Some Chemical and Physical Properties of the Effervescent Magnetic Peroxyborates. The Pseudo-Superoxides

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Abstract: Peroxyborate compounds, when heated carefully, can be modified so as to release appreciable quantities of gaseous oxygen when dissolved in water. In addition, these preparations exhibit unusually high paramagnetic susceptibilities. Because of these properties the preparations have been given the acronym EMPB (from Effervescent Magnetic Peroxy Borates). A monotonic relation was found between the amount of gaseous oxygen released on solution and the concentration of paramagnetic centers. Electron spin resonance measurements have resolved three magnetic centers and two of these have been identified as O_2^- and O_3^-; the third is a peroxyborate radical. A fourth center was resolved and identified in irradiated specimens. All centers are due to various chemically bound forms of oxygen. A quantitative discrepancy between the number of spins contributing to the resonances and the number of spins contributing to the susceptibility suggests the presence of O_2 molecules. Using the ^{18}O isotope, the path of oxygen atoms during preparation and aqueous decomposition was charted; only peroxide oxygen atoms end up in the evolved O_2 gas. The nature of the preparations was investigated using the techniques of X-ray, infrared spectra, reflectance spectra, nmr, and chemical analysis. A number of conclusions concerning structure and mechanism have been reached.

The fact that sodium peroxyborate compounds, when heated carefully, could be modified so as to release significant quantities of gaseous oxygen when mixed with water was discovered by Foerster.[2] Some hydrogen peroxide is simultaneously formed, and this only slowly decomposes. The discovery was extended to a variety of materials by Menzel[3] and others.[4] The effervescent behavior, which does not appear to depend on the nature of the cation but has only been reported for peroxyborates, is reminiscent of the superoxides.[5]

Recently the fact that these unusual compounds are strongly paramagnetic was communicated.[6] We present here additional experimental data on their physical and chemical properties. Similarities to and differences from the normal superoxides are pointed out for these "pseudo-superoxides," for which we will use the symbol EMPB (from Effervescent Magnetic Peroxy Borates).

Experimental Section

$H^{18}O^{18}OH$. Double-labeled peroxide was prepared by the electric discharge method.[7] The $H_2{}^{18}O$ starting material of 97–98% enrichment was supplied by YEDA Research and Development, Ltd. The resulting double-labeled hydrogen peroxide was diluted with 30% H_2O_2 of natural isotopic distribution supplied by FMC Corp.

$NaBO_3\cdot 4H_2O$. Samples containing a mixture of double-labeled and unlabeled peroxide groups were made from the hydrogen peroxide described above. The peroxide was added to a solution of sodium hydroxide and boric acid. The resulting crystalline precipitate was washed repeatedly with cold water and dried in air. By powder X-ray, the product was shown to be $NaBO_3\cdot 4H_2O$.

EMPB. Samples used in isotope studies were prepared by thermal treatment in a dry nitrogen atmosphere. The water of hydration in the $NaBO_3\cdot 4H_2O$ starting material was removed at 60°, and the EMPB samples were formed at 120–130°. Samples used in the esr and magnetic susceptibility studies were supplied by FMC Corp.

Ir Spectra. Spectra were recorded for $NaBO_3\cdot 4H_2O$, $NaBO_3\cdot H_2O$, and EMPB samples (in a KBr host matrix) using a Perkin-Elmer 337 spectrophotometer. $NaBO_3\cdot H_2O$ and EMPB samples were prepared for spectra in a dry nitrogen atmosphere.

Mass Spectra. Spectra were recorded with an Hitachi RMU 6D mass spectrometer.[8] Peak heights for the m/e range 28–36 were recorded. The isotope distribution in the molecular oxygen was determined from the peak heights at m/e values of 32, 34, and 36

Magnetic Susceptibility. The Gouy method was used for the susceptibility measurements. All values of χ_g (gram susceptibility) reported are the average of values obtained at four field strengths. For low-temperature measurements a calibrated copper–constantan thermocouple with four junctions in the low-temperature dewar was used to determine the sample temperature.

Magnetic Resonance Experiments. The electron spin resonance (esr) investigations of the preparations were carried out at microwave frequencies near 9.1 and 35 GHz[9] by means of a Varian Model V-4500 X-band spectrometer and a Varian Model V-4561 Ka-band bridge accessory. The magnetic field was modulated at 100 kHz, and the data were displayed on a recorder as the first derivative of the absorption spectrum. The g values[10] were assigned to spectral

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[1] (a) Department of Chemistry, Brown University; (b) Department of Physics, Brown University; (c) University Fellow, 1964–1965; (d) Du Pont Teaching Fellow, 1966–1967; (e) Oak Ridge National Laboratory.

[2] F. Foerster, *Z. Angew. Chem.*, **34**, 354 (1921).

[3] H. Menzel, *Z. Anorg. Allgem. Chem.*, 167, 193 (1927).

[4] (a) T. I. Taylor and G. G. Taylor, *Ind. Eng. Chem.*, 27, 672 (1935); (b) G. Schoenber, British Patent 312,664 (April 10, 1930); (c) H. Kloeper, to DEGUSSA, German Patents 528,873 (June 25, 1931) and 534,282 (Sept 10, 1931); (d) G. Bretschneider, to DEGUSSA, German Patent 855,737 (Feb 21, 1957).

[5] Reviews of superoxide compounds and their behavior have recently been published: (a) A. W. Petrocelli and D. L. Kraus, *J. Chem. Educ.*, 40, 146 (1963); (b) N. G. Vannerberg, *Progr. Inorg. Chem.*, **4**, 125 (1962); (c) I. I. Vol'nov, "Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals," Plenum Press, New York, N. Y., 1966.

[6] (a) R. Bruce, J. O. Edwards, D. L. Griscom, R. A. Weeks, L. R. Darbee, W. DeKleine, and M. McCarthy, *J. Am. Chem. Soc.*, **87**, 2057 (1965); (b) D. Griscom, R. A. Weeks, R. Bruce, and J. O. Edwards, *Bull. Am. Phys. Soc.*, 10, 614 (1965), Paper No. FE 6.

[7] R. E. Ball, J. O. Edwards, and P. Jones, *J. Inorg. Nucl. Chem.*, **28**, 2458 (1966).

[8] The mass spectrometer was purchased under a generous NSF equipment grant to Brown University.

[9] The notation "Hz" has the conventional meaning of cycles per second.

[10] Here, the measured g value is defined by $g = h\nu/\beta H$, where h = Planck's constant, ν = spectrometer frequency, β = Bohr magneton, and H = magnetic field position of the feature in question.

features according to standard procedures; detailed discussions of these measurements are given elsewhere.[11,12] Samples were prepared for esr investigation by sealing small amounts of material in evacuated fused-quartz tubes. Most X-band measurements were performed at either room temperature or 77°K. Measurements in the helium temperature range (4.2–1.4°K) were made on a superheterodyne X-band spectrometer.

The ^{60}Co γ irradiations were carried out with samples immersed in liquid nitrogen; the samples were investigated by esr techniques both before and after warming to room temperature. Electron irradiations were accomplished by Van de Graaf accelerators operated by the Air Force Cambridge Research Laboratories or by Electronized Chemical Corp.; these were carried out at 2.2 MeV and ambient temperatures between 20 and 40°.

Esr spin-concentration measurements were performed by means of comparison techniques,[13] although specialized procedures[11,12] were devised to handle cases where the spectrum consisted of a superposition of resonances of differing types. Determinations of *relative* spin concentrations (comparing the same resonance in two different samples) could be made to $\pm 10\%$ accuracy. The estimated accuracy of *absolute* measurements is usually $\pm 30\%$, although in some cases absolute determinations could have been in error by as much as a factor of 2 due to other complications.[11]

Nuclear magnetic resonance (nmr) studies of the boron-11 nucleus were performed on a Varian V-4200B wide-line spectrometer, employing a boron-free probe and operating at a frequency of 16 MHz in the absorption mode. Details are given elsewhere.[11]

Results

Preparations. The samples used in this study were prepared at FMC Corp. or at Brown University. Starting with $NaBO_3\cdot 4H_2O$ (the so-called "tetrahydrate" of commerce),[14] a compound of formula $NaBO_3\cdot H_2O$ (the "monohydrate") is prepared by reversible dehydration in the temperature range 55–60°.

$$NaBO_3\cdot 4H_2O \rightleftharpoons NaBO_3\cdot H_2O + 3H_2O$$

Further *careful*[15] heating in the range 100–130° converts, over a period of several hours, the monohydrate to EMPB.

The nature of EMPB was found not to depend on the presence or absence of oxygen gas during the preparation; similar runs with a dry nitrogen gas stream and with a dry air stream passing through the solid during transformation gave identical products. Conversion of monohydrate to EMPB apparently occurs therefore by a slow, solid-state reaction. Samples which had been heated to a high fraction of conversion still showed, by powder X-ray patterns (*vide infra*), the presence of some unreacted monohydrate.

Solvent Reactions. The EMPB samples react rapidly with water to give $H_2O_2(aq)$ and $O_2(g)$, not necessarily in 1:1 ratio. As expected the samples with highest percentage gaseous oxygen are more reactive in their effervescence and in their solution process. All samples give a pH of about 10 in aqueous solutions and give a positive starch–iodine test for H_2O_2 in water. Concentrated aqueous solutions of EMPB deposited (after effervescence) crystals of $NaBO_3\cdot 4H_2O$. These were identified by their X-ray powder pattern.

Table I. Apparent Molecular Weights of Samples from EMPB Preparation No. A-1

Sample[a]	H^+,[b] g/equiv	OH^-,[b] g/equiv
1	85.15	85.82
2	88.85	90.58
3	89.85	89.91
4	86.90	86.30

[a] Each weighed sample was dissolved in water in a volumetric flask and brought up to mark. From this solution, separate aliquots were taken for the titrations. [b] These values are chemical formula weights (CFW); see Table II.

Table II. General Properties of Some Preparations

Preparation no.	CFW[a]	% gO[b]	% aO[c]	% ox. power[d]
A-1	88	2.2	7.1	9.3
A-2	89	4.7	8.1	12.8
A-3	92	8.4	6.8	15.2
B-4	91	3.96	11.15	15.11
B-16	94	7.00	6.91	13.91
C-7[e]	..	3.5	5.41	8.91
C-10[e]	..	8.0	3.99	11.99
C-18[e]	..	10.0	2.50	12.50

[a] Chemical formula weight; average weight (of several samples) in grams of EMPB containing one gram formula weight of boric acid. [b] Weight of gaseous oxygen released per gram of EMPB, times 100. [c] Weight of "active oxygen" (titrated as hydrogen peroxide from iodometric procedure) released to solution per gram of EMPB, times 100. [d] Total available oxidizing power per gram of EMPB, times 100. This is the sum of % gO and % aO. For $NaBO_3\cdot H_2O$ the theoretical value is 16.0%. [e] Preparations from the same sample of $NaBO_3\cdot H_2O$ were heated varying lengths of time at 130–135° under static dry N_2 atmosphere. Pressures were 0.25 to 0.5 atm. Analysis for "active oxygen" was by ceric ion titration

The samples were insoluble in many solvents (benzene, carbon tetrachloride, dimethyl sulfoxide, ethanol, diethyl ether, dimethylformamide, and nitrobenzene). No gas evolution was observed. (Presumably care should be exercised in experiments of this type since the possibility of an explosion seems real.)

Analyses. Chemical analyses of many samples have been carried out. The alkalinity was determined by titration with standard acid, and the total boric acid content was determined by the addition of excess acid followed by pH titration with standard base in the presence and absence of mannitol. Gaseous oxygen released on dissolution of sample in water was determined by a manometric procedure. The remaining active oxygen in the resulting aqueous solution was determined by iodometric method for hydrogen peroxide.

As would be expected from the starting material which has one sodium atom per boron atom, the titrations for alkalinity and boric acid agree well for each sample,[16] but the results obtained from one sample to another of the same preparation are significantly more variable than can be explained by the usual error in these analyses; some of these data for one preparation

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(11) D. L. Griscom, Ph.D. Thesis, Department of Physics, Brown University, June 1966.

(12) D. L. Griscom and P. J. Bray, submitted for publication.

(13) R. H. Silsbee, *Phys. Rev.*, **103**, 1675 (1956).

(14) Unless otherwise noted the formulas given are to indicated stoichiometry but not structure. The formulas and names are those commonly employed by peroxide chemists.

(15) If carried out rapidly and/or at high temperature, a vigorous exothermic decomposition of peroxyborate monohydrate to give sodium

$$2NaBO_3\cdot H_2O \longrightarrow 2NaBO_2 + O_2 + 2H_2O$$

metaborate, steam, and oxygen obtains. The EMPB is somewhat more resistant to decomposition than its precursor, the monohydrate.

(16) Since the effervescent compounds are not homogeneous, it is appropriate to employ the word *preparation* for a batch of material made in a single experiment and the word *sample* to designate the small part of a preparation that was used for a specific determination.

are presented in Table I and similar results were obtained with other preparations. Such behavior is, of course, not unexpected for heterogeneous solids. The results are reported in terms of apparent molecular weight (*i.e.*, the weight of sample in grams that contains one formula weight of sodium borate). By way of comparison, the molecular weight of the monohydrate when calculated on the same basis is 99.8, and the corresponding weight of the hypothetical anhydrous sodium peroxyborate is 81.8.

In Table II, data on the chemical behavior of a number of preparations are presented. It is noted that (a) all of the CFW values lie between those of the monohydrate and the anhydrous peroxide, (b) in some cases, a significant amount of % ox. power is lost in the conversion from monohydrate to EMPB, (c) unlike KO_2, there may be little "hydrogen peroxide" left in a preparation which still has a significant % ox. power; however, this condition usually obtains when the reaction temperature exceeds 130°. In some preparations heated at moderate temperatures, $\approx 120°$, the per cent gaseous oxygen and per cent active oxygen appeared to asymptotically approach the same value. Though suggestive of a stoichiometric reaction analogous to that of superoxide with water, these results appear to be specific for only one carefully defined set of reaction conditions.[17] The per cent oxidizing power (sum of % gO and % aO) can increase slightly during the early stages of conversion of monohydrate to EMPB. The fact that the pressure over the solid in the reaction vessel increases in the early stages is in agreement with the analysis, provided some water is lost in this early stage.

X-Ray. A large number of EMPB samples were studied using powder X-ray techniques. In all cases, diffuse scattering with some sharp superimposed lines was observed. The lines detected were due to $NaBO_3 \cdot H_2O$, that is to say, unreacted starting material. Since some samples studied by X-ray had significant fractions converted to the effervescent form and since no new lines were observed, it is apparent that this form is not sufficiently crystalline to give coherent X-ray scattering.

Ir Spectra. The spectra of $NaBO_3 \cdot 4H_2O$, $NaBO_3 \cdot H_2O$, and several EMPB preparations have been recorded in the region 4000–400 cm^{-1}. The spectra of EMPB preparations show relatively sharp bands at 850, 770, and 650 cm^{-1}, characteristic of the $NaBO_3 \cdot H_2O$ starting material. These decrease in intensity and nearly disappear with increasing conversion. Bands which were already broad in $NaBO_3 \cdot H_2O$ appear increasingly broadened in the EMPB samples. No new spectral features were seen for any of the EMPB samples.

Visible Spectra. The EMPB preparations have an off-white appearance similar to but less intense than that of Na_2O_2. The color appears early in the heating process but levels off at about 10% conversion and does not intensify with continued heating. No significant reflectance spectrum in the range 7000–4000 Å was found.

Boron Nmr. Boron-11 broad line nmr data for solid borates (both crystalline and amorphous) have been found useful for distinguishing between three- and four-coordinate boron atoms.[18–21] Several EMPB samples were investigated, in addition to samples of (unreacted) $NaBO_3 \cdot H_2O$; in each case, a single, slightly asymmetric resonance line was observed with a width between derivative peaks of about 5 G. The relative narrowness of this line is consistent with the interpretation that the resonance arises from boron-11 nuclei situated in locally tetrahedral environments. Since all the experiments were performed at a relatively high frequency (ν_0 16 MHz), only a very crude upper limit[20] of 0.9 MHz can be placed on the quadrupolar coupling constant eqQ.

Searches for broader resonance lines (possibly indicative of three-coordinate borons) were carried out at high radiofrequency power levels, but no additional responses were observed. However, a negative result of this nature does not necessarily preclude the presence of some three-coordinate borons; up to 5% of the total borons could be in well-defined trigonal sites and still escape detection, while a larger number of three-coordinate borons could go unobserved if the trigonal sites were subject to random distortions (such as would be expected in the heterogeneous, amorphous material being investigated).

Quantitative measures of the number of four-coordinate borons can be made by measuring the areas under the absorption curves of the narrow resonance lines.[20,21] The nmr intensities per boron for samples of EMPB preparations with high gaseous oxygen contents (such as No. A-3) were 13–18% lower than the intensity per boron measured for unreacted $NaBO_3 \cdot H_2O$. Assuming that all of the borons in crystalline $NaBO_3 \cdot H_2O$ are four-coordinate, it was concluded[11] that between 13 and 18% of the borons in heavily reacted preparations have probably changed their coordination numbers from 4 to 3 in the course of the reaction. An alternative conclusion that 13–18% of the (still four-coordinate) borons have their nmr response broadened out or totally removed by hyperfine interactions with nearby paramagnetic electrons is not completely ruled out.

Magnetic Susceptibility. The room-temperature susceptibilities of six EMPB samples were determined. Figure 1 shows a plot of spin concentration, determined from room-temperature susceptibilities of six samples, against the % gO for these samples. (In this calculation, it was assumed that all magnetic centers had spin $^1/_2$.) The straight line gives an approximate fit to the data. The linear relation between gaseous oxygen and spin concentration as calculated from susceptibility measurements, and between gaseous oxygen and spin concentration from esr data (*vide infra*) over a large range of each parameter, indicates a good correlation of these disparate phenomena (*i.e.*, the magnetic properties and the ability to evolve oxygen when dissolved in water).

The susceptibilities of five EMPB samples have been measured as a function of temperature between 77 and 300°K. A linear relation between the reciprocal of

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(17) L. R. Darbee, FMC Corp., private communication.

(18) A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **29**, 984 (1958)

(19) P. J. Bray, J. O. Edwards, J. G. O'Keefe, V. F. Ross, and I. Tatsuzaki, *ibid.*, **35**, 435 (1961).

(20) P. J. Bray and J. G. O'Keefe, *Phys. Chem. Glasses*, **4**, 37 (1963).

(21) S. Greenblatt, Ph.D. Thesis, Department of Physics, Brown University, 1965.

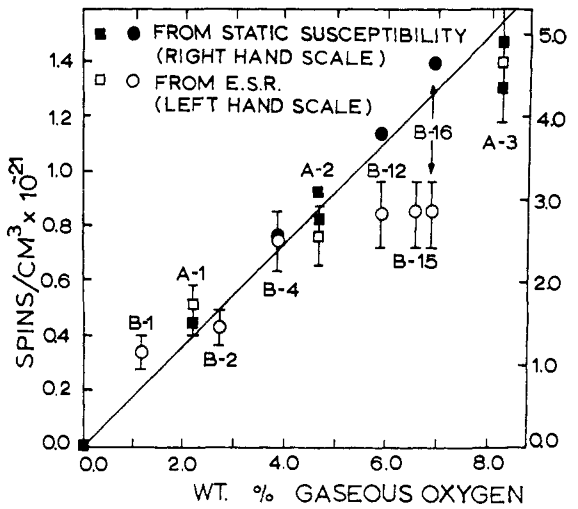

Figure 1. Density of unpaired electron spins in several thermally reacted sodium EMPB preparations *vs.* the weight per cent gaseous oxygen evolved on solution in water. Esr data are the X-resonance concentrations. The susceptibility data were taken from ref 21. The scatter in susceptibility data for the "A series" samples has been attributed to sample heterogeneity.[21] The error bars apply to *relative esr* spin-concentration measurements only; error estimates take into account variations in sample packing factor and spectrometer gain, as well as sample heterogeneity. Gaseous oxygen determinations were performed at FMC Corp. Error bars for weight per cent gaseous oxygen are not included here. However, the error in this measurement is estimated to be ±0.5 wt %.

the susceptibility and the absolute temperature was observed for each preparation in the temperature range studied. No significant dependence of susceptibility upon field strength was observed at any temperature. Figure 2 shows the plots of $1/\chi_g$ *vs.* T for these preparations. The extrapolated values of θ in the Curie–Weiss law

$$\chi = C/(T - \theta)$$

were obtained by a least-squares fit. In every case, the value of θ was negative as may be seen in the caption for Figure 2.

Electron Spin Resonance Results. All thermally prepared EMPB preparations were found to display three distinct types of resonances, each centering on or near $g = 2.0$ but otherwise differing radically in such aspects as shape, width, temperature dependence (see Figure 3), and behavior with frequency. At X-band frequencies, the broadest response shows a width between derivative maxima of the order of 3000 G, the narrowest shows a width of the order of 30 G, and the third response covers a field range of the order of 300 G; these have been denoted[6,11,12,22] the X, Y, and Z resonances, respectively. It is found that irradiation by ^{60}Co γ rays or by 2.2-MeV electrons results in the appearance or intensification of each of these types of esr responses in either reacted or unreacted peroxyborate materials. In addition, however, these irradiations are found to induce copious numbers of a fourth type of paramagnetic center, the spectrum of which has been designated the Z′ resonance.[11,12] The latter resonance also appears in the vicinity of $g = 2.0$ and, while bearing a slight resemblance to the Z resonance, covers a field range of only 90 G at X-band. Unirradiated noneffervescent peroxyborates exhibit no esr spectra. The four types of esr spectra are discussed individually in the following sections.

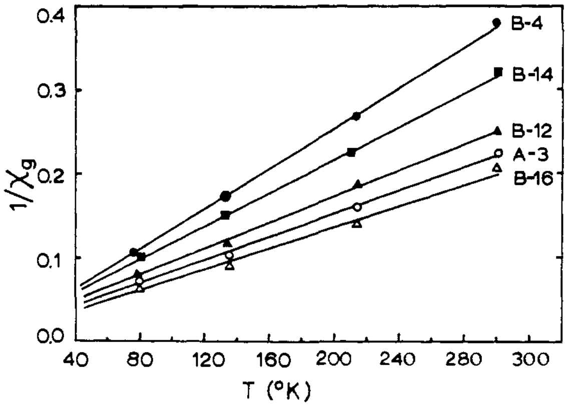

Figure 2. Relationship between absolute temperature and reciprocal of χ_g for five EMPB preparations. Extrapolated values of θ obtained by least-squares fit are: B-4, $\theta = -19$°K; B-14, $\theta = -35$°K; B-12, $\theta = -17$°K; A-3, $\theta = -24$°K; B-16, $\theta = -35$°K.

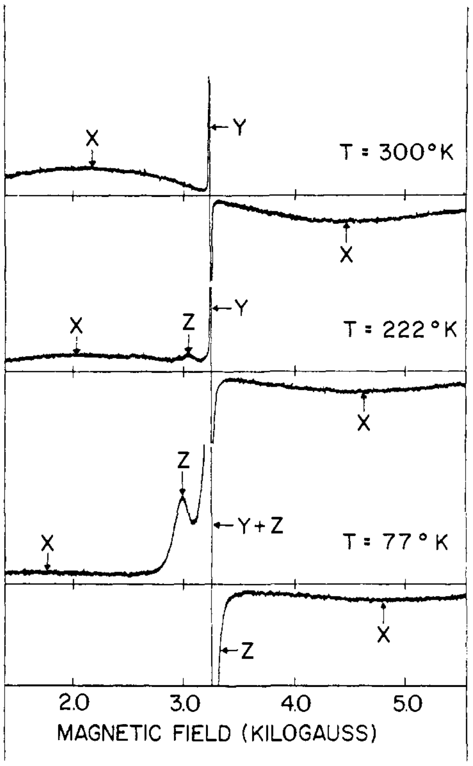

Figure 3. First derivative of the esr absorption in preparation A-3 obtained at X-band for three temperatures and otherwise identical instrument parameters. The spectra shown represent superpositions of resonances due to three distinct types of paramagnetic centers, the characteristic responses of which have been denoted the X, Y, and Z resonances (see text).

The X Resonance. Esr studies were undertaken in an effort to identify the magnetic species responsible for the large spin densities indicated by Gouy balance measurements. The extremely broad X resonance, which is by far the most intense esr response and is

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(22) R. Bruce, M.Sc. Thesis, Department of Chemistry, Brown University, June 1965.

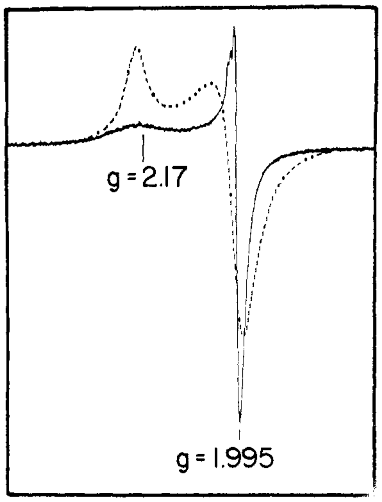

Figure 4. The Z resonance in a potassium EMPB sample as observed at X-band and 77°K. The small amount of structure on the high point of the central derivative peak is due to a superposition of the Y resonance (in sodium EMPB specimens the interference between the Y and Z resonances is seen to be more severe). The dashed curve provided for comparison is the observed spectrum for O_2^- in sodium peroxide.

centered on $g = 2.0$, accounted for approximately one-third of the susceptibility. Figure 1 shows a plot of the X-resonance spin concentrations *vs.* gaseous oxygen content for a series of preparations.

The X resonance is found to be nearly Lorentzian in shape with a peak-to-peak width approximately proportional to the -0.4 power of absolute temperature in the region 77–373°K. This width (≈ 2500 G at room temperature) is too great to be accounted for by dipole–dipole interactions alone (even at spin concentrations of the order of 10^{21} cm^{-3}), and the unusual temperature dependence is counter to that which would be expected of a lifetime broadening mechanism. It is proposed, therefore, that the mechanism probably responsible for the observed line shape is an exchange interaction. Some arguments for this interpretation are given elsewhere.[11,12]

The X resonance is attributed to oxygen in some combined form. The principal evidence for this conclusion is (1) spin concentrations are approximately proportional to the amount of gaseous oxygen evolved (Figure 1); (2) impurity concentrations (*e.g.*, Cu, Fe, Cr, Mn, etc.) are less by a factor of at least 100 than the spin concentration; (3) hyperfine interactions with boron nuclei have not been detected. However, the X resonance bears no resemblance to the spectrum of O_2^- in either potassium or sodium superoxide[23] or in magnetically dilute sodium peroxide,[23,24] and studies described elsewhere[11,12] of the relative growth rates of the various centers with increasing electron irradiation have indicated that the X resonance center is probably more complex than a simple O_2^- ion.

Y Resonance. For thermally reacted material observed at room temperature, the narrow part (termed the Y resonance) of the esr spectrum appears to be due to a single paramagnetic species characterized by a g tensor with three unequal principal components and no resolved hyperfine structure. It is proposed that the weak Y resonance arises from the presence of interstitial O_3^- (ozonide) ions in concentrations typically of the order of 1×10^{17} cm^{-3}. Evidence for this interpretation is found in the comparison of the g values observed for the Y resonance with the values previously reported for O_3^- in solid sodium ozonide[24,25] and in γ-irradiated potassium chlorate,[26] as well as values given for the isoelectronic molecules SO_2^-[27,28] and ClO_2.[25,26] Other evidence is presented elsewhere.[11,12]

Z Resonance. The room-temperature esr spectra of thermally reacted preparations are seen to consist of only two well-defined resonances: the 2500-G-wide X resonance and the narrow Y response near $g = 2.0$ (see two preceding sections). Only a very weak, poorly resolved bump in the vicinity of $g = 2.13$ suggests that another center may be present. As the temperature is lowered toward 77°K, the diffuse bump grows in amplitude by a factor of nearly 40, with the center of this feature generally shifting to the vicinity of $g = 2.17$ (see Figure 4). Accompanying the growth of this bump, or shoulder, is the appearance of a sharp negative derivative excursion at $g = 1.995$. In most preparations investigated, the height of the $g = 1.995$ excursion bears a constant ratio of about 13:1 to the height of the $g = 2.17$ shoulder, and in *potassium* peroxyborate[29] materials both responses are easily distinguishable from the X and Y resonances at 77°K. It is concluded, therefore, that both new spectral features belong to a third type of resonance, distinct from the X and Y varieties. This new spectrum is referred to as the "Z resonance."

The Z resonance shows striking similarities to the spectrum of O_2^- in sodium peroxide, with the values $g_{\parallel} = 2.175 \pm 0.005$ and $g_{\perp} = 2.002 \pm 0.005$ given by Bennett, *et al.*,[30] for the latter radical corresponding closely to the broad shoulder and sharp peak, respectively. The g-value theory of O_2^- in solids, as worked out by Känzig and Cohen,[31] shows that $g_{\parallel}$ is strongly dependent on the ratio λ/Δ, where λ is the spin–orbit coupling constant and Δ is the splitting of the $2p\pi_g$ electronic level effected by electrostatic or covalent interactions with neighboring atoms, while $g_{\perp}$ is only weakly dependent on λ/Δ. It is suggested here that in the EMPB preparations (which are both amorphous and somewhat heterogeneous) there exist ensembles of O_2^- ions which experience random distributions of

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(23) (a) J. E. Bennett, D. J. E. Ingram, M. C. R. Symons, P. George, and J. S. Griffith, *Phil. Mag.*, 46, 443 (1955); (b) R. A. Weeks and M. M. Abraham, private communication, 1967.

(24) J. E. Bennett, D. J. E. Ingram, and D. Schonland, *Proc. Phys. Soc.*, 69A, 556 (1956).

(25) A. D. McLachlan, M. C. R. Symons, and M. G. Townsend, *J. Chem. Soc.*, 952 (1959).

(26) P. W. Atkins, J. A. Brivati, N. Keen, M. C. R. Symons, and P. A. Trevalin, *ibid.*, 4785 (1962).

(27) M. C. R. Symons, Advances Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 76.

(28) J. M. deLisle and R. M. Golding, *J. Chem. Phys.*, 43, 3298 (1965).

(29) It is appropriate here to point out that the majority of EMPB samples investigated had sodium as the cation. In these samples the Y resonance is found to merge with the $g = 1.995$ excursion, making separation of the Y and Z resonances difficult. In order to accomplish this separation, the sample chosen had potassium as the cation. All reported data pertain to sodium EMPB samples except when explicit reference is made to potassum-containing preparations.

(30) J. E. Bennett, D. J. E. Ingram, M. C. R. Symons, P. George, and J. S. Griffith, *Phil. Mag.*, 46, 443 (1955).

(31) W. Känzig and M. H. Cohen, *Phys. Rev. Letters*, 3, 509 (1959).

Table III. Oxygen Isotope Tracer Data

Source of oxygen	$\%^{32}O_2$	$\%^{34}O_2$	$\%^{36}O_2$	Total $\%^{18}O$
H_2O_2	97.3 ± 0.2	0.5 ± 0.1	2.2 ± 0.2	2.45
$NaBO_3 \cdot 4H_2O$	97.2 ± 0.2	0.6 ± 0.1	2.2 ± 0.2	2.50
EMPB reacted with water	95.5 ± 0.2	4.2 ± 0.2	0.3 ± 0.1	2.50
EMPB oxidized in solution by Ce(IV)	96.9 ± 0.2	0.9 ± 0.1	2.3 ± 0.2	2.75
Gas in contact with EMPB during its formation	96.3 ± 0.2	2.8 ± 0.2	1.0 ± 0.1	2.40

environments, giving rise to statistical variations of Δ over the ensemble. The resulting esr spectrum would then be characterized by a statistically weighted superposition of O_2^- powder patterns representing a wide range of $g_{\parallel}$ values and only a comparatively narrow range of $g_{\perp}$ values. By fitting procedures, it was shown[11,12] that the Z resonance may be reconciled with the O_2^- g-value theory of Känzig and Cohen.[31] Nevertheless it is still not possible on the basis of this agreement to say whether the particular radical being observed is interstitial O_2^- or a radical of the type RO_2 (which would obey essentially the same theory). The growth rate of the Z resonance in electron-irradiated specimens supports the "interstitial-O_2^-" hypothesis.[11,12] Typical spin concentrations for the Z resonance were found to be of the order of 10^{19} cm^{-3}.

The Z′ Resonance. Exposure of peroxyborate materials to energetic radiations leads to the generation of a fourth type of esr response, which has been labeled the Z′ resonance. (This labeling was inspired by a superficial resemblance between the new response and the Z resonance.) The Z′ resonance is devoid of hyperfine structure and is characterized by an axially symmetric g tensor with $g_{\parallel} = 2.045 \pm 0.001$ and $g_{\perp} = 2.0038 \pm 0.0004$. A γ-ray dose of 10^8 R at 77°K induced a Z′ resonance spin concentration of 1.6×10^{20} cm^{-3}. Upon warming to room temperature, some 1.2×10^{19} spins cm^{-3} remained.

A large number of simple borate and peroxyborate compounds were irradiated with γ-rays at 77°K. Large concentrations ($\approx 10^{19}$ spins cm^{-3}) of Z′ resonance center were formed in the peroxy compounds $NaBO_3 \cdot 4H_2O$, $NaBO_3 \cdot H_2O$, $KBO_3 \cdot 0.5H_2O$, $LiBO_3 \cdot 2H_2O$, and samples of sodium EMPB. The simple borates $NaBO_2 \cdot 4H_2O$, $Na_2B_4O_7$, and $Na_2B_4O_7 \cdot 10H_2O$ exhibited (after irradiation) spectra one or two powers of ten less intense and qualitatively quite different from the Z′ resonance. (Details can be found in ref 11 and 12.) Thus, the formation of Z′ is related to the presence of peroxide groups in the materials.

Isotopic Studies. To learn more about the source of oxygen atoms in the product O_2, we have carried out experiments using ^{18}O. Some results are given in Table III. Peroxide from double-labeled H_2O_2, the starting point in most of the tracer experiments, was oxidized to oxygen gas using ceric ammonium sulfate in acidic solution. It has been shown[32] that this reaction does not involve cleavage of the oxygen–oxygen bond; thus the product O_2 contains the same isotope distribution as the H_2O_2 from which it is formed, enabling mass spectrometric measurement of this distribution for the parent material.

The $NaBO_3 \cdot 4H_2O$ prepared from the H_2O_2 can be analyzed in a similar manner. The agreement in the results listed in Table III for the H_2O_2 and the $NaBO_3 \cdot 4H_2O$ shows that no oxygen–oxygen scrambling or exchange occurs during formation of the peroxyborate.

Several EMPB samples prepared from labeled peroxyborate were dissolved in water, and the oxygen gas evolved during effervescence was analyzed both for content and distribution of ^{18}O. The observation that most of the oxygen label appeared as $^{34}O_2$ indicated that scrambling of peroxidic oxygens had occurred. Peroxide bonds had been broken and re-formed, presumably during the thermal treatment which converts $NaBO_3 \cdot H_2O$ to EMPB. The fact that the total content of ^{18}O atoms in the molecular oxygen was the same as that in the peroxide positions of the peroxyborate excludes the possibility of exchange with nonperoxidic oxygen atoms. This is further supported by experiments in which the nonperoxidic oxygens in the tetrahydrate starting material contained isotope label and some experiments in which the water used to dissolve the EMPB contained isotope label; in neither case was any ^{18}O found in the product O_2. A possible mechanism by which scrambling takes place is given in the Discussion section.

Since the EMPB samples contain some unreacted $NaBO_3 \cdot H_2O$, it was of interest to determine the extent of scrambling in the hydrogen peroxide remaining in water solution after effervescence of an EMPB sample. (The O_2 formed during effervescence was pumped off.) The peroxide in solution was oxidized by ceric ion and the resultant O_2 was analyzed. The results for these experiments are given in Table III. Little scrambling is observed in these O_2 samples.

The sum of the weight percentages of gaseous oxygen and peroxide in the more concentrated EMPB preparations is usually, but not always, somewhat less than the weight percentage of peroxide in the starting material. This difference suggests a release of oxygen during thermal preparation of an EMPB sample. Using labeled samples, the release was confirmed and the isotopic distribution in this portion of the O_2 was studied as follows. Double-labeled $NaBO_3 \cdot H_2O$ was placed in a dry, oxygen-free atmosphere and heated to about 130° to form an EMPB. The gas in contact with the sample after heating was found to contain O_2 which had the same percentage of ^{18}O atoms as did the peroxide positions in the peroxyborate starting compound. Considerable scrambling (about 55%) had taken place.

Discussion

General Nature. The EMPB preparations appear to be mixtures of an amorphous phase and some unreacted

(32) (a) C. A. Bunton and D. R. Llewellyn, *Research*, 5, 142 (1952); (b) M. Anbar, *J. Am. Chem. Soc.*, 83, 2031 (1961).

starting material, $NaBO_3 \cdot H_2O$. The unpaired spins and the easily released oxygen apparently are located in the amorphous portion. Since the preparations involve solid-state reactions, their heterogeneous nature is not surprising. This heterogeneity makes difficult any attempts to prove structure or to separate the phases. Nevertheless, we have been able to reach some rather definite conclusions about these materials. Evidence for heterogeneity has been the CFW variation from sample to sample, the type and number of separable esr responses, and the X-ray pattern. The preparations are heterogeneous not only in respect to having two phases, but also in respect to the properties (*e.g.*, esr) of the amorphous phase itself. Some consequences of this heterogeneity are mentioned below.

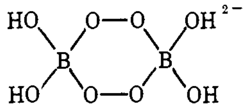
Possibility of Interstitial Oxygen. An important question not answered by our experiments is: Are oxygen molecules present in the interstices of the EMPB solids? We feel that there probably are some such molecules for the following reasons.

The susceptibility measurements have indicated the presence of up to 4.6×10^{21} $S = {}^1/_2$ paramagnetic states per cm^3 in certain preparations (or, alternatively, 1.7×10^{21} $S = 1$ states). The Gouy method used had a nominal accuracy of 1%, while a ±10% scatter in the data was attributed to sample heterogeneity. On the other hand, esr spin concentration measurements were able to account for no more than 1.4×10^{21} $S = {}^1/_2$ states per cm^3. The accuracy of the esr technique is normally estimated at ±30%, although the peculiar line shape of the X resonance could conceivably account for a larger error figure. Nevertheless, there is reason to doubt that the esr measurements could be in error by as much as a factor of 3. Thus, it is necessary to consider the possible existence of a *fifth* type of paramagnetic center—a center which does not show any esr response but which contributes substantially to the static susceptibility. One possible candidate for this center is the interstitial oxygen molecule. An investigation[33] of the magnetic susceptibility of oxygen molecules caged in the clathrate host β-quinol suggests that an esr spectrum due to oxygen molecule would not be expected in our studies. The evoluton of small amounts of O_2 gas during the preparation of an EMPB also is evidence for the formation and retention of such molecules in the solid state.

Comparison with Superoxides. There are some similarities between the EMPB preparations and the true superoxides such as KO_2. One is the effervescence when samples are dissolved in water. From KO_2, O_2 gas and H_2O_2 are formed in equal quantities. Under some conditions, the same stoichiometry is observed for EMPB samples; however, the ratio of O_2 to H_2O_2 can significantly deviate from this stoichiometry. The fact that the per cent O_2 can be considerably larger than the per cent H_2O_2 is again evidence for the presence of O_2 molecules in the solid.

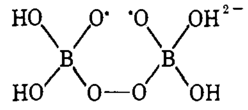
There are also similarities in magnetic properties. Both materials have a large paramagnetic susceptibility at room temperature, and at low temperatures there is evidence for magnetic phase changes in the superoxides. Although the esr spectra of the superoxides are significantly different from the spectra of the EMPB, there are similarities in the temperature dependence of the spectra. A broad intense resonance is observed for the superoxides in the temperature range 4–300°K, which decreases in intensity with decreasing temperature and disappears between 4 and 2°. This behavior is somewhat analogous to the EMPB in which the X resonance is not detectable at 4°K or less. Resonances which are much less intense and with a much smaller width are still observed at the lowest temperatures in the region of $g = 2.0$[34] in both the simple superoxides and the EMPB.

Formation Mechanism. From the data given, it is possible to construct a reasonable mechanism for formation of the magnetic centers in EMPB. Starting with $NaBO_3 \cdot 4H_2O$ for which the structure is known,[35] the complex polyanion



is present in the solid state. The stoichiometry and the readily reversible nature of the dehydration to form the monohydrate suggests that the polyanion structure is still present therein. However, the data on the formation of EMPB from monohydrate indicate that a deep-seated and irreversible change takes place.

It is known that most disubstituted peroxides have bond dissociation energies for the oxygen–oxygen single bond of 30–38 kcal mole^{-1}. Using this energy, a normal frequency factor, and the Arrhenius equation, it would then be predicted that peroxides should undergo homolytic scission at a measurable rate around 100°, as is the case. This temperature is, of course, just in that temperature range wherein EMPB is formed from monohydrate at a convenient rate. Therefore the first step in the thermal transformation is postulated to be the reaction of the anion to form the diradical



by homolytic scission of a peroxide bond. The oxygen radicals thus formed could do several things: (a) recombine to re-form stable bonds, and perhaps even the polyanion, (b) react with a nearby peroxide bond by radical displacement, or (c) react with a nearby boron–oxygen link to form a peroxy radical. In fact, supporting evidence for the existence of the diradical and for the three types of reaction is available.

When the monohydrate is irradiated by γ rays (at 77°K) or high-energy electrons (at ambient temperature of the irradiation facility), a type of paramagnetic center is generated with properties unlike those of the centers formed thermally. This new type of center, termed Z′, has magnetic properties which are consistent with those predicted[11,12] for a $RO\cdot$ radical. This is expected if the assumption is made that radiation damage is largely located at the sites of the weakest bond. In terms of

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[33] H. Meyer, M. C. M. O'Brien, and J. H. Van Vleck, *Proc. Roy. Soc.* (London), **A243**, 414 (1958).

[34] H. G. Smith, R. M. Nicklow, L. J. Raubenheimer, and M. K. Wilkinson, *J. Appl. Phys.*, 37, 1047 (1966).

[35] A. Hansson, *Acta Chem. Scand.*, **15**, 934 (1961).

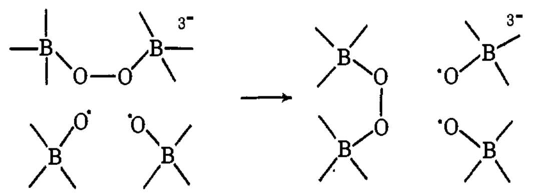
energy required per bond, scission of the O–O bonds would seem to be the "easiest" process by which paramagnetic centers might be produced upon irradiation of a peroxyborate compound. On the other hand, bond dissociation energies for O–H and B–O bonds in hydrated borates are generally greater than 100 kcal mole^{-1} and therefore less susceptible to cleavage.

The resulting oxygen radicals, although easily formed, would not be stable above room temperature. Indeed the Z′ resonance is largely annealed out as the temperature rises from 77°K to room temperature. Most of the residual esr properties after annealing the irradiated samples are like those of the EMPB samples prepared by heating.

It is apparent that a diradical of the above type is quite probably formed both thermally at 100° and by high-energy radiation at lower temperatures. It is not unexpected that such a diradical might exist for a long time at the lower temperatures and yet might only be an unstable and undetectable intermediate at the high temperature; thus the Z′ resonance is tentatively attributed to such a source.[36]

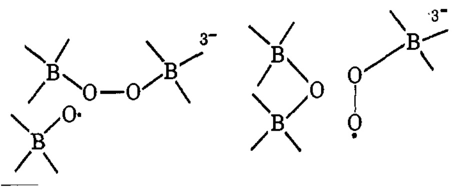
As mentioned above, there are three possible reactions which can occur with an RO· radical. The first involves recombination to form stable bonds. Ninety per cent of the Z′ resonance spins formed at 77°K is lost on bringing the sample up to room temperature. The data available do not allow us to state unequivocally that peroxide bonds are re-formed, but this certainly would be an expected fate.

As the second possibility for reactions of these radicals, they can react with a nearby peroxide bond by radical displacement. This would generate a new peroxide group and a new oxygen radical as in the scheme



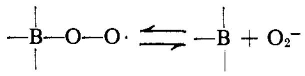
In this way, atoms in the peroxide groups could interchange among themselves, yet not exchange with nonperoxidic oxygens. This is exactly what is observed for the oxygen molecules derived from a labeled EMPB; extensive scrambling has taken place without exchange, and it may have happened previous to or simultaneous with the formation of the paramagnetic centers which lead to evolution of oxygen gas on dissolution in water.

The radicals can also react with a nearby boron–peroxide link to form a peroxy radical (this is the third possibility mentioned above). If an electron from a boron–peroxide oxygen bond is abstracted, as in the scheme



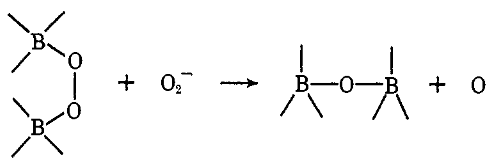
a peroxy radical is seen to be formed. This new radical is more stable than its parent radical; in general peroxy radicals are less reactive (more "stable") than are other oxygen radicals.[37] It is to be noted that the new species is one which fits the esr data for the X resonance.

The superoxide ion, which we believe is the source of the Z resonance, could be formed from the peroxy radical by the path



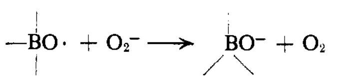
$$-\overset{|}{\underset{|}{B}}-O-O\cdot \rightleftharpoons -\overset{|}{\underset{|}{B}} + O_2^- \quad (1)$$

which (as will be seen below) may be an equilibrium reaction.[11] The ozonide ion, which presumably is the source of the weak Y resonance, can be formed from a peroxide group and a superoxide ion. This could be written schematically as



(2)

If oxygen molecules are indeed present, a probable mode of formation would be a reaction of the type



$$-\overset{|}{\underset{|}{B}}O\cdot + O_2^- \longrightarrow \overset{|}{B}O^- + O_2 \quad (3)$$

Reaction 1 to form superoxide ions would account for the presence of three-coordinate boron atoms indicated by nmr. The fact that the concentration of superoxide ions as measured by the Z resonance is at least two orders of magnitude less than the concentration of three-coordinate boron could be explained by (3) which converts the superoxide ions to oxygen molecules. Thus the presence of large quantities of molecular oxygen in EMPB samples is consistent with the presence of up to 15% three-coordinate boron in these samples.

Conclusions

The evidence obtained in this investigation leads to some important conclusions. The extensive scrambling in the evolved oxygen and the presence of ozonide ions in the EMPB preparations indicate that the peroxidic oxygens can react with each other significantly during reactions wherein radicals are involved. Chains of oxygen atoms are formed and broken with relative ease, yet there is little exchange of oxygen with the oxygen atoms in hydroxyl groups or water molecules. Oxygen chains have been postulated[38] as intermediates, and some compounds of the type ROOOR have sufficient stability to be isolated and identified.[39] Thus one conclusion is that chains with more than two oxygen atoms are likely intermediates in peroxide systems and that such chains are formed and broken with relative ease without involving oxygens in the −2 oxidation state.

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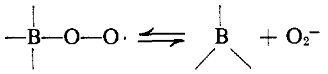
[36] It should be pointed out that the esr data do not eliminate the possibility that the Z′ resonance could arise from a species of peroxy radical, but even in such an event the postulated role of the diradical in the EMPB formation mechanism is still supported by the other data.

[37] G. A. Russell in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 6.

[38] (a) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956); (b) P. D. Bartlett and P. Gunther, *ibid.*, **88**, 3288 (1966), and references therein.

[39] (a) L. R. Anderson and W. B. Fox, *ibid.*, **89**, 4313 (1967); (b) P. G. Thompson, *ibid.*, **89**, 4316 (1967).

The presence of three distinct paramagnetic oxygen-containing species in the thermally reacted EMPB samples, plus a relatively unstable fourth species observed only in irradiated samples, invites the question: Are these species in equilibrium with each other or are they formed in separate, competitive paths? This question can be partially answered from the data on irradiated samples. It was found[11,12] that during irradiation of various EMPB samples the ratio of number of Z centers to number of X centers remained essentially constant after an initial period wherein the X centers were observed but no significant Z centers. Therefore, it seems possible that the chemical species giving rise to these two signals are in some type of equilibrium (or steady state) when the reaction is "turned on," *i.e.*, when the irradiation is being carried out or when the material is maintained at a temperature sufficient for the reaction to proceed thermally. It would not be surprising to find that the equilibrium



$$-\overset{|}{\underset{|}{B}}-O-O\cdot \rightleftharpoons \overset{|}{\underset{/\ \backslash}{B}} + O_2^-$$

is set up. Addition of oxygen bases to three-coordinate borons and the reverse process are known to be facile.[40] Similarly, the ratio of Y to Z was constant as both increased during the course of the irradiation. On the other hand, the intensity of the Z′ resonance first increased and then decreased with length of irradiation, suggesting that this signal is due to a percursor for the species which gives the other signals.[11,12]

The unusual nature of the EMPB preparations has led us to experiments which have in turn given a variety of specific and interesting results, as, for example, the esr and isotope data. We feel, moreover, that these systems give results and allow conclusions which may have broader generality and which may be applied to other systems.

Acknowledgments. The authors greatly appreciate the aid of FMC Corp., especially Dr. Leonard R. Darbee, in providing many chemical samples as well as valuable suggestions and discussion regarding some of the chemical aspects of the problem. We also wish to thank Professor P. J. Bray for helpful discussions regarding the nmr and esr studies, and Dr. E. G. Terezakis for generous assistance with the Gouy balance measurements. This work has been supported by generous grants from the Atomic Energy Commission (Grants No. AT(30-1) 1983 and AT(30-1) 2024), from the U. S. Air Force Office of Scientific Research (Grant No. 1027-66), and from the Advanced Research Projects Administration. R. B. J. and K. L. W. are grateful for the University Fellowship and Du Pont Teaching Fellowship, respectively, which partially supported these studies.

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[40] R. P. Bell, J. O. Edwards, and R. B. Jones "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 4.

The Oxidation of Tris(1,10-phenanthroline)iron(II) Ion by Chlorate and Chlorite Ions and Chlorine Dioxide[1a]

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Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742. *Received August 9, 1968*

Abstract: The reactions of chlorate and chlorite ions and chlorine dioxide with $Fe(phen)_3^{2+}$ have been studied. In the case of ClO_2^-, the rate of the reaction is controlled by the first dissociation step of $Fe(phen)_3^{2+}$ and the iron(III) product is a dimeric species. Chlorine dioxide reacts *via* an outer-sphere path, since the iron(III) product is the monomeric species $Fe(phen)_3^{3+}$. Chlorate ion is unreactive with $Fe(phen)_3^{2+}$. The results are compared with those of other investigations which involve the chlorine oxidants and the aquated Fe^{2+} ion and also other metal ions and complexes. A general classification of $Fe(phen)_3^{2+}$ redox reactions is suggested.

It has been suggested[2] that the reactions between the chlorine oxidants and certain metal ions proceed *via* an inner-sphere path. The chlorine oxidants can be reduced in both one- and two-electron steps. For example, in the reduction of chlorate ion to chloride ion in acid solution, chlorine dioxide, chlorous acid, hypochlorous acid, and chlorine are possible intermediates. These intermediates can either interact with one another or they can, in turn, be reduced ultimately to chloride ion if the rates of their further reduction are faster than the rates of their self-interaction.

The reaction between chlorine and tris(1,10-phenanthroline)iron(II) ion[3] is postulated[4] to proceed *via* an outer-sphere path with the formation of a chlorine radical, Cl_2^-, as a reactive intermediate.

The purpose of this paper is to present our results of the reduction of the other chlorine oxidants by $Fe(phen)_3^{2+}$.

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[1] (a) Part of the thesis presented by B. Z. Shakhashiri to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1967; (b) Postdoctoral Research Associate in Chemistry, University of Illinois, Urbana, Ill., 61801; (c) Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.

[2] R. C. Thompson and G. Gordon, *Inorg. Chem.*, 5, 562 (1966).

[3] Hereafter $Fe(phen)_3^{2+}$.

[4] B. Z. Shakhashiri and G. Gordon, *Inorg. Chem.*, 7, 2454 (1968).