

If the p-orbital model for the thiadiazole is accepted, it is apparent that the electron density of the sulfur atom is less than the electron density of the oxygen atom in the oxadiazole. This could explain why the additional electrons in the radical anions have a greater preference for sulfur than for oxygen. On the other hand, the d-orbital model of the sulfur atom leads to the conclusion that sulfur has a higher electron density than oxygen in the parent heterocyclics and a still higher spin density than oxygen in the radical anions. Such behavior seems more consistent with the inductive effect associated with mercapto and alkoxy substituents in the benzoic acids than the effect predicted on the p-orbital picture.^{24,25}

(24) The charge densities of sulfur (p-orbital model) and oxygen are +0.372 and +0.194, respectively, in the parent heterocyclics. If the inductive effect is restricted to polarization of σ -bonds alone, the ob-

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served inductive effects of mercapto and alkoxy substituents in the benzoic acids can be explained with the involvement of only the p-orbitals of the sulfur atom.

(25) The σ_1 -constants (inductive parameter for a *meta*- or *para*-substituted benzene derivative [R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 1045 (1957)]) are +0.19 (CH₃S) and +0.26 (CH₃O). Thus, inductively the methoxy group is the strongest electron attractor. The σ -constants [D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958)] are +0.15 for *m*-CH₃S, +0.115 for *m*-CH₃O, 0.00 for *p*-CH₃S, and -0.268 for *p*-CH₃O. The σ^+ -values (substituent constants wherein direct conjugation is prohibited [R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960)]) are +0.13 for *m*-CH₃S, +0.06 for *m*-CH₃O, and -0.12 for *p*-CH₃O. The σ^0 -values (substituent constants for reactions wherein direct conjugation is not important [H. v. Bekkum, P. E. Verkade, and B. M. Webster, *Rec. trav. chim.*, **78**, 815 (1959)]) are +0.225 for *m*-CH₃S, +0.076 for *m*-CH₃O, +0.220 for *p*-CH₃S, and -0.111 for *p*-CH₃O. Values quoted are those listed by Wells.⁴

Nuclear Magnetic Resonance Studies of the Uranyl-Citrate System in Deuterium Oxide at Low pD

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Nuclear magnetic resonance spectra of uranyl nitrate-citric acid mixtures in D₂O, having citric acid concentrations 0.1 M and higher, showed that a uranyl-citrate complex exists at unexpectedly high acidity. This "high acidity" species is different from the dimer existing in H₂O solution at lower concentration (0.01 M and less) and higher pH (>2). From the line-width broadening of citric acid transitions in the presence of uranyl nitrate, an average lifetime of the order of 0.006 sec. was calculated for the "high acidity" complex species. From the mean chemical shift of the methylene protons, a value of 3.16 ± 0.08 was obtained for the logarithm of the stability constant of this complex under the assumption that it is the monomer UO₂D₂Cit⁺. A calculation is presented relating the low-field shift of the methylene deuterons to the electrostatic field and the magnetic anisotropy of the uranyl entity in the complex.

Introduction

This work is a continuation of an extensive investigation of uranyl-hydroxypolycarboxylate systems.⁴ Previous work treated aqueous systems at pH above 2 and reactant concentrations 0.01 M and lower. The present

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(4) The most recent paper in this series is: I. Feldman, C. A. North, and H. Hunter, *J. Phys. Chem.*, **64**, 1224 (1960).

paper concerns n.m.r. studies on solutions of higher concentrations and higher acidities in D₂O.

Experimental

Proton spectra were obtained with a Varian 4300B spectrometer converted to operate at 100 Mc./sec., and with a Perkin-Elmer R-60 spectrometer at 60 Mc./sec. The Varian spectrometer was calibrated with audiofrequency side bands from a Muirhead-Wigan decade oscillator. Spinning samples of 4.5-mm. internal diameter were used. Spectra at 100 Mc./sec. were recorded at $25 \pm 1^\circ$, those at 60 Mc./sec. at $33.4 \pm 0.1^\circ$. All chemicals used were A.R. grade. As a general rule, spectra were obtained from solutions prepared by weighing the appropriate components into volumetric flasks and adding DCl, D₂O, or NaOD solution, as appropriate, to the proper volume. This procedure was not adopted during the addition of excess UO₂²⁺ to 0.1 M acid solutions. Here, a concentrated solution of uranyl nitrate was added from a microburet to the 0.1 M acid solution, and each sample was returned to the bulk acid solution before further samples were taken. In this manner, the concentration dropped slightly but the ratio of uranyl ions to acid was always accurately known.

Results

The results of n.m.r. studies of uranyl-citrate, -malate, and -tartrate systems are presented in graphical form (Figures 1-3). As far as possible, we have kept the coordinates of similar graphs on the same scale

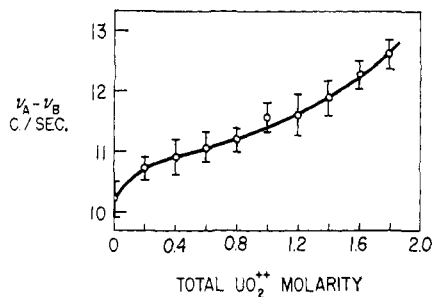


Figure 1. Variation of the internal chemical shift of the methylene protons of 1 *M* citric acid solution as a function of added uranyl ion concentration (spectrometer frequency, 60 Mc./sec.).

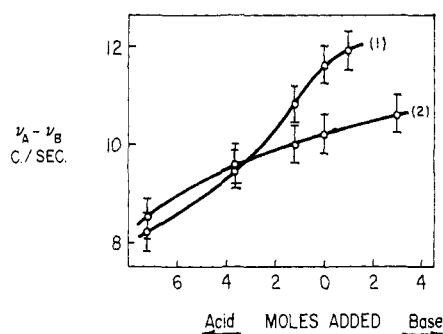


Figure 2. Variation of the internal chemical shift of the methylene protons of 1 *M* citric acid solutions as functions of added acid and base concentration (spectrometer frequency, 60 Mc./sec.): curve 1, in presence of 1 *M* uranyl nitrate; curve 2, in absence of uranium.

and, where necessary, indicated 90% confidence limits by vertical lines through the points. Our analysis has been concentrated on the citrate system. Some general remarks may be made which cover all three systems. Experiments in D_2O indicate that all carboxyl and hydroxyl protons and deuterons exchange rapidly with solvent protons and deuterons. The spectra therefore show a chemical shift as a time average over all electronic environments of the protons and deuterons, resulting in a single absorption predominantly that of water. These experiments in D_2O further confirmed that all other protons remain intact. Qualitatively, spectra in H_2O were very similar but more difficult to interpret because of the large water resonance which obscured some of the other nuclear transitions. *t*-Butyl alcohol has been used as an internal reference. It was established that negligible chemical change was caused by the butyl alcohol and that we did not reach the pH where butoxide ion was formed. An acetone reference provided a check on this point.

In 3 *M* HCl, citric acid in 0.1 and 1.0 *M* concentrations gives a four-transition spectrum characteristic of an AB system,⁵ that is, two protons of coupling constant J greater than or similar to the chemical shift, $\nu_0\delta$, between them. At 100 Mc./sec., these four transitions are well resolved and confirm that within each CH_2 group the protons are inequivalent, as found also for the methyl esters of citric acid.⁶ Coupling from one CH_2 group to the other has been neglected in our

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(6) A. Lowenstein and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2705 (1960).

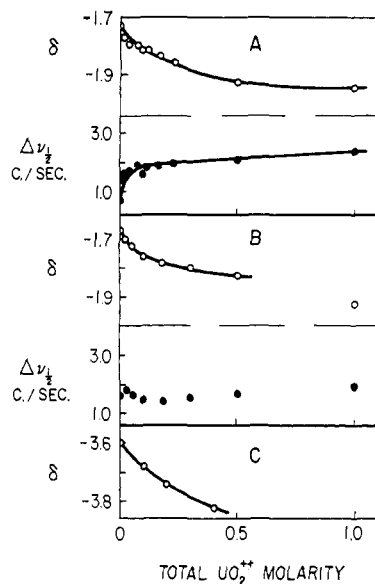


Figure 3. Mean chemical shift, in p.p.m. relative to *t*-BuOD, of methylene protons and line width of methylene proton transition of (A) citric acid, (B) malic acid, and (C) tartaric acid as a function of varying uranyl ion concentration (spectrometer frequency, 100 Mc./sec.).

analysis. For equimolar uranyl nitrate-citric acid solutions, the spectra are similar, but there is a noticeable increase in the line width, $\Delta\nu_{1/2}$ (defined as the width at half-maximum height), of the four transitions. This system has been studied in detail by gradually changing the molar ratio of uranyl nitrate to citric acid (0.1 *M*) from zero to 10:1 and by adding acid and alkali to 1 *M* citric acid in the presence and absence of uranyl ions. The results are shown in Figures 1-3A.

Malic acid in 0.5 *M* solution in D_2O is an ABX system⁵ with $|J_{AB}| = 16.7$, $|J_{AX}$ or $J_{BX}| = 4.1$, $|J_{BX}$ or $J_{AX}| = 7.3$, all ± 0.3 c./sec., the latter two coupling constants having the same sign. δ_{AB} for the above solution was 0.025 p.p.m. Because of this small chemical shift, it is not possible to use the AB transitions for accurate line-width studies. This shift is pH dependent and varies with the concentration of other cations in solution.⁷ A plot of mean AB shift and of line width of the narrowest AB transition against added uranyl ion concentration is shown in Figure 3B (top and bottom curves, respectively). The shift behavior parallels the citrate situation. As the uranyl ion concentration is increased, the slight increase in line width precludes observation of J_{AB} from the weak outer transitions, and the X part moves under the water peak and is obscured. However, the sum $|J_{AX} + J_{BX}|$ can be followed from the AB part. The small decrease in this sum observed when uranyl ion is added is on the borderline of being measurably significant. Other work with alkali malates shows a decrease as the salt concentration is increased.⁷

Tartrate ion has two equivalent protons and gives a single line spectrum. The δ -behavior of this absorption upon addition of uranyl ions to 0.1 *M* tartaric acid is shown by Figure 3C. The spectral line moves too close to the water absorption to allow a reliable measurement of line width and is eventually obscured by the water peak.

(7) L. E. Erickson and R. A. Alberty, *J. Phys. Chem.*, **66**, 1702 (1962).

Discussion

The n.m.r. spectra show that in D₂O a uranyl-citrate complex exists to a much larger extent than expected (*vide infra*) at acidities below pH 2 and that this "high acidity" complex is a different species from the dinuclear complex known⁴ to be predominant above pH 2 in aqueous solution. These facts were learned by considering three features of the n.m.r. spectra: (i) shift inequivalence of the methylene protons, (ii) mean chemical shift of these protons, and (iii) line-width changes.

First, the chemical shift inequivalence of the protons within the methylene groups of citric acid increases as uranyl nitrate is added to citric acid (Figure 1) or as the acidity of a 1:1 mixture of uranyl nitrate and citric acid is decreased from 3 M acid to 1 M base (Figure 2). These two trends indicate that the citrate adopts a preferred configuration in the presence of uranyl ions when the acidity is not high enough to reduce the D₂Cit⁻ concentration to insignificance. If there were rapid rotation about a C-C bond in citric acid and if all possible rotational configurations were equally populated, then a very small magnetic inequivalence of the CH₂ protons would be expected.⁸ However, if the molecules favored a particular configuration, then the chemical shift between the methylene protons would most probably increase.⁹

Second, the line widths of citric acid transitions change substantially in the presence of uranyl ions (Figure 3A, bottom curve). The line width is the same for 0.1 and 1.0 M citric acid solutions and rises from about 0.7 to about 2 c./sec. as the initial ratio of UO₂²⁺ to citric acid increases from zero to 10:1 (as far as solubility and viscosity permitted us to go). When exchanging species, chemically distinct, are not magnetically resolved, the line-width expression is⁵

$$\pi\Delta\nu_{1/2} = \frac{p_i}{T_{2i}} + \frac{p_j}{T_{2j}} + 4\pi^2 p_i^2 p_j^2 (\nu_i - \nu_j)^2 (\tau_i + \tau_j) + \text{small terms} \quad (1)$$

where $p_{i,j}$ are mole fractions of the two species, $\nu_i - \nu_j$ is their relative chemical shift in c./sec., and $\tau_{i,j}$ are their average lifetimes. The increased line width could arise in two ways: (i) the increased size of the citrate-containing species upon complexation could lead to an increased correlation time¹⁰ and thus to a decrease in T_{2j} in the above equation; or (ii) the chemical exchange lifetimes could be of magnitudes comparable with the inverse of the frequency separation, $(\nu_i - \nu_j)^{-1}$.

Measurements of line width of citric acid were carried out on 60- and 100-Mc./sec. spectrometers. The last term of eq. 1 should differ by almost a factor of three for the two measurements. In fact, the change in the line width is less than 10%. Consequently, almost the whole of the line width must be due to terms involving T_2 , implying that the exchange between free and complexed citric acid must be very rapid. (This 10% increase is of the order of the error of the line-width measurements and could be accounted for by the slightly lower temperature of the 100-Mc./sec. measurements.) From eq. 1 and the observed line width, it is

(8) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

(9) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

(10) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

possible to ascribe a maximum limit to both τ_i and τ_j ; the limit, of course, depends on the p_i and p_j values chosen. As a typical case, consider the citrate to be half-complexed, *i.e.*, $p_i = p_j$. Then taking 2 c./sec. as the maximum possible value of the last term in the equation, one obtains 0.006 sec. as the maximum lifetime of either species in solution.

Third, the addition of uranyl ions to a 0.1 M solution of citric acid (up to a ratio of 10:1) caused a definite decrease in the mean chemical shift of the CH₂ protons (Figure 3A, top curve). An idea of the stability of the complex can be obtained by assuming that the initial and final shifts represent free and complexed citric acid, respectively. The asymptotic behavior of the δ -plot supports this assumption. Since the citrate group exchanges rapidly between citric acid and complex, the mole fractions of free citric acid, p_1 , and of complexed citrate, p_2 , can be calculated from the expression

$$\delta_{av} = p_1\delta_1 + p_2\delta_2$$

The calculated percentages of the total citrate in complex form in the 0.1 M mixture as a function of the initial stoichiometric molar ratio of uranyl nitrate to citric acid are given in Table I. Theoretically, each of

Table I. Stability Constant of UO₂D₂Cit⁺ Complex

Total (UO ₂ ²⁺ /Cit) molar ratio	% citrate complexed	Log K _m
0.2	17	(3.59) ^a
0.5	29	2.27
0.7	31	3.07
0.9	38	3.18
1.2	38	2.98
1.6	48	3.12
2.3	59	3.22
5.0	93	
10.0	97	Av. 3.14 ± 0.08

^a This value ignored in averaging K_m.

the calculated "% citrate complexed" entries in Table I should consist of a dimer contribution⁴ and a contribution from the new high acidity complex species, which we assume to be the monomer, UO₂D₂Cit⁺. Because of the high acidity (pD < 2) we may assume almost all uncomplexed citrate to be the molecular D₃Cit species. If we further assume negligible dimer concentration (*vide infra*), then the deuteron concentration (D⁺) is approximately equal to the monomer concentration (C⁺) according to the equation: UO₂²⁺ + D₃Cit → UO₂D₂Cit⁺ + D⁺.

Then (D⁺) = (C⁺) = 0.1(% citrate complexed)/100%; the uncomplexed citrate concentration = (D₃Cit) = 0.1 - (C⁺); and the uncomplexed uranyl ion concentration (UO₂²⁺) = 0.1 (initial U/H₃Cit ratio) - (C⁺). One may then calculate the stability constant of the monomer

$$K_m = (C^+)/(\text{UO}_2^{2+})(\text{D}_2\text{Cit}^-) = (C^+)(\text{D}^+)/(\text{UO}_2^{2+})(\text{D}_3\text{Cit})K_1$$

where K_1 is the first ionization constant of citric acid in D₂O. pK_1 in D₂O may be obtained^{11,12} by adding 0.5

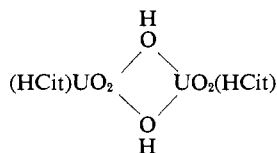
(11) N. C. Li, P. Tang, and R. Mathur, *J. Phys. Chem.*, **65**, 1074 (1961).

(12) A. O. McDougall and F. A. Long, *ibid.*, **66**, 249 (1962).

to the pK_1 in an H_2O solution of the same ionic strength μ . In this study, except for the first value which we ignored in averaging, μ varies from 0.15 to 0.7. We choose as a compromise K_1 for $\mu = 0.3$ since this is the value in the equimolar mixture (0.1 M) and the experimental error probably does not warrant considering the μ -effect too closely. pK_1 in H_2O for $\mu = 0.3$ may be calculated from the equation of Bjerrum and Unmack¹³ to be 3.03, giving a pK_1 of 3.53 in D_2O .

Our calculated values for the stability constant, K_m , of the monomer are presented in Table I. An average value of $\log K_m = 3.14 \pm 0.08$ was obtained. The apparent constancy with the small deviation in $\log K_m$ is quite surprising since it would be caused by only a 5% experimental error in determining “% citrate complexed” and since we have neglected ionic strength effects.

Some justification for our having ignored any dimer concentration in the calculation may be obtained by considering previous work⁴ in which a value of 6500 was found for the dimer formation constant, *i.e.*, (dimer)^{1/2} (H⁺)/(UO₂²⁺)(HCit²⁻), at $\mu = 0.14$ in H_2O . A number of factors, some positive and some negative, would cause the formation constant in D_2O and H_2O to be different, but the situation is too complex to allow an unequivocal prediction of their relative magnitudes at the present time.^{12,14} For this particular system, however, there is one very evident factor not operative in all complex ion systems. The (H⁺) term in the dimer constant above is due to formation of olation bridges,⁴ *i.e.*, in



The constant 6500 therefore is a function of K_w , the ion product of H_2O . (Ordinarily K_w does not openly enter into a stability constant because the protons are released only from the organic ligand. In such a case, the K_w term cancels out because of its inclusion also in the ionization constant of the parent organic acid.) The fact that the ion product of D_2O is one-sixth as large as K_w would tend to cause a 36-fold decrease in the over-all dimer constant for D_2O solution. In addition since K_1K_2 of citric acid in D_2O is about one-tenth as great in H_2O ,^{11,12} the DCit²⁻ concentration should be considerably smaller than (HCit²⁻) for a given citric acid concentration. From the formation constant, 6500, in water one can calculate that about 10% of the citrate is complexed in a water solution 0.1 M in both uranyl nitrate and citric acid. It might be expected, therefore, that only a relatively small amount of dimer should exist in D_2O solution having the same reagent concentration. This seems to be the case since a good monomer constant was obtained when the dimer contribution was completely neglected. Also, consistent

(13) N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **9**, 1 (1929).

(14) P. K. Glasoe and J. R. Hutchison, *J. Phys. Chem.*, **68**, 1562 (1964).

with this conclusion is the fact that the pD (= pH meter reading + 0.4)¹⁵ of the 0.1 M equimolar mixture in D_2O is 1.64, *i.e.*, 0.3 log unit higher than the pH of the same mixture in H_2O . This pD value agrees within experimental error with our expected value, if we assume a D^+ ion activity coefficient close to the 0.74 value of H^+ ion at $\mu = 0.3$, for if $(D^+) = (C^+) = 0.038 M$, we expect $pD = -\log(0.038 \times 0.74) = 1.55$.

It was not possible to use the plot of methylene proton internal shift vs. uranium concentration in Figure 1 to study the stability of the complex in 1 M citric acid because, in accord with our calculation above for 0.1 M solution, no asymptote was obtained.

Consideration can be given to the cause of the low-field shift. It is most probably brought about by two factors: the electrostatic field of the uranyl ion, and the magnetic anisotropy of this ion. Presumably the D_2 -Cit⁻ ligand will tend to orient bidentately with a carboxyl oxygen and an alcoholic oxygen near the equatorial plane around the linear O-U-O axis. In this configuration the field effect of the positively charged uranyl ion will cause a low-field shift of the methylene protons. Using Buckingham's equation,¹⁶ we calculate a shift of about -0.3 p.p.m. for an assumed U-H distance of 6 Å. and an assumed effective charge of +1. The susceptibility of the uranyl ion is markedly anisotropic, since it is linear and has a temperature-independent paramagnetism of $+57 \times 10^{-6}$ c.g.s. unit.¹⁷ For the magnetic field parallel to the O-U-O axis, the ion is diamagnetic; in the perpendicular orientation, it must be paramagnetic. For calculation purposes assume: $\chi_{\parallel} = 0$. Then $\chi_{\perp} = +80 \times 10^{-6}$ unit, since $\frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) = +57 \times 10^{-6}$ c.g.s. unit. χ_{\parallel} is in fact negative,¹⁷ so this anisotropy is a minimum value.

The equation predicting the chemical shift arising from this anisotropy is¹⁸

$$\delta = \frac{1}{3R^3}(\chi_{\parallel} - \chi_{\perp})(1 - 3 \cos^2 \theta)$$

For a reasonable range of θ -values, within the previously assumed geometry, this shift is negative and less than 1 p.p.m. As an example, if R (U-H distance) is 6 Å. and θ is 10° (U-H angle with respect to the plane), a contribution of -0.2 p.p.m. is obtained. Since $\Delta\chi > 80 \times 10^{-6}$ c.g.s. unit, the -0.2 p.p.m. value is a minimum value of the low-field shift for the assumed configuration. Thus, a reasonable assumed geometry of the complex gives a low-field shift of its methylene protons in essential agreement with the shift observed as uranyl ions were added to citric acid solutions.

Acknowledgment. The authors are pleased to acknowledge that the Perkin-Elmer spectrometer was provided by a grant to University College, London, from the Department of Scientific and Industrial Research, England.

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(16) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(17) J. C. Eisenstein and M. H. Pryce, *Proc. Roy. Soc. (London)*, **A229**, 20 (1955).

(18) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).