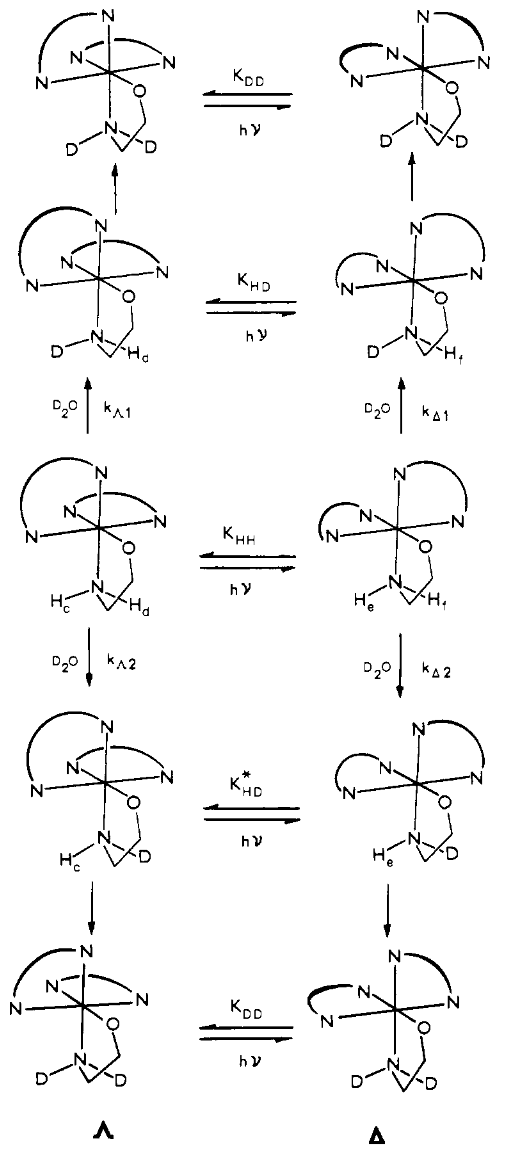

Figure 4. Possible deuterium-exchange processes and photocatalyzed chiral equilibria. Results indicate $k_{\Delta 1} > k_{\Lambda 2} >> k_{\Delta 2} > k_{\Lambda 1}$, K_{HH} = 1.24 (4), and K_{DD} = 1.13 (2). K_{HD} and K^*_{HD} are indeterminant.

were to form in the reaction reported here, with the deprotonation step being stereospecific and assisted by a solvent (or OD^-) interaction, then attack at that intermediate by D_2O also must be sterically controlled so as to allow complete formation of the mono-N-deuterated forms as observed (Figure 3).

If the mechanism for the photoinduced chiral equilibration were to involve "bond rupture",[11,12] then the rotations thus allowed should mean that exchange at the amine group would be nonspecific. If the Ru-NH_2 bond in particular were to break, then H-D exchange with the solvent should be rapid, and the rate of disappearance of the amine proton signals would be determined by that of the equilibration process at the metal. A fluxional "twist" mechanism,[11,12] if slow, would demonstrate a constant equilibrium ratio of all four N-H ^{1}H NMR signals until complete exchange is observed, with this ratio reflecting to a large extent the relative rates of the two processes. However, if the "twist" process were comparatively rapid, then an approximately equal amine proton ratio would persist until exchange is complete. At this stage of our investigations no distinction can be made between these two mechanisms. However, as the rate of attainment of chiral equilibrium may be controlled by the incident light intensity[10] and the rate of proton-deuteron exchange is pD dependent, then manipulation of these parameters should allow a distinction to be made between the two mechanisms. Such a study has begun.

Acknowledgment. The authors are indebted to Mr. A. Tseng of the School of Chemistry, Macquarie University, for the recording of ^{1}H NMR spectra. P.A.W. wishes to thank the British Council for a travel grant.

Registry No. Λ-[(L-Alaninato)bis(2,2'-bipyridine)ruthenium(II)] perchlorate, 83692-85-7; Δ-[(L-alaninato)bis(2,2'-bipyridine)ruthenium(II)] perchlorate, 83730-07-8; hydrogen, 1333-74-0.

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Reinvestigation of 18-Crown-6 Ether/Potassium Superoxide Solutions in Me_2SO

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It was recently reported[1] that optical absorption measurements are unsatisfactory for determining superoxide ion (O_2^-) concentrations in dimethyl sulfoxide (Me_2SO) solutions. Solutions of KO_2 in Me_2SO are often prepared with use of 18-crown-6 ether to increase the solubility of the salt.[2] The concentrations of these solutions are measured spectroscopically.[3] Spectra of KF, KCl, KCN, and KH_2PO_4 in 0.3 M 18-crown-6 ether in Me_2SO were published,[1] showing a large maximum at ~275 nm with $\epsilon \approx 3000\ M^{-1}\ cm^{-1}$. If such a spectral band did arise from 18-crown-6 ether potassium complexes in Me_2SO, spectrophotometric determinations of the superoxide concentrations in crown ether solubilized KO_2 used in many laboratories including our own[4] would be unreliable. We were therefore prompted to undertake this reinvestigation of potassium crown ether complexes and of the stability of superoxide ion in Me_2SO.

Experimental Section

Potassium chloride (Fisher Certified) and potassium bromide (Baker Analyzed) were finely ground in a mortar, dried at 150 °C, and stored under vacuum. Potassium fluoride (Baker Analyzed) was heated in a platinum crucible over a Bunsen burner for 2 h and finely ground after cooling. Potassium superoxide (Alfa, 95%, stored under N_2) was finely ground and kept in a Vacuum Atmospheres drybox. 18-Crown-6 ether (Aldrich, Recrystallized[4]) was dissolved in Me_2SO (Aldrich spectrophotometric grade, freshly distilled over CaH_2 at a reduced pressure of N_2) to give a 0.08 M stock solution. Weighed amounts of KF, KCl, KBr, and KO_2 were dissolved in this crown ether solution in a glovebag filled with dry N_2. For the solutions of KCl and KBr, the concentration of potassium was determined by atomic absorption spectroscopy (Galbraith Laboratories, Knoxville, TN).

UV spectra were recorded at 25 °C with use of a Cary 118C spectrophotometer and 0.1-mm path length matched quartz cells. Dimethyl sulfone was determined by gas chromatography on a Varian Aerograph 1400. The carrier gas was N_2, Carbowax 20 M on Chromosorb was used as the column material, and the column temperature was 150 °C.

Results

The spectra of 18-crown-6 ether and its complexes of KCl, KBr, and KO_2 in Me_2SO are shown in Figure 1. They clearly

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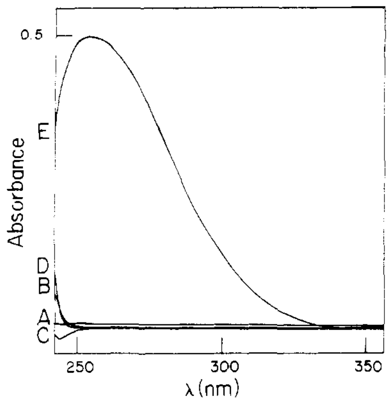

Figure 1. Absorption spectra of potassium salts in Me_2SO containing 18-crown-6 ether as a solubilizing agent: (A) empty cells; (B) 0.08 M 18-crown-6 ether in Me_2SO; (C) 0.012 M KBr; (D) 0.014 M KCl; (E) 0.019 M KO_2. In B–E, Me_2SO was in the reference cell.

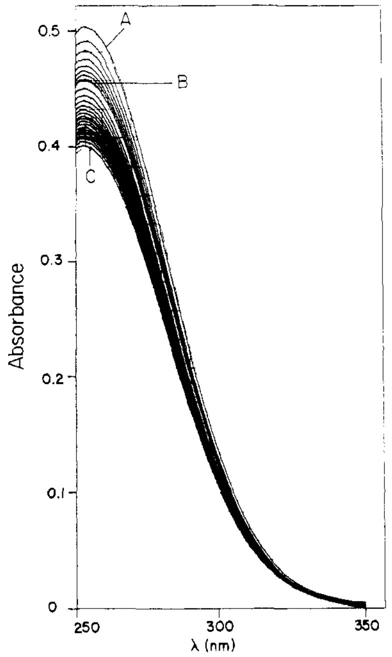

Figure 2. Time dependence of the absorption of 0.019 M KO_2 in 0.08 M 18-crown-6 ether in Me_2SO: (A) taken 30 min after preparation of the solutions; (A–B) taken in 19-min intervals; (B–C) taken in 52.5-min intervals.

indicate that, between 250 and 350 nm, the crown ether complexes of KF (not shown), KCl, and KBr do not significantly absorb, whereas that of KO_2 does.

As can be seen from Figure 2, superoxide solutions in Me_2SO containing 18-crown-6 ether undergo a spectral change with time. The decreasing absorbance suggests decomposition of the superoxide ion. A logarithmic plot of the maximum absorbance vs. time is given in Figure 3. After a rapid initial reaction, an approximately first-order decay with a half-life of about 100 h occurs. The decomposition of the superoxide solutions is further indicated by increasing amounts of dimethyl sulfone found in these solutions. Freshly prepared 0.019 M

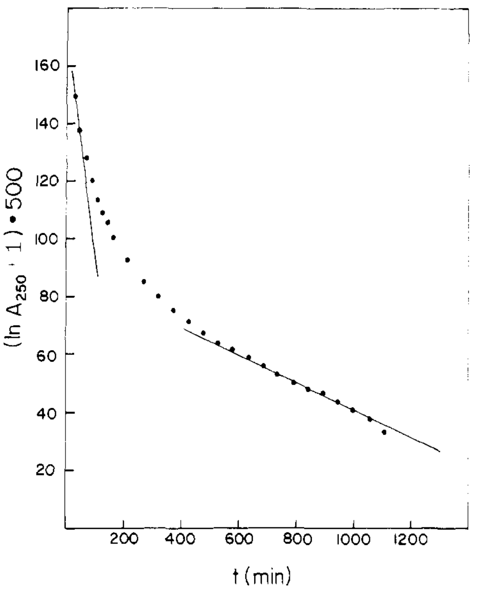

Figure 3. Plot of the logarithm of the absorbance at 250 nm vs. time for 0.019 M KO_2 in 0.08 M 18-crown-6 ether in Me_2SO.

KO_2 contained only about 0.001 M sulfone. Two 0.0235 M KO_2 solutions stored for 2 months at room temperature were found to be 0.010 and 0.011 M, respectively, in sulfone. Formation of sulfone was also observed for a frozen solution stored for 2 months at 0 °C.

Discussion

Since none of the KF, KCl, and KBr crown ether complexes absorb significantly between 250 and 350 nm, we conclude that the spectrophotometric determination of superoxide suggested in the early report by Valentine and Curtis[2] is not affected by the potassium crown ether complex and is a reliable method. Extrapolating the data in Figure 3 to zero time gives a molar absorptivity, $\epsilon_{250} = 2715\ M^{-1}\ cm^{-1}$, a value within the error limits of the literature value ($\epsilon_{250} = 2686 \pm 29\ M^{-1}\ cm^{-1}$).[3] It should be noted, however, that crown ether solubilized potassium superoxide solutions slowly decompose. The stoichiometry of this decomposition, based on the quantitative determination of sulfone, can be formulated as in eq 1. In

$$2O_2^- + 2Me_2SO \rightarrow O_2 + Me_2SO_2 + OH^- + MeSO(CH_2)^- \quad (1)$$

this reaction superoxide disproportionates and Me_2SO serves both as a reducing agent and as a proton source to stabilize the O^{2-} that is formed. Alternatively, if water were present in the solvent, the decomposition of superoxide might occur according to eq 2 and 3. Our results do not distinguish

$$2O_2^- + H_2O \rightarrow HO_2^- + OH^- + O_2 \quad (2)$$

$$HO_2^- + Me_2SO \rightarrow OH^- + Me_2SO_2 \quad (3)$$

between these two alternatives. In any case, the concentration of superoxide should be checked spectrophotometrically prior to any experiment in which it is used.

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Registry No. KBr, 7758-02-3; KCl, 7447-40-7; KO_2, 12030-88-5; Me_2SO, 67-68-5.

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