Science Foundation regional instrumentation facility (CHE 8211164), performed mass spectrometric analyses.

Supplementary Material Available: Spectroscopic and analytical data for all new compounds and tables of thermal parameters, positional parameters, bond distances, and bond angles for **13d** (5 pages). Ordering information is given on any current masthead page.

Characterization of the ESR Spectrum of the Superoxide Anion in the Liquid Phase

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The anion radical O_2^-, which is of considerable importance in living matter,[3,4] has been shown to be moderately stable in low-temperature aprotic media.[5-8] Consequently, ESR studies on O_2^-[9-23] generally have been undertaken in frozen media containing aprotic solvent[9-19] or at low temperatures on various solid oxide surfaces.[20-23] For example, Bray et al.[9] studied the low-temperature ESR spectrum of O_2^- generated in aqueous dimethyl sulfoxide media by using pulse radiolysis followed by a rapid freezing method. The intensity of the two-line spectrum was found to be extremely temperature dependent, and the disappearance of the ESR lines at temperatures prior to melting of the solvent was attributed to line broadening resulting from fast relaxation. In contrast only brief reports at single temperatures are available on the solution phase O_2^- ESR spectrum.[24,25]

This communication reports that ESR spectra of O_2^- can be obtained in solution at temperatures well above the melting point of aprotic solvents[26-28] such as butyronitrile (mp −112.0 °C) and propionitrile (mp −92.9 °C) and that frozen or solid-state media are not required for temperature-dependent studies.

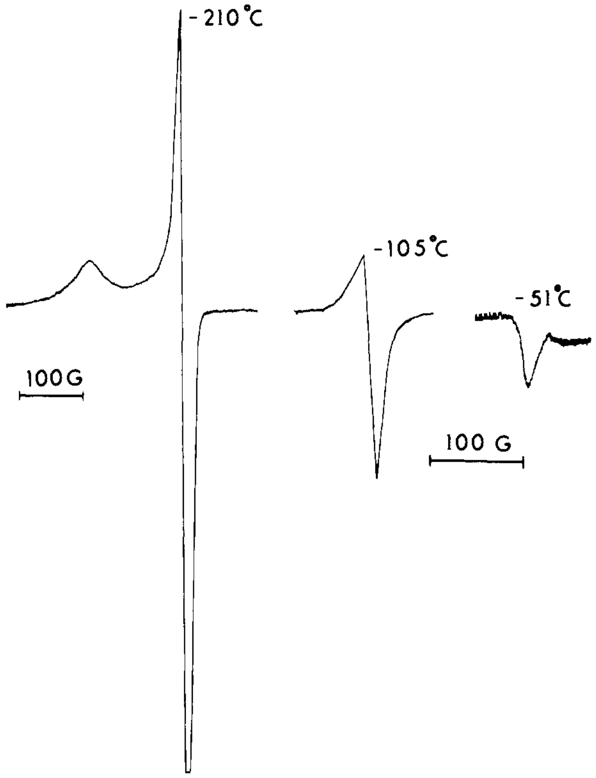

Figure 1. ESR spectra at various temperatures of the superoxide anion O_2^- generated by electrochemical reduction of molecular oxygen in butyronitrile containing 0.1 M Bu_4NClO_4.

Figure 1 shows the ESR spectra of electrochemically generated O_2^- in butyronitrile in the frozen solvent at −210 °C and in the liquid phase at −105 and −51 °C. Obviously it is possible to detect the ESR signal or O_2^- as high as 60 °C above the melting point (−112 °C) of butyronitrile. A similar study was undertaken in propionitrile, and the temperature dependence of the ESR signal amplitude in this solvent is shown in Figure 2 over a temperature range encompassing frozen solvent and the liquid phase. The temperature dependence is much greater than expected on the basis of the Curie law. For comparison purposes, Figure 2 also includes the temperature-dependent behavior of the well-known stable 4-hydroxy-2,2′,6,6′-tetramethylpiperidine-*N*-oxyl (TEMPOL) radical.

TEMPOL is a much larger molecule than O_2^- and has a much smaller *g*-factor anisotropy. Data for TEMPOL are in complete agreement with the Curie law.

The ESR spectra of O_2^- in frozen butyronitrile and propionitrile are characterized by $g_\parallel = 2.072$ (broad line) and $g_\perp = 2.009$ and are similar to the results reported in frozen solutions of dimethyl sulfoxide.[5] However, there are two unusual features of the solution ($g_{av} = 2.031$) spectra: (a) the signal height decreases sharply with

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(26) The ESR spectra of O_2^- were recorded on samples prepared by electrochemical reduction at platinum electrodes of molecular oxygen, O_2, dissolved in butyronitrile and propionitrile (purified by standard procedures) containing 0.1 M Bu_4NClO_4 as the supporting electrolyte. A newly developed in situ electrochemical ESR cell[27] or a conventional bulk electrolysis cell was used for the reduction and for obtaining voltammetric data. ESR spectra of O_2^- also were obtained by dissolution of KO_2, supported by dibenzo-18-crown-6 ether, in the same solvents. The ESR spectra were recorded over a wide temperature range (−210 °C to 20 °C) in both the frozen and solution phases either with a "home made" ESR spectrometer[28] or a Varian E4 spectrometer.

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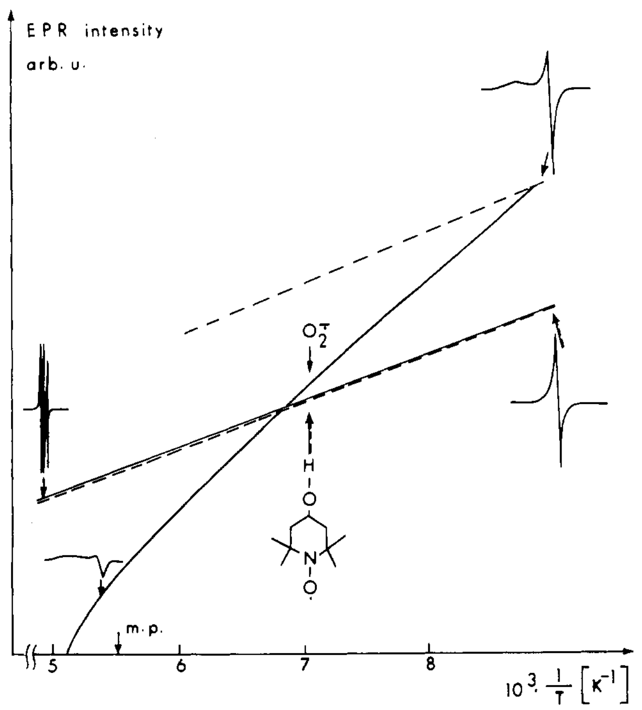

Figure 2. Plot of relative ESR signal amplitude versus reciprocal temperature for (a) O_2^- and (b) the TEMPOL radical in propionitrile. The broken line represents the expected change of intensity with temperature on the basis of the Curie law.

temperature and (b) *g*-anisotropy remains virtually unchanged over a wide range of temperature and is observed even in the liquid phase.

The remarkably similar temperature dependence of the ESR signal of O_2^- in butyronitrile or propionitrile solution, frozen solutions of dimethyl sulfoxide,[9] or O_2^- generated on a silica gel surface[29] can be explained by assuming that the dominant temperature-dependent effect arises from changes in the mobility of O_2^- entities in the solvent matrix and variation of spin–lattice relaxation time.[30] The major temperature-dependent term effecting the mobility is presumably related to fluctuations in the O–O bond length (*z*-axis). This term would explain the pronounced line broadening of $g_{\parallel}$ that is observed with increasing temperature. The nature of the organic solvent or matrix should not effect this phenomenon to any significant extent as appears to be the case from experimental data. However, when the solvent is in the liquid phase, and in absence of large orbital momentum contribution or orbital degeneracy, a one-line symmetrical spectrum of O_2^- would normally be expected, due to complete averaging of the *g*-anisotropy caused by rapid tumbling of O_2^- entities. However, an *asymmetric* one-line spectrum is observed, whose amplitude continues to decrease rapidly with temperature, even in the liquid phase. To understand this interesting and relatively unusual phenomenon, one has to bear in mind that (i) the matrix of the frozen solvent softens and remains soft at temperatures much below the melting point and (ii) that a certain degree of order may be preserved at temperatures above the melting point accompanied by retention of relatively high viscosity. The large drop in signal intensity over a wide temperature range encompassing both the frozen state and solution phase can be rationalized in terms of these two phenomena. The increased mobility of O_2^- with increasing temperature and spin–lattice relaxation would lead to enhanced averaging of the *g*-anisotropy resulting in a broad line in the solution phase instead of two separate lines corresponding to $g_{\parallel}$ and $g_{\perp}$. However, the retention of an anisotropic spectrum of O_2^- in the liquid phase indicates that *g*-anisotropy is too large to be completely averaged out.

A study with TEMPOL (Figure 2) shows that in contrast with O_2^- (i) the expected (Curie) dependence of integrated signal intensity on temperature is observed and (ii) hyperfine structure is observed to be resolved at temperatures immediately above the melting point of the solvent. TEMPOL is a large molecule relative to O_2^- with an almost totally quenched orbital momentum and almost zero *g*-anisotropy. Under these circumstances, the temperature dependence of the ESR signal intensity simply mirrors changes in viscosity. In contrast the very small change in *g*-anisotropy indicates that the orbital momentum of O_2^- is modulated by the fluctuations in the O–O bond length[29,30] leading to a shortened spin relaxation time with increasing temperature.

The spectrum of O_2^- in frozen solvent was essentially independent of the preparation technique (KO_2 dissolution in the presence of crown ether or electrolytic generation). It was also found that no change in the line shape of the ESR signal could be detected in the solution phase after bubbling argon through the solvent to remove molecular oxygen. This indicates that negligible electron exchange occurs between O_2 and O_2^- on the ESR time scale in the solution phase. The stability of O_2^- solutions in the organic phase over the temperature range of interest was confirmed by the constancy of repeated experiments performed after a number of freeze–thaw cycles.

As a precursor to performing the electrochemical generation of O_2^-, cyclic voltammetric measurements on the reduction of O_2 were made with mercury, glassy carbon, platinum, and gold electrodes in butyronitrile. The formal reversible potentials, calculated as the average of the reduction and oxidation peaks, are −1.01 (Hg), −1.01 (glassy carbon), −1.00 (Pt), and −1.05 (Au) V vs SCE. The formal potentials are essentially independent of electrode material as expected theoretically. However, the values in butyronitrile are more negative than in dimethyl sulfoxide.[31] The large difference between the formal potentials reported in butyronitrile and the standard potential of O_2/O_2^- redox couple in water ($E° = -0.33$ V vs NHE)[32] can be attributed to solvation affects.[5]

Registry No. TEMPOL, 2226-96-2; O_2^-, 11062-77-4.

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Light-Sensitive Oscillations in the Hydrogen Peroxide Oxidation of Ferrocyanide[1]

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We recently designed a new pH oscillator using a continuous-flow stirred tank reactor (CSTR) in which sulfite ions and hexacyanoferrate(II) ions are simultaneously oxidized by hydrogen peroxide in water solution.[3] Further study of this system reveals that, in a significant excess of H_2O_2, pH oscillation occurs without sulfite in the hexacyanoferrate(II)–hydrogen peroxide reaction. This new mode of oscillation is extremely sensitive to visible light.

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