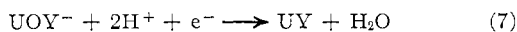the U(V) resulting from the first electron transfer involves protonation and subsequent removal of the uranyl oxygen atoms followed by the second electron transfer to yield a nonoxygenated U^{IV}–EDTA species

$$UO_2HY^{2-} + H^+ \rightleftharpoons UOY^- + H_2O \qquad (6)$$

$$UOY^- + 2H^+ + e^- \longrightarrow UY + H_2O \qquad (7)$$

Additional information on the actual reaction sequence could have been obtained if the intermediate U^V–EDTA species had been isolated. Attempts to generate the U(V) complex by controlled-potential electrolysis at pH 6.5 (where $E_2{}^{\circ\prime}$ lies slightly cathodic of $E_1{}^{\circ\prime}$) were not successful, probably because the two reduction potentials are still not sufficiently separated. The desired intermediate possibly could be prepared by first generating a stable solution of the U(V) cation and then adding EDTA to this. However, U(V) tends to disproportionate to form mixed valence state complexes and makes such a procedure infeasible.

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Proton Nuclear Magnetic Resonance Studies of Uranium(IV)–Ethylenediaminetetraacetic Acid Complexes

BY DEWAYNE L. EHMAN AND DONALD T. SAWYER

The proton nmr spectrum of a 1:1 paramagnetic uranium(IV)-ethylenediaminetetraacetic acid complex (prepared by dissolving $U^{IV}(EDTA)\cdot 2H_2O$ in aqueous Na_2SO_4 solutions) has been studied as a function of pH and temperature. The magnetic moment of the complex is 3.01 BM as determined from the nmr data. Because of the anisotropy of the U(IV) unpaired electron spin at the ligand protons, the spectra exhibit extensive contact shifts (10–35 ppm). Above 45° the spectrum consists of an AX pattern for the ligand acetate protons plus a singlet for the ethylenic group; the resonances broaden as the temperature is lowered. Below 7° the broadened A resonance splits into two singlets and the X resonance becomes narrower; the ethylenic resonance splits into two singlets. On the basis of the nmr data a plausible solution structure for the complex is proposed as well as an exchange mechanism for the ligand protons. The exchange rates and their energies of activation have been determined. Clear evidence that the nmr spectral displacements are due to pseudocontact shifts is given by the large differences in the chemical shift values for the methylenic protons of the ligand acetate groups.

The complexes of uranium(IV) with the ethylenediaminetetraacetic acid tetraanion (EDTA) have been the subject of a number of investigations.[1-14] There is general agreement that the coordination number of U(IV) is 8,[1] which makes possible a variety of complexes with the sexadentate EDTA ligand. Complexes with metal-to-ligand ratios of 1:1,[2-11] 1:2,[4] 2:1,[5] and 2:3[5] have been reported.

A potentiometric study[5] has indicated that the stable form of the 1:1 complex is $U^{IV}(EDTA)(H_2O)_2$ between pH 0.0 and 3.5 with a formation constant,[8] K_f, of 6 × 10^{25}. At higher pH values the complex apparently loses a proton to form $U(EDTA)(H_2O)(OH)^-$, which undergoes an olation reaction

$$2U(EDTA)(H_2O)(OH)^- \rightleftharpoons [U(EDTA)(OH)]_2{}^{2-} + 2H_2O \qquad (1)$$
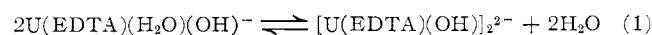
to form a dimeric hydroxy-bridged species. Previous work has established that the limited solubility of $U(EDTA)(H_2O)_2$ in water (6.45 mM at 25°) can be increased by dissolving the complex in solutions containing ionic complexing agents such as oxalate, carbonate, sulfate, citrate, tartrate, or fluoride ions; apparently these replace one or both of the coordinated waters of the complex.

A dodecahedron or a quasi-dodecahedron with trigonal faces has been suggested for the structure of $U^{IV}(EDTA)(H_2O)_2$ on the basis of its similarity to the Th(IV) complexes.[12] However, a cubic or slightly perturbed cubic symmetry has been proposed as more reasonable because of the low magnetic moment of the complex (2.8 BM);[13] U(IV) complexes with orthorhombic symmetry, such as $U(SO_4)_2\cdot 4H_2O$, have magnetic moments of about 3.6 BM.[13] The structure of $U^{IV}(acetylacetonate)_4$ has been shown to be a square antiprism on the basis of its isomorphism with Th^{IV}-

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(acetylacetonate)$_4$,[14,15] and a straight cubic structure has been postulated for U^{IV}(oxalate)$_4^{4-}$ with $5f6d^37s7p^3$ hybridization.[16]

There is general agreement that U(IV) has two unpaired electrons with the electronic configuration $5f^2$ (instead of 5f6d or $6d^2$);[1] thus, U(IV) complexes are expected to be paramagnetic. The potential value of nmr studies of paramagnetic species was first demonstrated in 1958 by the experimental[17,18] and theoretical[19,20] work of McConnell and coworkers. The required condition for the observation of an nmr spectrum for a paramagnetic molecule is[21]

$$T_1^{-1} \text{ or } T_e^{-1} \text{ or both} \gg \frac{\gamma_e}{2\pi} a_i \qquad (2)$$

where T_1 is the electronic relaxation time, T_e the electronic exchange time, γ_e the gyromagnetic ratio of the electron, and a_i the isotropic hyperfine interaction constant resulting from contact interaction at proton i. The interactions of the unpaired electrons of a metal ion with the ligand protons (through delocalization of unpaired electron spin density, anisotropy of unpaired electron spin density, or both) cause chemical shift values to be displaced from those of a diamagnetic complex.

Wiedenheft[22] has obtained proton nmr spectra of U^{IV}(dibenzoylmethane)$_4$ and U^{IV}(1-phenyl-1,3-hexanedione)$_4$ in deuteriochloroform which indicate displacements in the chemical shift values of about 6 ppm from those of the diamagnetic Th(IV) counterparts. Displacements in the chemical shift values also have been observed in the proton nmr spectrum of U^{IV}(diethyldithiocarbamate)$_4$.[23] Larger displacements of chemical shift values (on the order of 150 ppm) have been observed in the proton nmr spectra of the Co(II) and Ni(II) complexes with EDTA.[24]

The present study has been undertaken to determine the proton nmr spectra of the 1:1 U^{IV}–EDTA complexes in aqueous (D$_2$O) 1.0 F Na$_2$SO$_4$ solutions, to determine the solution structures for the complexes, and to determine the rates of interconversion of ligand protons. Proton nmr spectra have been obtained at 60 and 100 MHz, and solution structures have been proposed which are consistent with the nmr data, magnetic susceptibility measurements, and results of acid–base titrations. The rates and activation parameters for EDTA proton interconversions have been determined by using computer analysis of the nmr line shapes.[25]

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Experimental Section

Equipment.—The proton nmr spectra were recorded with a Varian Model A-60 spectrometer (60 MHz) and a Varian Model HA-100 spectrometer (100 MHz) operated in the HR mode. The latter was calibrated with the side bands from a Hewlett-Packard audio oscillator connected to the modulation input of the fixed-frequency radiofrequency unit (Model V-4311) on the spectrometer; the audio oscillator was calibrated with the frequency counter (Model V-4315) of the spectrometer. The temperatures of the nmr samples were established with Varian variable-temperature controllers (Model V-4343 for the HA-100 spectrometer and Model V-6040 for the A-60 spectrometer). Temperatures below 28° were obtained by using a Dry Ice–acetone slurry in a dewar for the heat exchanger. The sample temperatures were calibrated by measuring the peak separations in the nmr spectra of ethylene glycol (from 383 to 310°K) and of methanol (from 305 to 265°K) and using the equations developed by Van Geet[26]

$$T = 466.0 - 1.694|\Delta \nu_1| \qquad (3)$$

$$T = 464.0 - 1.775|\Delta \nu_2| \qquad (4)$$

where T is the absolute temperature, $\Delta \nu_1$ the peak separation (in hertz at 60 MHz) for ethylene glycol, and $\Delta \nu_2$ the peak separation for methanol. Chemical shifts were measured downfield (δ) from an internal TMS* standard (sodium 2,2-dimethyl-2-silapentane-5-sulfonate).

The magnetic susceptibilities of the U^{IV}–EDTA complexes were determined by using the nmr method developed by Evans[27] and modified by Rettig.[28] The U^{IV}–EDTA complexes in 1.0 F Na$_2$SO$_4$ solutions containing TMS* as an internal reference were placed in an outer tube; 1.0 F Na$_2$SO$_4$ solutions containing TMS* were placed in an inner tube. The displacement in the chemical shift value of TMS* in the paramagnetic solution from its value in the diamagnetic solution was recorded on the A-60 spectrometer at probe temperature (38°). The concentrations of the U^{IV}–EDTA complexes were determined before and after the nmr measurements with K$_2$Cr$_2$O$_7$.[29]

Adjustment of solution acidity and acid–base titrations were performed with a Leeds and Northrup line-operated pH meter which was standardized with Sargent standard buffer solutions. No correction was made for the large abundance of D$_2$O in the aqueous solutions; all reported pH values refer to the pH meter reading for the solutions at room temperature.

Reagents and Solutions.—All chemicals were reagent grade or better and were used without further purification. The D$_2$O was obtained from Mallinckrodt Chemical Works and had an isotopic purity of 99.8%. The UO$_2$(ClO$_4$)$_2 \cdot x$H$_2$O used to generate U(IV) was obtained from the G. Frederick Smith Chemical Co., H$_4$EDTA from J. T. Baker Chemical Co., and TMS* from Eastman Organic Chemicals and Merck Sharp and Dohme of Canada, Ltd. HCl and NH$_3$ were used for adjusting the acidity of the U^{IV}–EDTA solutions, and HClO$_4$ was used for the supporting electrolyte for the electrochemical reduction of UO$_2^{2+}$. Solutions of NaOH and NH$_3$ standardized with primary standard potassium biphthalate were used in the acid–base titrations.

Perchloric acid solutions of U(IV) were prepared by the electrochemical reduction of 70-ml quantities of 0.35 F UO$_2$(ClO$_4$)$_2 \cdot x$H$_2$O in 4 F HClO$_4$, using a Hewlett-Packard dc power supply connected to a mercury-pool cathode and a platinum-wire anode.[8,30,31] The cell consisted of a 100-ml beaker with a tungsten wire sealed into the bottom to maintain contact with the mercury-pool electrode, a fritted glass tube for the anode com-

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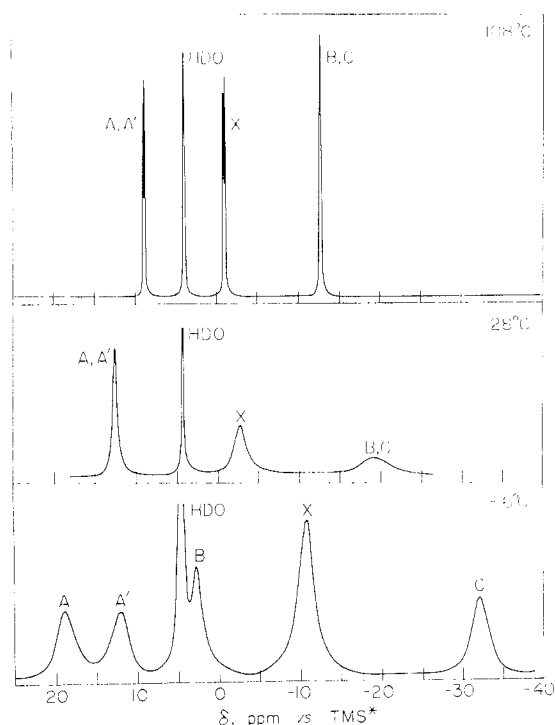
Figure 1.—The 100-MHz proton nmr spectra of 0.3 F U^{IV}-(EDTA) in 1.0 F Na$_2$SO$_4$ and 0.01 F TMS*at pH 2.00; sweep rate, 12.9 Hz/sec.

partment, and a Leeds and Northrup saturated calomel electrode (sce) to reference the potential of the mercury-pool electrode. The potential of the mercury-pool electrode *vs.* sce was kept at or above -0.5 V by adjusting the power supply.

The resulting dark green U(ClO$_4$)$_4$ solutions were standardized with K$_2$Cr$_2$O$_7$[29] using barium *p*-diphenylamine sulfonate as the indicator. U^{IV}(EDTA)(H$_2$O)$_x$ was prepared by adding 1 equiv of dry H$_4$EDTA to a standardized acidic U(ClO$_4$)$_4$ solution and adjusting the pH to 1.0 with NH$_3$. The grayish green precipitate was filtered while the solution was hot (to prevent any NH$_4$-ClO$_4$ from precipitating) and then washed twice with water and once each with acetone and anhydrous diethyl ether.[5] The resulting grayish green powder was analyzed for C and H by Elek Microanalytical Laboratories, Torrance, Calif., and for U(IV) using K$_2$Cr$_2$O$_7$.[29] The results indicate that the composition is U^{IV}(EDTA)(H$_2$O)$_3$. *Anal.* Calcd for UC$_{10}$H$_{18}$O$_{11}$N$_2$: C, 20.70; H, 3.13; U^{IV}, 41.01. Found: C, 20.58; H, 3.15; U^{IV}, 41.77.

Aqueous (D$_2$O) solutions of 0.3 F U^{IV}(EDTA) and 0.005 or 0.01 F TMS* in 1.0 F Na$_2$SO$_4$ were prepared by adding D$_2$O to the TMS* and the anhydrous Na$_2$SO$_4$ with stirring and heating (just to boiling) until all the solid dissolved and then adding U^{IV}-(EDTA)(H$_2$O)$_3$ and again stirring and heating until the U^{IV}(EDTA) complex dissolved. The resulting solutions were then cooled and their acidities were adjusted with either HCl or NH$_3$. The D$_2$O solutions of 0.3 F U^{IV}(EDTA) and 0.005 F TMS* containing no Na$_2$SO$_4$ were prepared by adding D$_2$O to the U^{IV}(EDTA)(H$_2$O)$_3$ powder and TMS* and then stirring and adding NH$_3$ until all the solid dissolved (at about pH 5.2). Solutions containing 0.1 F U^{IV}(EDTA) and 0.02 F TMS* for magnetic susceptibility measurements were prepared in a similar manner.

Exchange Rates.—Each of the EDTA proton-exchange processes was treated as a two-site exchange[32–34] in conjunction with two Fortran IV computer programs to determine the exchange rates from the nmr data. The nmr curve-fitting program of

Neuman and Jonas,[35] based on the total line-shape equation of Gutowsky and Holm,[36] was used to calculate the standard deviations between experimental and calculated line intensities for a range of values of τ (equal to $1/2k$) and $\delta\nu_\infty$, where τ is related to the average lifetimes of the exchanging protons at each site, k the first-order rate constant for the transfer of a proton from one site to the other, and $\delta\nu_\infty$ the nonexchanging chemical shift difference between the two protons. The values of τ and $\delta\nu_\infty$ that gave the smallest standard deviations between the experimental and calculated line intensities were then used in a computer program based on the equation of Gutowsky and Holm[36] to plot the calculated line shapes for comparison with the experimental spectra. Values for T_2 (equal to $2/W_{1/2}$, where $W_{1/2}$ is the peak width at half-intensity for the unbroadened resonance of the exchange process) were taken from the nmr spectra at 108°.

Results

The 100-MHz proton nmr spectra of the paramagnetic U^{IV}(EDTA) complex at pH 2.00 in 1.0 F Na$_2$SO$_4$ for three different temperatures are shown in Figure 1. Above 45° the spectra consist of one AX pattern and an upfield singlet with relative intensities of 2:1. The coupling constant between the A and X protons, J_{AX}, is 16.4 Hz at 100 and 60 MHz, and the chemical shift difference between protons A and X, $\delta_A - \delta_X$, is 9.76 ppm at 100 MHz and 108°. The value for the coupling constant agrees with those obtained for other metal–EDTA complexes.[37] Below 45° all of the U^{IV}(EDTA) peaks broaden so that the coupling between the A and X protons is not observed. At 20° the upfield singlet splits into two broad singlets (B and C), and below 7° the A peak also splits into two broad singlets (A and A'); the X peak remains a broad singlet. The temperature dependence of the chemical shift values for HDO and for the A,A', X, and B,C protons of the U^{IV}(EDTA) complex are summarized in Figure 2. The extrapolated chemical shift values at infinite temperature ($1/T \rightarrow 0$) for all types of protons are similar to those expected for a diamagnetic EDTA complex.[37]

The nmr spectra of U^{IV}(EDTA) solutions (1.0 F Na$_2$SO$_4$) at high temperatures (>45°) exhibit AX patterns and an upfield singlet from pH 1.00 to 3.00. At pH values below 1.00 all of the U^{IV}(EDTA) peaks become smaller and broader, so that no AX coupling is observed, and peaks due to uncomplexed EDTA appear at pH 0.00; at pH -0.50 only peaks due to uncomplexed EDTA are observed. Above pH 3.00 the U^{IV}(EDTA) peaks become broader and undergo large displacements in their chemical shift values with increasing pH (see Figure 3). Above pH 6.50 the U^{IV}-(EDTA) solutions are sensitive to air oxidation. The pH dependence of the chemical shift values for the A,A', X, and B,C protons at 92° is illustrated by Figure 4. Assignment of the resonances for regions of crossover in Figures 2 and 4 have been made on the basis of peak area measurements and a large number of spectra in the vicinity of the temperatures and pH values where overlapping peaks occur. A smooth, continuous change of chemical shift values also has been assumed.

At 28° the nmr spectra of U^{IV}(EDTA) solutions

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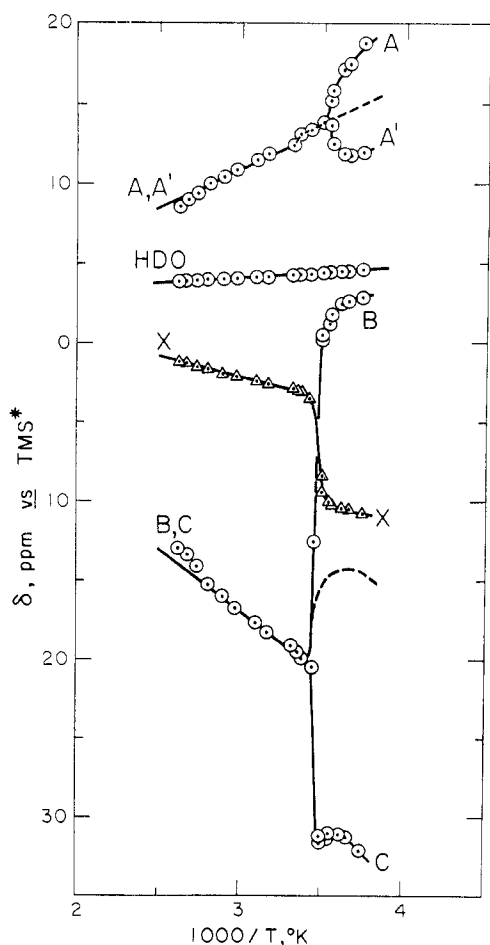(37) Y. O. Aochi and D. T. Sawyer, *Inorg. Chem.*, **5**, 2085 (1966).

Figure 2.—Temperature dependence of the chemical shift values for HDO and for A,A′, X, and B,C protons of U^{IV}(EDTA). Solution: 1.0 F Na$_2$SO$_4$, 0.3 F U^{IV}(EDTA), 0.01 F TMS*, pH 2.00.

Figure 3.—The 100-MHz proton nmr spectra of 0.3 F U^{IV}-(EDTA). Spectra at 92°: 1.0 F Na$_2$SO$_4$ and 0.005 F TMS*; sweep rate, 9.8 Hz/sec. Spectrum at 103°: 0.005 F TMS* and no Na$_2$SO$_4$; sweep rate, 19.2 Hz/sec.

Figure 4.—pH dependence of the chemical shift values for the A,A′, X, and B,C protons of U^{IV}(EDTA) at 92°. Solution: 1.0 F Na$_2$SO$_4$, 0.3 F U^{IV}(EDTA), and 0.005 F TMS*.

(1.0 F Na$_2$SO$_4$) between pH −0.50 and 6.50 are quite broad; below pH 2.50 the peaks become smaller and broader, and peaks due to uncomplexed EDTA appear at pH 1.00. Above pH 2.50 the U^{IV}(EDTA) peaks also become smaller and broader up to pH 6.50, where the peaks cannot be detected. The nmr spectra of the complex at −4° from pH 2.50 to 1.50 resemble the spectrum at −6° in Figure 1; below pH 1.50 peaks due to uncomplexed EDTA appear, while at pH 6.50 the nmr spectrum consists of ten ill-defined peaks.

The nmr spectra of U^{IV}(EDTA) solutions which do not contain Na$_2$SO$_4$ are different from those with 1.0 F Na$_2$SO$_4$; discernible peaks for U^{IV}(EDTA) are not observed at −2 or 28° in solutions containing no Na$_2$SO$_4$. However, at 103° the spectrum consists of three broad peaks (see Figure 3).

The splittings of the A,A′ and B,C peaks at low temperatures have been treated as two-site exchange processes.[32-36] Good agreement between calculated line shapes and experimental spectra occurs with $\delta\nu$ and T_2 values of 685 Hz and 0.1220 Hz^{-1}, respectively, for the A,A′ exchange process and 3595 Hz and 0.2994 Hz^{-1}, respectively, for the B,C exchange process at 100 MHz. The rate constants for the two exchange processes at several temperatures are summarized in
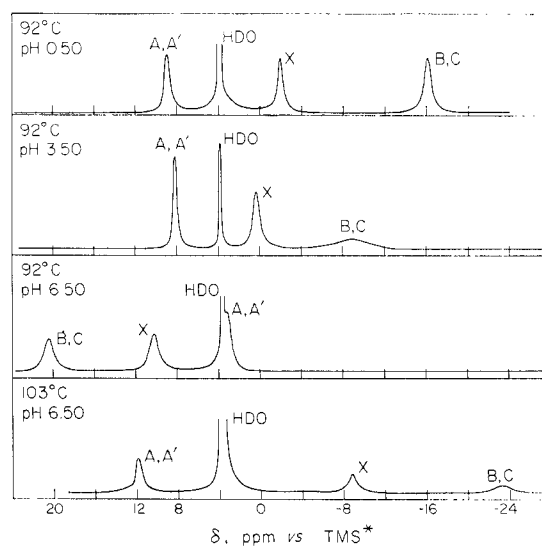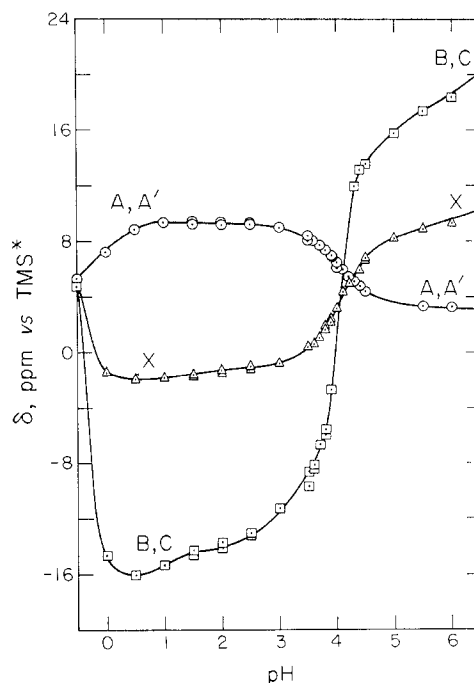
Table I. The coalescence temperature is 279°K for the A,A′ exchange process and 292°K for the B,C exchange process. Between pH 1.50 and 2.50, the apparent stability range for a single complex species, pH does not have a significant effect on the line widths and exchange kinetics. The limited solubility of the complex has precluded meaningful studies of the effect of concentration on the exchange rates.

An Arrhenius plot for the A,A′ exchange process yields a straight line for temperatures from 267 to 298°K; for the B,C exchange process a straight line is obtained between 301 and 366°K (see Figure 5).

TABLE I

RATE CONSTANTS FOR THE EXCHANGE OF PROTONS A AND A'
AND OF PROTONS B AND C IN THE U^{IV}(EDTA) COMPLEX
(1.0 F Na$_2$SO$_4$, pH 2.00)

A,A' exchange		B,C exchange	
Temp, °K	Log [$k_{A,A'}$(sec^{-1})]	Temp, °K	Log [$k_{B,C}$(sec^{-1})]
316	4.43	366	6.16
301	4.15	356	5.90
298	3.83	345	5.75
292	3.60	336	5.49
285	3.34	323	5.23
281	3.15	316	5.03
277	2.99	301	4.68
273	2.92	273	3.13
267	2.74	267	2.86

Above 298°K another process, such as the breaking of the acetate–uranium(IV) bonds, may commence and allow the A,A' exchange process to occur more easily; this in turn probably would make the B,C exchange process less hindered. Such a conclusion is supported by the discontinuity in the A,A' chemical shift curve of Figure 2 at 298°K and by the high values of the two high-temperature A,A' rate constants (Figure 5). Below 301°K the B,C nmr curves become difficult to match with calculated line shapes. However, the near coincidence of the A,A' and B,C rate constants at low temperatures supports the conclusion that the two exchange processes have a common mechanism.

Values for E_a and for log A, determined from the straight-line portions of the plots in Figure 5, are
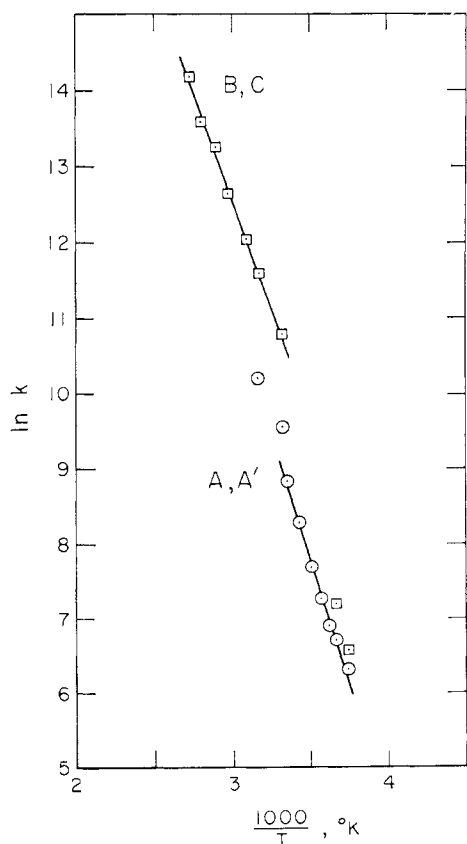

Figure 5.—Arrhenius plot for the A,A' and the B,C proton-exchange processes. Solution: 0.3 F U^{IV}(EDTA), 1.0 F Na$_2$-SO$_4$, 0.01 F TMS*, pH 2.00.

TABLE II

ACTIVATION PARAMETERS FOR THE A,A' AND
B,C PROTON-EXCHANGE PROCESSES

Exchange process	Temp, °K	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
A,A'	298	12.7 ± 0.7	11.8 ± 0.5	3.0 ± 2.0
B,C	301	10.8 ± 0.3	10.8 ± 0.3	0.0 ± 1.0

13.3 ± 0.7 kcal mol^{-1} and 13.6 ± 0.5, respectively, for the A,A' exchange process and 11.4 ± 0.3 kcal mol^{-1} and 12.9 ± 0.3, respectively, for the B,C exchange process. Other activation parameters for both exchange processes are summarized in Table II. The values for $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ have been calculated assuming that both exchange processes involve intermediates. Thus, the observed rate constants, $k_{A,A'}$ and $k_{B,C}$, have been doubled for these calculations because the rate of formation of an intermediate is twice the rate of exchange of protons between sites A and A' or between sites B and C; *i.e.*, half of the intermediates from sites A and B go to sites A' and C, respectively, and half revert to sites A and B.[38]

Molar magnetic susceptibilities of U^{IV}(EDTA) in 1.0 F Na$_2$SO$_4$ at pH 2.00 and at pH 6.50 have been determined by an nmr procedure. The magnitude of the TMS* nmr peak displacement is related to the molar magnetic susceptibility of the complex by the relation

$$\chi_M' = \frac{3\Delta\nu}{2\pi\nu C} + \chi_D \qquad (5)$$

where χ_M' is the molar magnetic susceptibility in cgs units, $\Delta\nu$ the displacement of the chemical shift value of the internal standard, ν the probe frequency, C the concentration of the complex in moles per milliliter, and χ_D the correction given by Pascal's constants[39] for the diamagnetism of substances present only in the paramagnetic solution (such as EDTA). For the U(IV) complex the values of χ_M' at 311°K are 3604 × 10^{-6} and 2304 × 10^{-6} cgsu at pH 2.00 and at pH 6.50, respectively; values for χ_D of 138 × 10^{-6} cgsu for EDTA and 18 × 10^{-6} cgsu for NH$_3$ have been used.[39] Assuming that the U^{IV}(EDTA) complexes obey the simple Curie law,[40] the magnetic moments of the complexes may be determined from the equation[40]

$$\mu = 2.84(\chi_M' T)^{1/2} \qquad (6)$$

where μ is the value of the magnetic moment and T is the absolute temperature. On this basis, the values for the magnetic moments of U^{IV}(EDTA) at pH 2.00 and at pH 6.50 are 3.01 and 2.41 BM, respectively.

Acid–base titration curves for U^{IV}(EDTA)(H$_2$O)$_3$ in H$_2$O with and without 1.0 F Na$_2$SO$_4$, using an NH$_3$ solution as titrant, exhibit end points at pH 6.0 after the addition of 1 equiv of NH$_3$. The curves are similar except at their beginnings, where, in the absence of Na$_2$SO$_4$, considerable U^{IV}(EDTA)(H$_2$O)$_3$ remains un-

(38) F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).

(39) A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, London, 1968, p 6.

(40) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966, pp 639, 640.

dissolved and the pH equilibrates slowly up to pH 5.2. The titration in the absence of Na_2SO_4 agrees with the results of Ermolaev and Krot,[5] who interpreted their results as the loss of a proton from one of the complexed waters of $U^{IV}(EDTA)(H_2O)_2$ at about pH 6 and the loss of another proton from the other complexed water at about pH 9.

The acid–base titration curve for $U(ClO_4)_4$ in excess $HClO_4$, using an NH_3 solution and an NaOH solution as titrants, exhibits an end point for the titration of $HClO_4$, an end point for the titration of U(IV), and an end point for the titration of NH_4^+. The end point for the titration of NH_4^+ in the presence of U(IV) is identical with the end point for the titration of NH_4^+ in the absence of U(IV), which indicates that there is no interaction between U(IV) and NH_3.

Discussion and Conclusions

The high-temperature (>45°) proton mmr spectra of $U^{IV}(EDTA)$ solutions containing 1.0 F Na_2SO_4 from pH 1.00 to 3.00 exhibit an AX pattern and an upfield singlet with relative intensities of 2:1. Thus, the AX pattern is assigned to the two nonequivalent methylenic protons (A,A' and X) on the four acetate groups of EDTA, and the upfield singlet is assigned to the four ethylenic protons (B,C) between the two nitrogen atoms of EDTA. Apparently the two X protons are equivalent either by symmetry or by accident. Observation of an AX (or AB) pattern for a metal–EDTA complex is caused by nonequivalency of the methylenic protons due to nonlabile bonding between the metal ion and the two nitrogen donor groups of the EDTA ligand. Several metal–EDTA complexes exhibit AB patterns for the nonequivalent methylenic protons and singlets for the equivalent ethylenic protons.[37] The line broadening of the nmr spectra below pH 1.00 is due to the exchange of uncomplexed EDTA with complexed EDTA.

Above pH 3.00 another $U^{IV}(EDTA)$ complex begins to form with a completely different nmr spectrum (see Figures 3 and 4). This new complex is not the dihydroxy dimer[5] indicated by eq 1, however, because the nmr spectra of $U^{IV}(EDTA)$ solutions at pH 6.50 with and without 1.0 F Na_2SO_4 are different; this also is true at low temperatures.

At temperatures below 45° the line broadening of the nmr spectra of $U^{IV}(EDTA)$ solutions is caused by a decrease in the rates of the exchange processes (A with A', B with C, and uncomplexed EDTA with complexed EDTA at low pH values). Also, the discontinuities in the temperature dependence of the chemical shift values of the A,A' and X protons in Figure 2 indicate that the acetate–uranium(IV) bonds may become labile above 27°. The breaking and re-formation of the acetate–uranium(IV) bonds will contribute to the line broadening of the nmr spectra if the chemical shift values of the methylenic protons depend upon the formation of the acetate–uranium(IV) bond. The two broad singlets for the A and A' protons and for the B and C protons for the nmr spectra of $U^{IV}(EDTA)$ solutions at temperatures below 7° indicate further

decreases in the rates of the A,A' and the B,C proton-exchange processes.

The $U^{IV}(EDTA)$ complexes in 1.0 F Na_2SO_4 are paramagnetic. At pH 2.00 the magnetic moment of the complex is 3.01 BM, which indicates the presence of two unpaired electrons and a cubic or slightly perturbed cubic structure.[13] In contrast, at pH 6.50 the magnetic moment is 2.41 BM; this implies considerable spin pairing, possibly through the formation of an oxo-bridged dimeric species.[41]

Large displacements of the chemical shift values in the nmr spectra of $U^{IV}(EDTA)$ solutions from those of diamagnetic metal–EDTA solutions are observed because of the interactions of the unpaired U(IV) electrons with the EDTA protons. The magnitude and direction of the displacement is related to the magnitude and sign of the unpaired spin density at the resonant nucleus. Displacements of chemical shifts due to delocalization of unpaired electron spin density at the resonating nucleus are true contact shifts; shifts due to an anisotropy of unpaired electron spin density at the resonating nucleus are pseudocontact shifts.[20] Thus, paramagnetic ions may cause true contact shifts, pseudocontact shifts, or both.

The magnitude and direction of the true contact shift due to unpaired electron spin density at a particular nucleus is given by[20]

$$\frac{\Delta H_i}{H_0} = \frac{\Delta \nu_i}{\nu_0} = -a_i \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT} \qquad (7)$$

where ΔH_i is the shift in resonance field at applied field H_0, $\Delta \nu_i$ is the shift in resonance frequency at applied frequency ν_0, a_i is the isotropic hyperfine contact interaction for the ith proton, q is the isotropic g factor, β is the Bohr magneton, S is the total spin state of electrons, k is the Boltzmann constant, T is the absolute temperature, and γ_e and γ_H are the gyromagnetic ratios for the electron and proton, respectively. The expression for the proportionality between the magnitude and direction of the pseudocontact shift contribution for axially symmetric complexes in solution is[20]

$$\frac{\Delta H_i}{H_0} = \frac{\Delta \nu_i}{\nu_0} \propto \frac{1}{r_i^3} \frac{\beta^2 S(S+1)}{kT} (3\cos^2 \psi - 1) \qquad (8)$$

where r_i is the distance between the metal atom and the nucleus of the ith proton and ψ is the angle between the metal atom–ith proton vector and the principal magnetic axis. These equations indicate that the paramagnetic chemical shift value approaches the diamagnetic value with increasing temperature. Reference to Figure 2 establishes that the temperature dependence of the chemical shift values for the U^{IV}-(EDTA) complex at pH 2.00 is in agreement with these expressions.

The large chemical shift differences between the methylenic protons (A,A' and X) can only result from pseudocontact shifts. Unpaired electron spin delocalization (true contact shifts) would affect these

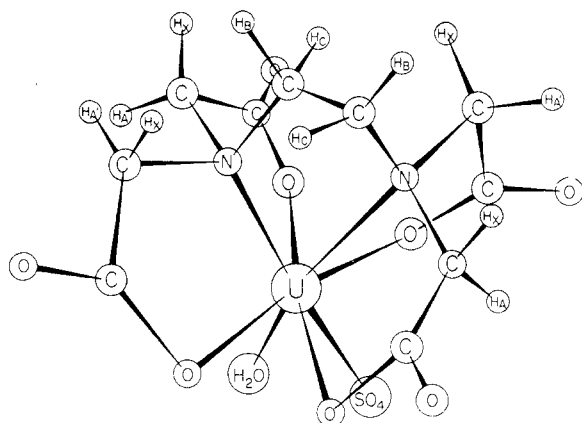(41) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967).

Figure 6.—Aqueous solution structure of $U^{IV}(EDTA)(H_2O)$-$(SO_4)^{2-}$.

protons to almost the same degree and would not cause the large splittings that are observed (see Figure 1).

Theoretical ratios for the displacements of the chemical shift values for the protons of $U^{IV}(EDTA)$ can be calculated assuming an axially symmetric structure for the complex and negligible true contact shift contributions.[22] These ratios are summarized in the last column of Table III along with values for ψ and for r_i.

TABLE III

THEORETICAL PSEUDOCONTACT SHIFT
MEASUREMENTS FOR CUBIC $U^{IV}(EDTA)$

Proton	ψ, deg	r_i, arbitrary unit	$(3 \cos^2 \psi - 1)/r_i^3$
A	70	0.109	−500
A′	56	0.093	−80
X	30	0.111	+910
B	5	0.114	+1330
C	25	0.086	+2330

The values for ψ and r_i have been determined assuming a cubic structure for $U^{IV}(EDTA)$ in 1.0 F Na_2SO_4 at pH 2.00, U(IV)–ligand bond lengths of 2.5 Å (which is slightly longer than the Zr(IV)–N bond length in the bis(nitrilotriacetato)zirconate ion[42]), and a principal magnetic axis lying on the line connecting the U(IV) nucleus with the center of the C–C ethylenic bond of the EDTA ligand. The theoretical ratios are in qualitative agreement with the chemical shift values of experimental nmr spectra. The lack of agreement for the relative position of the B resonance may indicate that the structure of the complex is not precisely cubic. However, prediction of the observed number of resonances supports the conclusion that the spectral displacements are due primarily to pseudocontact shifts.

The enhanced solubility of $U^{IV}(EDTA)(H_2O)_3$ in water containing Na_2SO_4 indicates that the SO_4^{2-} ions replace one or both of the coordinated water molecules when the complex dissolves. The acid–base titration of $U^{IV}(EDTA)$ in 1.0 F Na_2SO_4 indicates that each U(IV) ion has one coordinated water molecule. Thus, the data imply that the remaining two coordination sites on the eight-coordinated U(IV) ion in the $U^{IV}(EDTA)$ complex are occupied by one water molecule and one SO_4^{2-} ion and that the complex exists in

aqueous Na_2SO_4 solutions from pH 1.00 to 3.00 as $U^{IV}(EDTA)(H_2O)(SO_4)^{2-}$. The value for the magnetic moment of $U^{IV}(EDTA)(H_2O)(SO_4)^{2-}$ in solutions at pH 2.00 (3.01 BM) and the pseudocontact shift calculations agree with a cubic solution structure for the complex. Because the proton nmr spectra of the complex from pH 1.00 to 3.00 indicate a highly symmetrical structure in solution, a rapid exchange must occur between the coordinated water molecules and SO_4^{2-} ions. A structure which is consistent with all of the data is shown in Figure 6. The A,A′, B, and C protons of the EDTA ligand are shown "frozen" in one configuration, which conforms to the nmr spectra at low temperatures.

A recent study[43] of the exchange rates for the acetate groups in a palladium(II)–nitrilotriacetic acid complex has determined the activation parameters for the exchange reaction: $\Delta G^{\ddagger}$, 17 kcal mol^{-1}; $\Delta H^{\ddagger}$, 9.3 kcal mol^{-1}; $\Delta S^{\ddagger}$, −23 eu. These values are consistent with a process which involves an ionic transition state. The rate of chair-to-inverted-chair exchange for cyclohexane has been studied by Anet and Bourn[38] using proton nmr line broadening of C_6HD_{11}; the activation parameters are: $\Delta G^{\ddagger}$, 10.22 kcal mol^{-1}; $\Delta H^{\ddagger}$, 10.8 kcal mol^{-1}; and $\Delta S^{\ddagger}$, 2.8 eu. Such values are indicative of a ring-inversion process with six pathways for reaching the transition state.

Considering these two systems the exchange of the A and A′ and of the B and C protons of $U^{IV}(EDTA)$-$(H_2O)(SO_4)^{2-}$ is concluded to involve a ring inversion of the ethylenic "backbone" of the ligand without bond breakage. Such a mechanism accounts for both exchange processes and is consistent with their activation parameters (Table II), which are similar to those for the ring inversion of cyclohexane.[38] However, only one pathway is available for each of the A,A′ and B,C exchanges, which implies that the value of $\Delta S^{\ddagger}$ should be close to zero (in agreement with the data of Table II). At higher temperatures the metal–acetate bonds probably become more labile, which would reduce the hindrance to the "backbone" rocking process. The difference between the kinetic parameters for the A,A′ and B,C exchange processes probably is due to the fact that the former are for temperatures where the metal–acetate bonds are nonlabile; the latter are for temperatures where the bonds may be labile. The nmr data do not permit evaluation of the rate constants for the two processes over the same temperature range. However, two B,C rate constants of limited precision have been determined at low temperatures, and their values almost coincide with those for the A,A′ process (Figure 5). This supports the conclusion that a single mechanism is responsible for the two exchange processes.

The $U^{IV}(EDTA)$ complex that begins to form in 1.0 F Na_2SO_4 solutions above pH 3.00 has a magnetic moment at pH 6.50 (2.41 BM) which is indicative of spin-pairing through the formation of an oxo-bridged dimeric species. The appearance of ten ill-defined

(42) J. L. Hoard, E. Willstadter, and J. V. Silverton, *J. Am. Chem. Soc.*, **87**, 1610 (1965).

(43) B. B. Smith and D. T. Sawyer, *Chem. Commun.*, 1454 (1968).

proton nmr peaks at low temperatures can be explained by a decrease in the exchange rate for water molecules with coordinated SO_4^{2-} ions to give a stable solution structure of the form
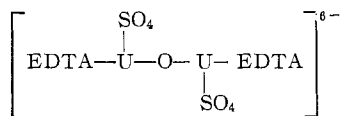
$$\left[\begin{array}{c} SO_4 \\ | \\ EDTA-U-O-U-EDTA \\ | \\ SO_4 \end{array} \right]^{6-}$$

Electrochemical Reduction of Elemental Sulfur in Aprotic Solvents. Formation of a Stable S_8^- Species

BY MARGARET V. MERRITT AND DONALD T. SAWYER

The electrochemical reduction of elemental sulfur has been investigated in several aprotic solvents using a gold electrode. Reduction occurs by two one-electron steps with S_8 the electroactive species. The stoichiometry and kinetics of the reduction have been studied by chronopotentiometry, cyclic voltammetry, and controlled-potential electrolysis. The first step has a voltammetric E_p value of -0.62 V *vs.* sce in DMSO; the second reduction step has an E_p value of -1.29 V *vs.* sce. Controlled-potential electrolysis at the first potential yields a new stable oxidizable sulfur species with an anodic E_p value of -0.23 V *vs.* sce. The electronic spectrum for the product of the first reduction step, "S_8^-," exhibits absorption maxima at 490 and 618 mμ. Concentration studies establish that the S_8^- species undergoes dimerization with a formation constant of 5000 M^{-1}.

The polarographic reduction of elemental sulfur in protic solvents has been studied extensively;[1-3] the final product is mercuric sulfide.[1,2] The electrochemical reduction of sulfur also has been examined in fused salts; sulfide is assumed to be the product in a LiCl–KCl eutectic.[4] The present paper summarizes the results of a detailed investigation of the electrochemistry of elemental sulfur in aprotic solvents.

Experimental Section

A solid-state potentiostat–amperostat[5] with a Sargent Model SR recorder, a Moseley Model 7035A X–Y recorder, and a Tektronix Model 564 oscilloscope was used for all electrochemical operations and measurements. A conventional two-compartment electrochemical cell with a three-electrode system was used for coulometric experiments; a large gold foil (reagent grade) functioned as the working electrode. For chronopotentiometric and cyclic voltammetric studies a gold billet sealed in a polyethylene tube (gold-inlay electrode) was used as the working electrode. The area of the gold-inlay electrode was determined by reduction of ferricyanide ion in water. An aqueous Ag–AgCl reference electrode was used which has been described previously;[6] its potential was 0.000 V *vs.* sce. The isolated counterelectrode was a large platinum gauze. All solutions were deaerated with prepurified nitrogen prior to electrochemical measurements.

(1) G. Hauck and M. v. Stackelberg, *Leybold Polarograph. Ber.*, **4**, 81 (1956); *Chem. Abstr.*, **54**, 15023*i* (1960).
(2) S. I. Zhdanov and B. A. Kiselev, *Collection Czech. Chem. Commun.*, **31**, 788 (1966).
(3) R. E. Humphrey, *Anal. Chem.*, **34**, 167 (1962).
(4) F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, **116**, 607 (1969).
(5) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).
(6) D. T. Sawyer and J. L. Roberts, Jr., *J. Electroanal. Chem.*, **12**, 90 (1966).

Baker Analyzed reagent grade dimethyl sulfoxide (DMSO) was used without further purification. The supporting electrolyte, tetraethylammonium perchlorate (TEAP) (Distillation Products Industries), was recrystallized three times from water. Elemental sulfur (Mallinckrodt) was recrystallized from benzene. A sample of sodium polysulfide was supplied by FMC Corp. The visible spectra were recorded with a Cary Model 14 spectrophotometer.

Results

Cyclic Voltammetry and Coulometry.—Figure 1 illustrates cyclic voltammograms of elemental sulfur in DMSO at a gold electrode. The curves indicate that the reduction proceeds by two steps, each of which involves the same number of electrons. Furthermore, the product of each reduction step can be reoxidized to the starting material on the time scale of Figure 1, even though these processes are irreversible by electrochemical criteria. That is, the peak potential for each reduction is separated from the corresponding anodic peak potential by more than 56 mV and the peak potentials are dependent on the scan rate. Qualitatively, the same electrochemical behavior is observed with sulfur in tetrahydrofuran and dimethylformamide at a gold electrode, or in DMSO at a platinum or graphite electrode; the peak potentials are slightly different. The sulfur system behaves most reversibly in DMSO with gold as the electrode material; consequently, this system has been used for the remainder of the studies.

A series of controlled-potential electrolyses at -0.60 V *vs.* sce have established that one electron per eight