TABLE III

CALCULATION OF k_{11}[a]

$T = 30.0°$, $[H^+] = [Cl^-] = 1.00$, $[Fe^{2+}]_0 = 6.57 \times 10^{-5}$, $[\Sigma Cl_2]_0 = 3.19 \times 10^{-5}$, $\bar{k} = 257\ M^{-1}\ sec^{-1}$

$10^5[Fe^{3+}]_{20\ sec}$	$10^5[Cu^{2+}]$	k_{11} from (13), $M^{-1}\ sec^{-1}$
2.43	0.33	148
2.43	0.67	73
2.73	1.00	115
3.81	5.00	225
4.60	10.00	211
		Av 154 ± 60

[a] All concentrations: F.

nique. The rather high degree of uncertainty in k_{11} may be attributed to experimental difficulties in the spectrophotometric method and to reaction half-lives of less than 20 sec in some cases. However, we were able to measure the slope of one plot of ln $[Fe^{2+}]$ *vs.* time at 20 sec and from this to calculate a single value of 162 ± 15 M^{-1} sec^{-1} for k_{11}, in good agreement with the average.

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The Electron Paramagnetic Resonance Spectrum of Chlorine Dioxide in Solution. Effect of Temperature and Viscosity on the Line Width

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An epr study was made of chlorine dioxide in solution for the temperature range 25 to −180°, using as solvents CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4. The g value obtained was 2.0103, and the isotropic hyperfine splittings were found to be 17.0 and 13.7 gauss for the Cl^{35} and Cl^{37} isotopes, respectively. The effect of temperature and solvent viscosity on the line width of the hyperfine components of ClO_2 was found to agree with the theory of spin-rotational interaction as developed by Kivelson. From this the viscosity of the solvent could be estimated.

Several previous studies have been made on ClO_2 in both the liquid and solid phases. Using ethanol, water, acetone, and benzene as solvents for ClO_2, a single epr line was observed at 273°K and a partially resolved quartet at 193°K. This gave a hyperfine splitting of 17 gauss, a line width of 8 gauss, and a g value of 2.010.[1]

With ClO_2 dissolved in H_2O, H_2SO_4, H_3PO_4, CCl_4, and glycerol at room temperature, a four-line spectrum was observed.[2] In the case of CCl_4, a single broad line was observed at 25° and this was partially resolved into a quartet at −35°, but no line-width measurements were reported. However, it was observed that the line width was less in the hydrogen-containing solvents than in the CCl_4. It was suggested that this was due to hydrogen bonding. For ClO_2 dissolved in H_2SO_4 at room temperature, a hyperfine splitting of 16.5 gauss and a g value of 2.0093 were observed.[3]

The ClO_2 free radical was formed in a single crystal of $KClO_4$ by X-ray irradiation.[4] The isotropic hyperfine splitting of 15.4 gauss and an average g value of 2.0102 were calculated from the observed anisotropic hyperfine splitting.

We have studied the epr spectrum of ClO_2 in various solvents down to very low temperatures. The solvents were chosen so that the isotropic spectrum of ClO_2 could be observed over a wide temperature range along with large variations in the solvent viscosity. With these temperatures and solvents, the hyperfine splittings of the two chlorine isotopes were resolved and their splittings were measured accurately. The line width of the hyperfine components was studied as a function of the temperature and solvent. These line-width data could be related to the viscosity of the solvent and were found to agree with the theory of spin-rotational interaction developed by Kivelson.[5] The line-width data also lead to estimates of the viscosity of the solvent for temperature ranges in which the viscosity has not been measured by other methods.

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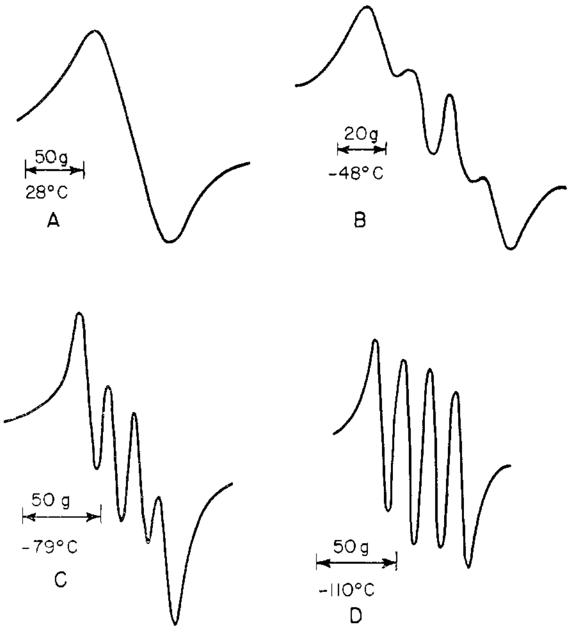

Figure 1.—The epr spectra of ClO_2 dissolved in CCl_3F.

Experimental Section

The chlorine dioxide was prepared by the usual method of heating a mixture of oxalic acid, potassium chlorate, and water to 60°. The by-products, Cl_2, CO_2, and H_2O, were removed by bubbling the reaction products through a concentrated sodium hydroxide solution and drying over P_2O_5. The CCl_3F, CCl_2F_2, $CClF_3$, and CF_4 were supplied by Allied Chemical Corp. under the trade names Genetron 11, 12, 13, and 14, respectively, and the CCl_4 was the Baker and Adamson reagent grade chemical.

The epr sample tube was 2-mm i.d. quartz. This was attached to a valve by means of a Swagelok compression fitting with Teflon ferrules. Approximately 0.25 ml of degassed solvent was added to 5–10 mg of ClO_2. About ten times more ClO_2 could be added without observing any concentration broadening of the epr spectral lines. The epr spectrum was observed for each solvent at several temperatures down to the freezing point of the solution.

The epr spectra were obtained with a Varian V4500-10A spectrometer and a 6-in. magnet. The microwave frequency was measured with a Sperry Model 14X1 cavity frequency meter which has an accuracy of 0.01%. The magnetic field strength was measured with a Varian F-8 fluxmeter equipped with a crystal controlled oscillator which has an accuracy of 0.005%. This gave magnetic field markers accurate to ±0.2 gauss. By interpolating between the field markers with a cathetometer, the magnetic field in gauss could be measured at any point on the spectrum. The accuracy of the hyperfine splitting, line width, and g value was determined by the line width of the epr spectrum and not by the frequency and magnetic field measurements. Temperature measurements were made on a Varian G-11A recorder with a copper–constantan thermocouple located close to the sample.

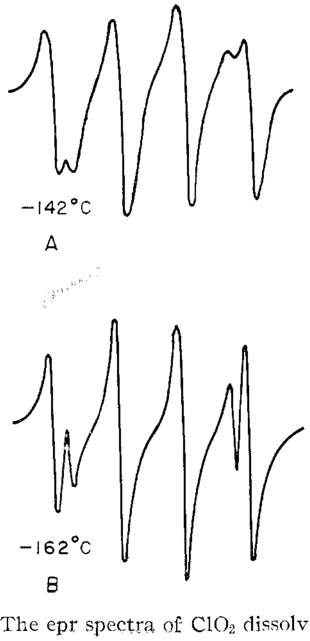

Figure 2.—The epr spectra of ClO_2 dissolved in CCl_2F_2.

Results

Epr Spectrum.—Typical spectra of ClO_2 in solution at different temperatures are shown in Figures 1 and 2. A single, broad line was observed at room temperature. By lowering the temperature to $-110°$, it was possible to resolve the spectrum into a quartet due to the chlorine nuclear spin of $^3/_2$ as shown in Figure 1. At lower temperatures, hyperfine splittings were observed for the Cl^{35} and Cl^{37} isotopes as shown in Figure 2. The different degrees of resolution are caused by the line widths of the hyperfine components as listed in Table I. Comparable line widths were obtained in the different solvents at different temperatures. Thus, the spectrum of ClO_2 in $CClF_3$ at $-180°$ was similar to ClO_2 in CCl_2F_2 at $-162°$ as shown in Figure 2B.

At temperatures above $-140°$ only the hyperfine splitting for the more abundant Cl^{35} isotope was observed. The Cl^{37} isotope caused line broadening and an apparent decrease in intensity for the outer hyperfine components as shown in Figure 1. The intensity of the lines as shown in Figure 2B agrees with the natural abundance ratio of 3:1 for Cl^{35} to Cl^{37} isotopes.

The average hyperfine splittings (hfs) were found to be 17.0 ± 0.3 and 13.7 ± 0.3 gauss for the Cl^{35} and the Cl^{37} isotopes, respectively. When the hfs for Cl^{37} was calculated from the hfs of Cl^{35} and the ratio of the nuclear magnetic moments, the hfs for Cl^{37} was 14.1 gauss. This could be due to an isotopic effect as observed in other radicals.[6] There was no observable variation in the hyperfine splitting due to different temperatures or solvents.

The g value was calculated from the microwave frequency and the magnetic field strength at the center of the spectrum. The value of 2.0103 ± 0.0005 is an average obtained from several different spectra and is the same for both chlorine isotopes.

Line Width.—In order to study the variations in resolution and line width, the ClO_2 spectra were observed in various solvents over a wide temperature range. Since the observed spectra as shown in Figures 1 and 2 are not completely resolved, they do not give the true line width. Thus, the experimental line-width data were corrected by reference to the calculated line shapes given by Lebedev.[7] This gave the true line width of the individual hyperfine components be-

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TABLE I

HYPERFINE LINE WIDTH AND VISCOSITY DATA FOR ClO_2 IN VARIOUS SOLVENTS

T, °C	Line width, gauss		η, cp[a]	°K/η
	Obsd	Calcd		
		CCl_4		
28		20	0.865	348
−1		16	1.371[b]	198
−10		15	1.629[b]	162
−21		13.3	2.063[b]	122
−25		12.8	2.270[b]	109
		CCl_3F		
28		36	0.4119	731
−11		20	0.6186	424
−37		16.0	0.9241	255
−48	10.4	15.0	1.164[c]	193
−66	9.1	12.5	2.024[c]	102
−82	7.8	10.3	5.667[b]	34
−95	7.2	7.8	(11.9)	(15)
−110	6.0	6.8	(16.3)	(10)
		CCl_2F_2		
28		45	0.253[c]	1190
			0.33[c]	912
−46		19	0.462[b,c]	491
			0.54[b,d]	420
			(0.67)	(340)
−73	9.8	14	(1.3)	(160)
−79	9.9	12.5	(2.4)	(80)
−91	8.0	11.8	(3.6)	(50)
−110	7.2	8.3	(10.9)	(15)
−142	3.8		(26)	(5)
−162	2.3			
		$CClF_3$		
−45			0.336[d]	623
−70			0.37[e]	549
−74		30	(0.31)	(650)
−93		26	(0.32)	(570)
−132		14	(1.2)	(120)
−150	7.1	8.2	(8.2)	(15)
−167	4.4		(21)	(5)
−180	2.9			
		CF_4		
−112		(22)	0.34[d,e]	474
−118		18	(0.5)	(310)
−178		15		

[a] R. Thorpe, *Phil. Trans. Roy. Soc. London*, **A185,** 397 (1895); "International Critical Tables," Vol. 7, p 212. [b] Extrapolated from straight-line equation. The values in parentheses were obtained from the T/η *vs.* line width plot in Figure 4. [c] A. F. Benning and W. H. Markwood, *Refrig. Eng.*, **37,** 243 (1939); private communication. [d] Allied Chemical Corp. data. [e] Du Pont Technical Bulletin No. 10.

tween points of maximum slope for all of the observed spectra as listed in Table I. The line shape was found to be Lorentzian.

The observed line widths listed in Table I were measured on the central hyperfine components of the spectra because of the line-broadening effect of the Cl^{37} isotope on the outer lines. Since there was additional broadening of the high-field hyperfine components of the spectrum in CF_4, accurate line-width values could not be obtained in the solvent. No spectra could be observed for ClO_2 dissolved in liquid nitrogen, possibly due to greater line broadening than in the CF_4.

An examination of the data presented in Table I shows that the corrected line width decreases as the temperature is lowered. This effect is shown graphically in Figure 3 for each solvent. Also, the line width for a given temperature decreases for the different solvents in the order CF_4, $CClF_3$, CCl_2F_2, $CClF_3$, and CCl_4. Reference to Table I shows that the viscosity, η, of the solvents increases in the same order. The relationship of the line width to the viscosity of the solvent is shown in Figure 4 by plotting the line width *vs.* $T°(K)/\eta$. The correlation between viscosity of the solvent and the line width of the ClO_2 was difficult to ascertain owing to lack of accurate viscosity data. The discrepancies in the reported values of the viscosity are shown by the dashed lines in Figure 4 (T/η = 600–1200). Where viscosity data were not available, the epr line-width data plotted in Figure 4 were used to obtain approximate viscosity values. These data are listed in parentheses in Table I.

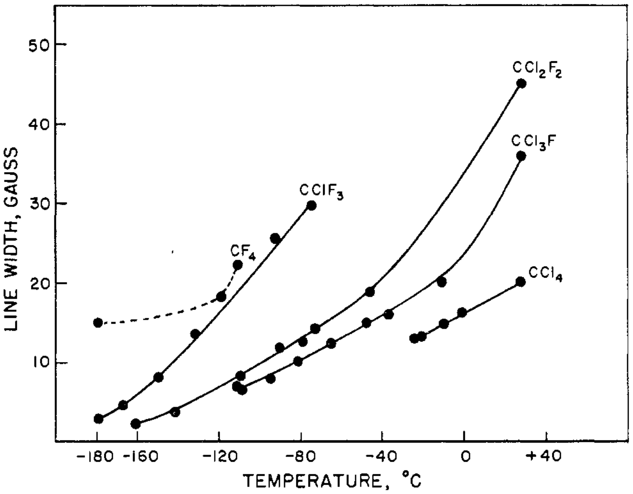

Figure 3.—Corrected line width of the hyperfine components of ClO_2 in various solvents as a function of temperature.

Discussion

The ClO_2 molecule provides a unique opportunity for testing the theory of spin-rotational interaction

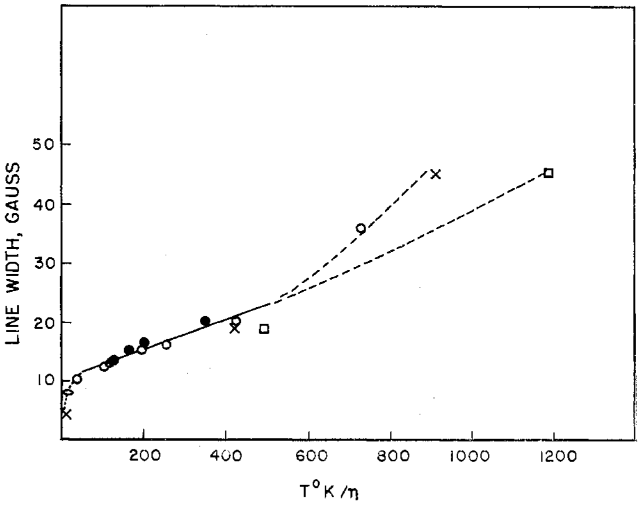

Figure 4.—Corrected line width of the hyperfine components of ClO_2 in solution as a function of the viscosity and temperature: ●, CCl_4; O, CCl_3F; □, CCl_2F_2 (see footnote *c* of Table I); ×, CCl_2F_2 (see footnote *d* of Table I).

as it relates to the line width of an epr spectrum. The ClO_2 radical is stable and has a suitable line-width variation with the viscosity of the solvent. By making sufficiently dilute solutions and choosing solvents with suitable liquid ranges and viscosities, the effect of spin-rotational interaction could be studied.

The theory developed by Kivelson[5] for spin-rotational interactions in liquids predicts that the line width of the epr spectrum should depend on the temperature and viscosity. The variation of line width as a function of T/η is given by

$$T_2^{-1} = \text{constant}\left(\frac{T}{\eta}\right) \qquad (1)$$

As shown in Figure 4, the line width is a linear function of T/η over a wide temperature and viscosity range. Therefore, in this linear region, ClO_2 appears to follow the spin-rotational interaction theory as given in eq 1. Also, the curves in Figure 4 for the different solvents are superimposed. This shows the line width is primarily a function of the temperature and viscosity of the solvent as predicted by eq 1.

The relationship of line width *vs.* T/η shown in Figure 4 was not linear over the entire range of the experimental data. This curvature, as indicated by the dashed lines, could be due to other line-broadening effects. However, in the line-width regions indicated by dashed lines in Figure 4, the available viscosity data are not accurate enough to test the theory. For the line-width region over which the T/η plot is linear, Figure 4 can be used to estimate the viscosity of the solvent. This is shown by the values in parentheses in Table I.

Atkins, *et al.*,[2] have suggested that there is a different relaxation mechanism for ClO_2 in noninteracting solvents (*e.g.*, CCl_4) than in hydrogen-bonding media (*e.g.*, N_2O, glycerol, H_2SO_4). However, their results could also be explained on the basis of the viscosity of the solvent. In each case in which they indicated that the resolution was increased, there was also an increase in the viscosity. However, from their data it is not possible to make a quantitative comparison with the viscosity of the solvent.

Summary

We have measured the line width of ClO_2 in solvents such as CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4 over temperature ranges of 25 to −180°. The isotropic hyperfine splittings due to the Cl^{35} and Cl^{37} isotopes were resolved and found to be 17.0 and 13.7 gauss. The peak height was in the same ratio as their isotopic abundance, and the hyperfine splitting was in almost the same ratio as the isotopic magnetic moment. The measured g value was 2.0103.

The line widths of the individual hyperfine components were found to vary with the solvent and the temperature. The viscosity dependence of the hyperfine line widths agreed with the theory of spin-rotational interaction proposed by Kivelson.

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Isotope Exchange in the Iron(II)-Iron(III)-Chloride Ion System in Dimethyl Sulfoxide

BY GORO WADA[1] AND WARREN REYNOLDS

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The isotope exchange reaction between iron(II) and iron(III) in dimethyl sulfoxide (DMSO) is catalyzed by chloride ion. Rate constants for the reaction paths involving $Fe^{2+} + FeCl^{2+}$ and $Fe^{2+} + FeCl_2{}^+$ are $(130 \pm 15)\ M^{-1}\ sec^{-1}$ and $(1020 \pm 150)\ M^{-1}\ sec^{-1}$, respectively, at 20°. The formation constants β_1 and β_2 for $FeCl^{2+}$ and $FeCl_2{}^+$ in DMSO are $(5.3 \pm 0.6) \times 10^3\ M^{-1}$ and $(5.7 \pm 1.2) \times 10^5\ M^{-2}$, respectively. The molar extinction coefficients of Fe^{3+}, $FeCl^{2+}$, and $FeCl^{2+}$ in DMSO at 20° are (840 ± 10), (1180 ± 16), and $(2350 \pm 130)\ M^{-1}\ cm^{-1}$, respectively, at 400 mμ.

Despite the fact that net transfer of a hydrogen atom was postulated[2,3] to be a possible mechanism for electron transfer as early as 1952, very few studies on mechanisms of electron-transfer reactions in essentially aprotic or other nonaqueous solvents have been carried out. Maddock[4] reported that electron transfer between iron(II) and iron(III) perchlorates in nitromethane had a half-time of "many days" at room temperature. Sutin[5] found that the rate of the same exchange reaction was about 10^{-8} times

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[1] Goro Wada wishes to gratefully acknowledge leave by Kobe University, Japan.

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