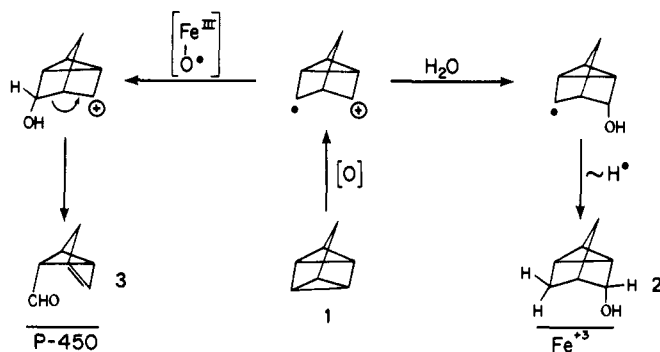


Table I. Cytochrome P-450 Catalyzed Oxidation of Quadricyclane

incubation conditions	yield of 3, nmol/nmol of P-450
control ^a	370
-NADPH	ND
+argon	95
+argon, -NADPH, +PhIO (1 mM)	1570
+argon, -NADPH, -microsomes, +PhIO	57
+CO	8
+1-aminobenzotriazole (1 mM)	11
+SKF 525A ^b (100 μM)	18
+benzphetamine (0.5 mM)	15

^aIncubation contained phenobarbital-induced rat liver microsomes (1.0 mg of protein/mL), glucose-6-phosphate dehydrogenase (0.5 units/mL), glucose 6-phosphate (4.5 mM), NADP (0.5 mM), MgCl₂·H₂O (2 mM), KCl (1.0 mM), diethylenetriaminepentaacetic acid (1.0 mM), and quadricyclane (1 mM) in 0.1 M NaKPO₄ (pH 7.4) buffer (20-mL incubation volume). Mixtures were incubated at 37 °C for 30 min (ND, not detectable). The argon experiments were carried out with microsomes from a different set of rats. ^bSKF 525A is (diethylamino)ethyl 2,2-diphenylpentanoate hydrochloride.

**Figure 2.**

chemical precedent and are therefore unlikely. The novel reactivity observed in the oxidation of quadricyclane by cytochrome P-450 indicates that the enzyme can oxidize hydrocarbons that have low oxidation potentials by sequential one-electron steps. The net outcome is oxidation of an otherwise unactivated carbon-carbon single bond.

Electron Paramagnetic Relaxation as a Probe for Structural Characterization of Paramagnetic Oxyanions

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The purpose of this note is to show that in some structural studies using electron paramagnetic resonance (EPR) spectroscopy, where conventional identification procedures (based on *g* values and hyperfine splitting) are insufficient for distinguishing between two species, the temperature-dependent line-width behavior may provide an important criterion. This situation may arise for a complex in which the ligand atoms exhibit little or no hyperfine structure, for example, paramagnetic oxyanions (CrO₃⁻, CrO₄³⁻, WO₄³⁻, etc.). The direct determination via EPR of the number of oxygen ligands is difficult since the dominant oxygen isotope (¹⁶O) has nuclear spin *I* = 0 and hence exhibits no hyperfine structure, and the natural abundance of its magnetic isotope ¹⁷O (*I* = 5/2) is too low (~0.04%) to be normally detected by EPR. We experienced such difficulty during the initial stages of studies aimed at characterizing the Cr(V) oxyanions CrO₃⁻ and CrO₄³⁻.

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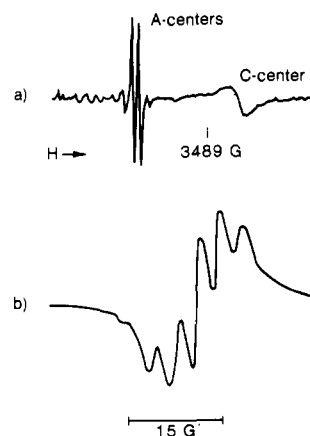


Figure 1. EPR spectrum of (a) γ -irradiated K₂Cr₂O₇ oriented with H//*a**-axis and (b) CrO₄³⁻ in KH₂PO₄. Note the (1:4:6:4:1) quintet structure from four H's hydrogen bonded to the four oxygens of the CrO₄³⁻, thus confirming the identity of this center. The temperature dependence of the overall line width of this signal provided an internal standard for identifying the C center. The spectra were recorded at room temperature under nonsaturating (~1 mW) microwave power. The modulation amplitude was about 0.5 G at 100 kHz.

Such Cr(V) oxyanions have been postulated as active sites in chromia-alumina and chromia-silica catalysts,^{2,3} but their identity has not been confirmed. Since both CrO₃⁻ and CrO₄³⁻ are paramagnetic (d¹), attempts have been made to produce and characterize (using EPR) these species in well-defined crystalline chromium-oxygen lattices such as K₂CrO₄,^{4,5} K₂Cr₂O₇,⁶⁻⁸ and Na₂Cr₂O₇.⁹ In all of these studies, the Cr(V) species were identified via electron Zeeman tensor (*g*) and in some cases the ⁵³Cr hyperfine tensor. However, the assignment of CrO₃⁻ in all of the above studies is in disagreement with recent additive ligand-field theoretical calculations of *g* values for a tricoordinate Cr(V) oxyanion.¹⁰ The theoretical results also suggest that the spectral features assigned to CrO₃⁻ should in fact be reassigned to CrO₄³⁻. To help solve this controversy preparation of an ¹⁷O-labeled host crystal (such as K₂Cr¹⁷O₄) was considered, but it was felt that the results might not be conclusive if the labeling were not 100% complete, a fairly difficult task. Alternatively it was decided to utilize the well-known fact that the electron spin-lattice relaxation time (*T*₁) for a species is dependent upon its coordination and point symmetry.¹¹ Under identical conditions, a tetrahedral species such as CrO₄³⁻ will exhibit a shorter *T*₁ than a tricoordinate species such as CrO₃⁻. In EPR measurements a shorter *T*₁ would be observable as a larger signal line width. Since *T*₁ is a sensitive function of temperature (in general, sharply decreasing with increasing temperature), variation of the EPR line width with temperature should be characteristic of the coordination and symmetry.¹² Thus a comparison of the temperature dependence of the line width of an unknown with that of a selected set of known species should serve as a criterion for structural identification. The work summarized below, and described in greater detail elsewhere,¹³ demonstrates the feasibility of such a procedure.

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Table I. Principal Components and Their Orientations for the A and the C Centers in γ -Irradiated $K_2Cr_2O_7$, Site 1 at 77 K

center	principal g values	direction cosines with respect to axes			ref
		a^*	b^*	c	
A	$g_{zz} = 1.9840 \pm 0.0005$	0.2002	0.8754	-0.3710	present work
	$g_{yy} = 1.9674$	-0.4680	0.4419	0.7510	
	$g_{xx} = 1.9588$	0.8351	0.0100	0.5439	
	$g_{zz} = 1.9841$	-0.0660	0.9929	0.0987	ref 8
	$g_{yy} = 1.9685$	-0.6310	-0.1180	0.7625	
	$g_{xx} = 1.9592$	0.7650	-0.0127	0.6394	
C	$g_{xx} = 1.9908 \pm 0.0005$	0.5121	0.6299	0.5840	present work
	$g_{yy} = 1.9745$	-0.4062	0.7767	-0.4815	
	$g_{zz} = 1.9222$	-0.7570	0.0094	0.6536	
	$g_{xx} = 1.9886$	-0.5699	-0.2429	0.7849	ref 8
	$g_{yy} = 1.9671$	0.1885	0.9373	0.2894	
	$g_{zz} = 1.9148$	0.7997	-0.2500	0.5486	

This procedure was applied to the species earlier identified as CrO_3^- and CrO_4^{3-} in γ -irradiated $K_2Cr_2O_7$. The EPR measurements were made at X-band (~ 9.35 GHz) on single crystals of $K_2Cr_2O_7$ grown from saturated aqueous solution at room temperature. The γ -irradiation was carried out with a ^{60}Co (500 C) source for 24 h at room temperature. Figure 1a shows a typical EPR spectrum for the magnetic field (H) aligned along the crystalline a^* -axis. The crystal axis system (a^*b^*c) used was that of earlier workers.⁶⁻⁸ The observed spectra were quite similar to those reported earlier with the sharper lines labeled A and the broad signal labeled C assigned previously⁶⁻⁸ to CrO_4^{3-} and CrO_3^- , respectively. To ensure that our notation for the signals was indeed the same as used earlier⁶⁻⁸ we studied the angular dependence of the spectra in three mutually orthogonal crystallographic planes ca^* , a^*b^* , and b^*c . The g tensor principal components and their orientations are summarized in Table I. The agreement between the values reported previously⁸ and obtained in this work can be considered satisfactory. Further analysis¹³ of the g components, using McGarvey's procedure,¹⁴ confirmed that the ground states of the A and the C centers are d_{z^2} and $d_{x^2-y^2}$, respectively.

The temperature dependence of both the A- and C-center line widths, measured as the peak-to-peak distance of a first derivative signal, was studied from 230 to 350 K (Figure 2). The A-center line width was found to exhibit little temperature dependence while that of the C center showed a strong temperature dependence. These results indicated that the C center was perhaps CrO_4^{3-} . To confirm this the temperature dependence of CrO_4^{3-} was studied in several KH_2PO_4 -type crystal hosts between 200 and 350 K (Figure 2). These crystals were chosen since CrO_4^{3-} has been positively identified¹⁵ in these lattices via its quintet (1:4:6:4:1) hyperfine structure due to four OH hydrogens around a CrO_4^{3-} unit (Figure 1b). By comparison with the temperature-dependent line width of the CrO_4^{3-} signal in KH_2AsO_4 , $NH_4H_2PO_4$, and $NH_4H_2AsO_4$,^{15,16} the C center was assigned to CrO_4^{3-} in contrast with earlier reports⁶⁻⁹ where it was identified as CrO_3^- . This conclusion supports the assignment based on theoretical calculations.¹⁰ Moreover, the rather strong temperature dependence of the line width for the C center explains why its line shape appears to be different in the three earlier reports.⁶⁻⁸ Our results confirm Alybakov's conclusion⁸ that the C-center signal becomes stronger at 77 K and disagree with the reported⁶ disappearance at 77 K.

It seems worth emphasizing¹⁷ that this methodology can be used only when the EPR signals have been shown to be homogeneously broadened, i.e., the dominant line broadening mechanism is spin-lattice relaxation. In general the broadening can be shown to be homogeneous via a strong decrease in the line width at lower temperatures (as for the C center in Figure 2). This could be further confirmed via a strong decrease of the signal amplitude at high microwave power levels (power saturation), also found¹³ to be the case for the C center. On the other hand the relatively

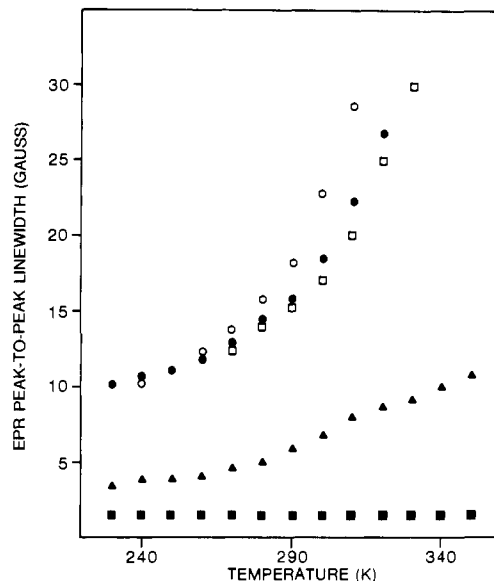


Figure 2. Temperature dependence of the first derivative peak-to-peak line width for CrO_4^{3-} in KH_4AsO_4 (○), CrO_4^{3-} in $NH_4H_2PO_4$ (●), CrO_4^{3-} in $NH_4H_2AsO_4$ (□), and the A center (■) and C-center (▲), in γ -irradiated $K_2Cr_2O_7$.

temperature-independent line width for the A center (cf. Figure 2) clearly indicates that spin-lattice relaxation makes little contribution to the line width, thus suggesting it to be CrO_3^- .

The above procedure was applied to the centers identified as CrO_4^{3-} and CrO_3^- in $(NH_4)_2SO_4$.^{18,19} Both of these centers have been used as probes of molecular motion near the ferroelectric transition in $(NH_4)_2SO_4$ at 223 K. Our studies found absence of temperature dependence in the line width of the spectra assigned to CrO_4^{3-} in $(NH_4)_2SO_4$, suggesting that this identification may not be correct. This conclusion is consistent with our observation¹³ that a frozen-glass solution of K_3CrO_4 in $(NH_4)_2SO_4$ yielded spectra totally different from that obtained from a glassy solution of $(NH_4)_2SO_4/CrO_4^{3-}$, thus casting doubt on its earlier^{18,19} assignment as CrO_4^{3-} . In fact, this work suggests a reexamination of other systems where CrO_4^{3-} and/or CrO_3^- have been identified (K_2CrO_4 ,^{4,5} and $Na_2Cr_2O_7$,⁹ $K_2SO_4/(NH_4)_2SO_4$ ¹⁸). Therefore, we have shown that by combining g - and A -tensor analysis with the temperature dependence of the line width(s), a more positive identification of a paramagnetic species is possible. In particular we anticipate that this procedure will be useful for the identification of other oxyanions such as those of tungsten and molybdenum, of topical interest in surface chemistry and catalysis.

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Registry No. $K_2Cr_2O_7$, 7778-50-9; CrO_4^{3-} , 14333-16-5; CrO_3^- , 37276-79-2.

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(16) The stronger temperature dependence of the CrO_4^{3-} line width in the KH_2PO_4 -type lattices than in $K_2Cr_2O_7$, may be understood in terms of the larger distortion of the CrO_4^{3-} tetrahedron in $K_2Cr_2O_7$, as discussed in ref 13. The larger residual line width in the phosphates results from the abundance of protons.

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