(*R*),26-Dihydroxycholesterol (**7a**) and 25(*R*),26-dihydroxycholecalciferol (**9a**) have positive Cotton effects centered at 318 nm (ϵ +2.6 ± 0.3). Conversely, 25(*S*),26-dihydroxycholesterol (**7b**) and 25(*S*),26-dihydroxycholecalciferol (**9b**) exhibit negative Cotton effects at 318 nm (ϵ −2.6 ± 0.3). The observed Cotton effects cannot predict the absolute configuration at C-25 based on the empirical model (secondary–tertiary α-diols) of Nakanishi and Dillon.[21] *However, we have unequivocally shown that for these first examples of primary–tertiary α-diols, the R compounds have positive Cotton effects and the S compounds have negative Cotton effects at 318 nm. This may be a general phenomenon for primary–tertiary α-diols.*

To prove unequivocally the absolute configuration of the natural human 25,26-dihydroxycholecalciferol, we compared the high-performance LC elution times of the tris(trimethylsilyl) derivatives of the natural metabolite and the synthetic 25(*R*),26- and 25-(*S*),26-dihydroxycholecalciferols. An approximately 1:1 mixture of the tris(trimethylsilyl) derivatives, individually made with (trimethylsilyl)imidazole (THF, 25 °C), gave the high-performance LC trace A of Figure 1. This tracing demonstrates that the 25*R* epimer is eluted before the 25*S* epimer in discrepancy with the Redel findings.[6,8] A sample of human metabolite was prepared by methylene chloride extraction of 72 mL of human serum and purification of the fraction containing the desired metabolite on a Sephadex LH-20 column. This sample was purified further by high-performance LC (μ Porasil column; 87:13 hexane–2-propanol as eluant) and then silylated. Addition of this silylated derivative[22] to the ca. 1:1 mixture of silylated synthetic epimers previously described gave the high-performance LC tracing B shown in Figure 1, which clearly shows that *the human 25,26-dihydroxycholecalciferol possesses the 25S absolute configuration.*[23]

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Supplementary Material Available: Crystallographic data for **7a** and Eu(fod)$_3$-induced shift CD spectra for **7a**, **7b**, **9a**, and **9b** (8 pages). Ordering information is given on any current masthead page.

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(21) Nakanishi, K.; Dillon, J. *J. Am. Chem. Soc.* **1975**, 97, 5417; Nakanishi, K.; Schooley, D. A.; Koreeda, M.; Dillon, J. *J. Chem. Soc. Chem. Commun.* **1971**, 1235. In all cases secondary–tertiary α-diols were studied.

(22) The silyl derivative of the human metabolite was identified by its characteristic ultraviolet spectrum and high-resolution mass spectrum. For the ^{13}C NMR spectrum of 25(*S*),26-dihydroxycholecalciferol, see: Williams, T. H., Greeley, D. N.; Baggiolini, E. G.; Partridge, J. J.; Shiuey, S.-J.; Uskoković, M. R. *Helv. Chim. Acta* **1980**, *63*, 1609.

(23) Since 25(*S*),26-dihydroxycholecalciferol is further metabolized to calcidiol lactone and 1α,25,26-trihydroxycholecalciferol, these substances should also possess the 25*S* absolute configuration. Portions of this work were presented at the Third IUPAC Symposium on Organic Synthesis. See: Partridge, J. J.; Shiuey, S.-J.; Chadha, N. K.; Baggiolini, E. G.; Confalone, P. N.; Kulesha, I.; Wovkulich, P.; Uskoković, M. R. "Abstracts of the Third I.U.P.A.C. Symposium on Organic Synthesis"; Madison, WI, June 15–20, 1980; p 74.

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^{13}C NMR Spectra of the Uranyl Tricarbonate–Bicarbonate System

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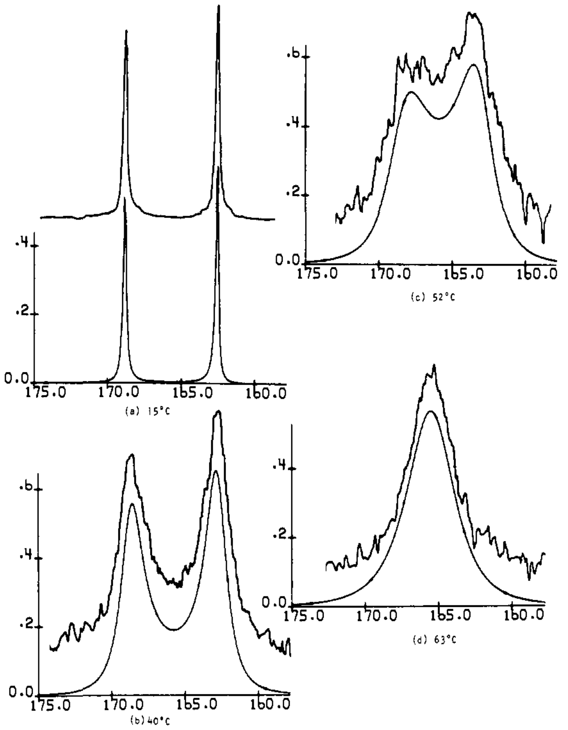

Figure 1. Experimental (above) and theoretical (below) ^{13}C NMR spectra of the uranyl tricarbonate–bicarbonate system at various temperatures, pH 9.1.

We report the ^{13}C NMR identification of the important uranyl tricarbonate complex. This complex is of great commercial significance as the vehicle for extracting uranium from ore by solution mining and conventional carbonate leaching.[1] The uranyl tricarbonate complex is a rare example of a soluble carbonate complex and is extremely stable. A recent compilation[2] indicates that the formation constant for this complex is in the range 10^{18}–10^{23}. The NMR spectra of the uranyl tricarbonate–bicarbonate system also show the transition from slow to fast carbonate exchange between uranyl ion and bulk water in an easily accessible temperature range. The carbonate δ value in the complex is surprisingly close to the δ value of uncomplexed carbonate.

A room temperature, 15-MHz ^{13}C NMR spectrum was taken of a solution 0.0295 M in UO_2^{2+} and 0.242 M in HCO_3^- with 10% ^{13}C label at pH 8.84 in 75:25 H_2O–D_2O. If UO_2^{2+} complexes three carbonates, the carbonate concentration should be 0.0885 M in $UO_2(CO_3)_3^{4-}$ and 0.1535 M in HCO_3^-. The spectrum in fact shows two peaks. The smaller peak is at 168.86 ± 0.2 ppm, and the taller peak is at 162.31 ± 0.2 ppm.[3] In simple carbonic systems we find that uncomplexed CO_3^{2-} has a δ value of 169.6 ± 0.2 and uncomplexed HCO_3^- has a δ value of 162.1 ± 0.2, in substantial agreement with earlier reported measurements.[4] Carbonate–bicarbonate mixtures give an averaged, singlet spectrum whose spectrum δ value is weighted by the relative proportions of each. The simplest interpretation is that the taller peak at 162.31 ppm is from HCO_3^-, and the smaller peak at 168.86 ppm arises from the uranyl tricarbonate complex.[5]

Variable temperature studies offer persuasive evidence that this interpretation is correct. With increasing temperature the peaks

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(1) See: Merritt, R. C. "The Extractive Metallurgy of Uranium"; U.S. Atomic Energy Commission: Washington, DC, 1971; pp 83–108.

(2) Cinnéide, S. Ó.; Scanlon, J. P.; Hynes, M. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1013–1018.

(3) An external reference of 90% $^{13}CH_3OH$ was used whose δ value was taken as 49.3 to the left of tetramethylsilane.

(4) The δ value of CO_3^{2-} is given as 170 and that of HCO_3^- as 160 in Stothers' book (Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 304), as calculated by Stothers from the original work: Patterson, A. Jr.; Ettinger, R. *Z. Electrochem.* **1960**, *64*, 98–110.

(5) Spectra of uranyl tricarbonate complex were not mistaken for those of uncomplexed carbonate, whose δ value is similar, because in later experiments at pH 12 separate peaks could be seen for uncomplexed and complexed carbonate.

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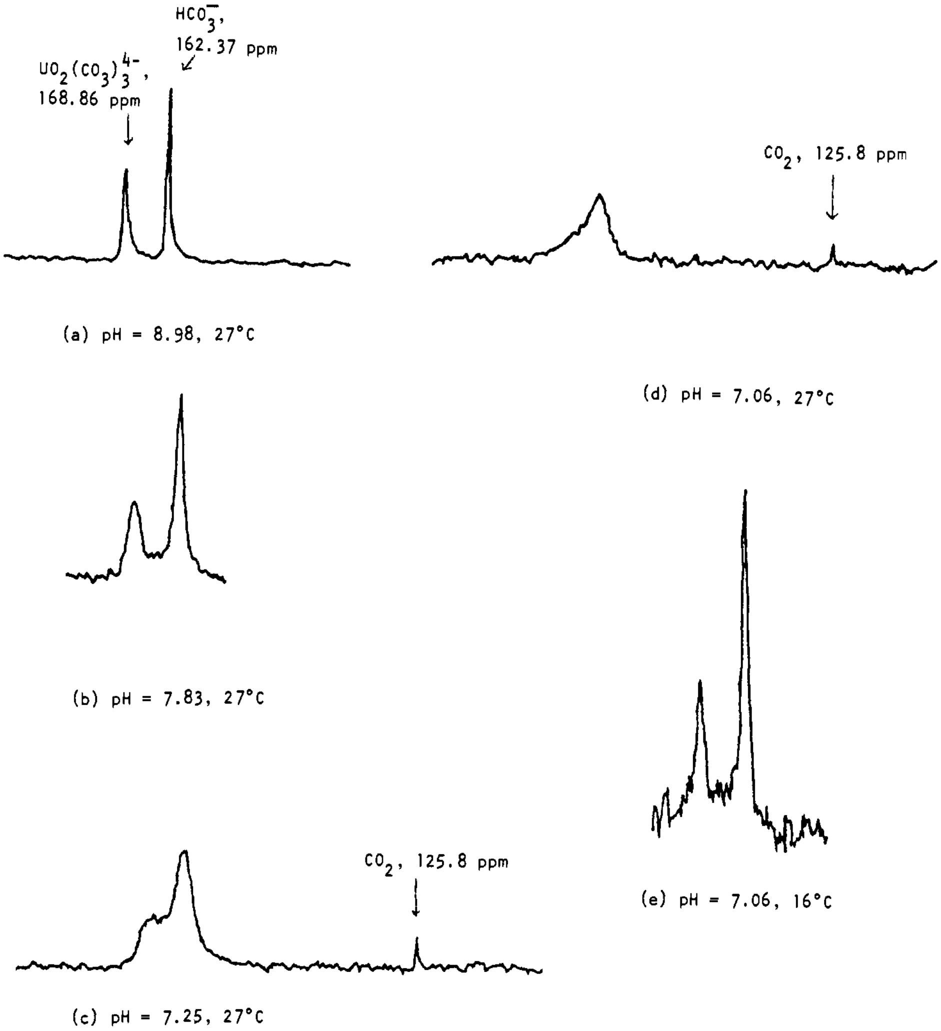

(a) pH = 8.98, 27°C

(b) pH = 7.83, 27°C

(c) pH = 7.25, 27°C

(d) pH = 7.06, 27°C

(e) pH = 7.06, 16°C

Figure 2. ^{13}C NMR spectra of the uranyl tricarbonate–bicarbonate–carbonic acid system. Scale is shown on the a spectrum. The d and e samples are identical.

broaden, collapsing to a 164.77-ppm singlet at 58 ± 2 °C.[6] When the room temperature δ values are used, the position of the fast exchange singlet can be calculated from eq 1, by using standard

$$\delta_{CO_3^{2-},av} = \delta_{HCO_3^-} + (1 - x_{HCO_3^-})(\delta_{UO_2(CO_3)_3^{4-}} - \delta_{HCO_3^-}) \quad (1)$$

NMR theory.[7] Assuming the complex is indeed the tricarbonate complex, its mole fraction $(1 - x_{HCO_3^-})$ would be 0.366. If the appropriate numbers are substituted in eq 1, the δ value for the collapsed singlet is given by

$$\delta_{CO_3^{2-},av} = 162.31 + 0.366(168.86 - 162.31) = 164.71$$

which is in excellent agreement with the measured value.

More extensive variable temperature studies were undertaken to gain a measure of the E_a for carbonate exchange. The spectra were obtained at pH 9.1 by using a 90% ^{13}C label. Theoretical spectra were calculated by assuming relaxation and instrumental broadening were negligible compared to the observed line widths. The derived rates were found by systematically adjusting the input exchange rates to reproduce the observed spectra. Trial values were obtained by using the slow and rapid line width (T_2) approximations[8] for the low- and high-temperature experimental cases. The program used was similar to that of Binsch.[9] Figure 1 shows examples of some of these experimental and theoretical curves. An Arrhenius plot gives an E_a value of 13.00 kcal with a preexponential factor of 9.24×10^{10}.

It was observed that carbonate transfer increased markedly with lowering of pH. This is illustrated in Figure 2. Note that at pH 7.06 at room temperature the spectrum is almost a singlet, but the separate peaks can be resolved at 16 °C. Also note the presence of dissolved CO_2 (125.8 ppm) at the lower pH's.

At pH <7 considerably more complex spectra are obtained. They feature a sharp peak at 169.9 ppm plus envelopes of broader peaks at smaller δ values. These spectra probably stem from uranyl carbonate dimers or trimers and will be the subject of our further investigations.

Concerted Ring-Opening Reaction of Cyclobutenes. The Extraordinary Accelerating Effects of Arylsulfoxy and Sulfonyl Carbanion Substituents

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Over the years, thermal ring opening of cyclobutenes has held the attention of physical organic chemists[1] and has proven to be

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[6] Only insignificant changes were noted in the δ value of the $^{13}CH_3OH$ reference in the temperature range 7–70 °C.

[7] Gutowsky, H. S.; Saika, A. *J. Chem. Phys.* **1953**, *21*, 1688–1694.

[8] Woessner, D. E.; *J. Chem. Phys.* **1961**, *35*, 41–48.

[9] Binsch, G. *Top. Stereochem.* **1968**, *3*, 97.

[1] (a) Frey, H. M. *Trans. Faraday Soc.* **1962**, *58*, 957. (b) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.