **172**, 723 (1948).