rotation about one of the axes which correspond to the fourfold inversion axes of a conventional Keggin unit. This produces the F-centering (see Figure 2). Therefore, the arrangement resembles an enlarged NaCl structure, with the Na^+ ions replaced by a set of Keggin-like units having one orientation and the Cl^- ions replaced by Keggin-like units with an orientation at right angles to the first set. This arrangement makes possible some extraordinary thermal properties.

Adjacent Keggin-like structures in such an arrangement each have six oxygen atoms (in two parallel rows of three each) which project closest to the corresponding six oxygen atoms from the next Keggin-like structure, thus forming a channel between the four parallel rows (three oxygen atoms in each row). These channels are of appropriate size for water molecules, H-bonded together, and H-bonded *very* weakly[6] to the oxygen atoms of the complexes.

A Keggin structure has two sets of tetrahedrally oriented faces. One set consists of four "flat faces" of the complex. Each flat face consists of six close-packed oxygen atoms in a planar triangle. The other set of tetrahedrally oriented faces consists of four "reentrant faces," that is, faces with deep indentations in their centers.

In the structure described (see Figure 2), two types of rather large octahedral pockets (big enough for the cations and hydrate H_2O's) are formed between the complexes. One type is bounded by the flat faces of the eight adjacent Keggin-like units. The other type of large pocket is similarly bounded by eight reentrant faces. The channels between the anions interconnect the large pockets.

The electron density maps, for crystals X-ray photographed at 25–32°, show that the channels and large pockets contain electron density, but it is smeared out on the maps, with the exact locations of cations and H_2O's not evident. This is probably the characteristic result of disorder in those spaces.

Unusual Thermal Behavior. When the cubic salts are heated or desiccated, the crystals shrink reversibly. At about 45°, each has changed so that it no longer has an F space group, although it is still cubic. A cubic cell containing eight complexes has a definitely shorter edge than at low temperature (*e.g.*, 15°) and high humidity.

The case of $(NH_4)_7Na_2[GaO_6H_2O_4W_{11}O_{30}]\cdot 15H_2O$ is especially interesting. An air-dried sample of this solid has a unit cell edge which shrinks rapidly, reversibly, and *continuously*, *e.g.*, from 22.17 A at 10° to 21.84 A at 47° (a 4.6% shrinkage in volume). The cell edge immediately returns reproducibly to a given value for each temperature. The cell is cubic at all times. Most of the change occurs between 25 and 40° (see Figure 3). The change was monitored by taking, at various temperatures, single crystal X-ray photographs and complete powder patterns, and by observing the effect on a single sharp powder line for which 2θ moved from 63.3 to 64.4°. The line never decreased in intensity or broadened, but shifted continuously through several times its width as the temperature varied.[13]

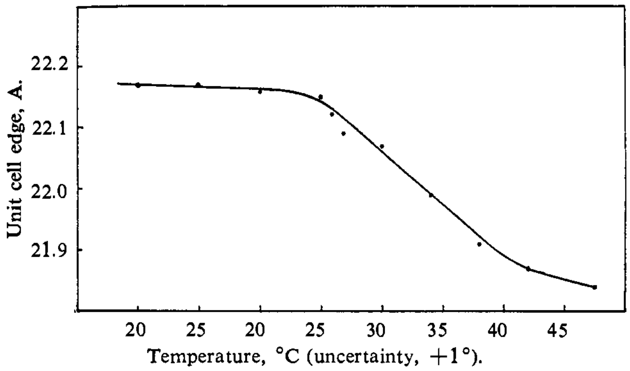

Figure 3. Continuous and reversible shrinkage of the cubic unit cell edge with increasing temperature for an air-dried sample of $(NH_4)_7Na_2[GaO_6H_2O_4W_{11}O_{30}]\cdot 15H_2O$. Thermal equilibrium had been attained at each point.

A probable explanation would depend upon reversible thermal disorganization of H-bonding patterns of H_2O molecules (and NH_4^+ ions) in the large octahedral pockets and/or the channels, allowing the heteropoly complexes to move continuously closer as the temperature goes up. This bears a rough analogy to the much less dramatic shrinkage of liquid water upon heating from 0 to 4°. Reversible movement of H_2O molecules from the channels into vacancies in the large octahedral pockets (in the case of a partly dried crystal) might also be involved. A more exhaustive investigation is underway.

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[13] A powder pattern of NaCl in the same apparatus did not change with temperature.

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Pentadienyl Cations and Their Rearrangements in FSO_3H-SbF_5 Solution[1]

Sir:

The solvent system FSO_3H-SbF_5 is one of the most acidic media yet studied. It has been shown to be an extremely useful solvent for studying carbonium ions.[2a,b] Using this method[2b] we have now studied the pentadienyl cations I and IV and their rearrangements. Ions I and IV are readily and clearly formed by dissolving the precursor dienols in FSO_3H-SbF_5 at −75 to −60°. Previous work has shown that in 96% H_2SO_4 at −30° only III is observed.[3] In FSO_3H at −50° although ion I is observed initially it readily rearranges to II and then very quickly to III.[4] In FSO_3H-SbF_5, I is stable for hours at −75°, but at 10° R_1 has $t_{1/2}$ = 185 sec. Ion II is stable at −10° and III is only formed by prolonged warming at 35°, R_2 $t_{1/2}$ = 8 to 12 min. In contrast to FSO_3H alone, these rates

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[1] Stable Carbonium Ions. XXVI. Part XXV: G. A. Olah and M. S. Comisarow, *J. Am. Chem. Soc.*, in press.

[2] (a) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964); (b) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).

[3] T. S. Sorensen, *Can. J. Chem.* **42**, 2768 2781 (1964).

[4] T. S. Sorensen, *ibid.*, **43**, 2744 (1965).

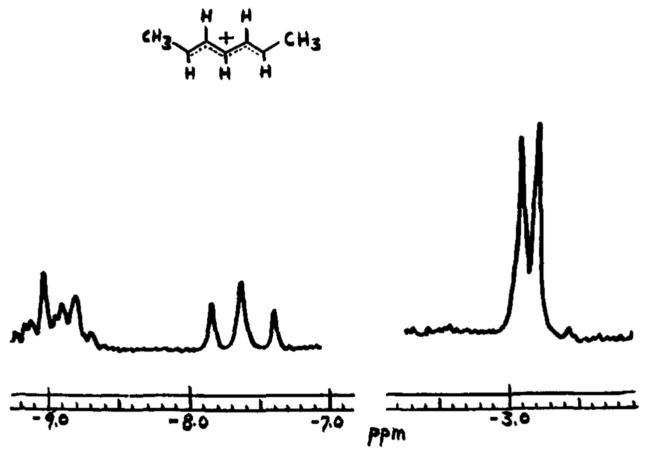
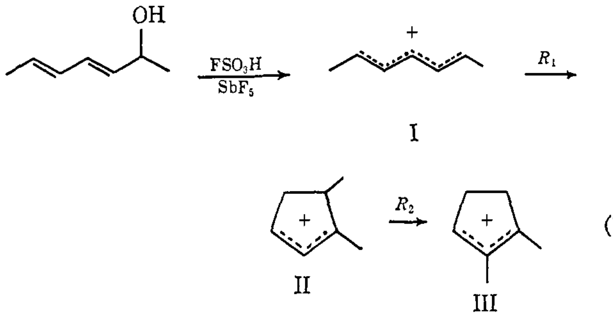
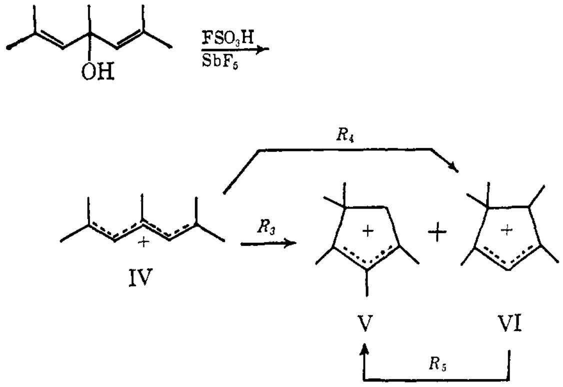


Figure 1.

are sufficiently separated, timewise, so as to be considered as independent first-order reactions.



(1)



(2)

The nmr spectrum of I is shown in Figure 1. As in the case of other dienylic cations the conjugating hydrogens at C$_2$, C$_4$, and C$_6$ (−8.6 to 9.3 ppm, multiplet) are further downfield than the nonconjugating hydrogens at C$_3$ and C$_5$ (−7.41 ppm, triplet, $J_{\text{HH}} = 13.5$ cps).

Similarly (eq 2), IV is generated quantitatively in FSO$_3$H-SbF$_5$ at −60° and is stable for over an hour. At −30° V and VI are simultaneously and independently formed from IV ($t_{1/2} = 45$ sec for disappearance of V), but a much higher temperature is required for conversion of VI to V (R_5 $t_{1/2} = 12$ min at 27°). The independent formation of V and VI has been shown[3] but the ion IV has not previously been observed.[4]

The nmr spectrum of IV (Figure 2) demonstrates that all the methyl groups are deshielded to approximately the same degree (3.05 ppm, broadened).

Other trienes described previously[3] are now being studied in FSO$_3$H-SbF$_5$. The low-temperature capabilities of this system allow one to observe dienylic open-chain cations which at higher temperatures undergo rapid rearrangement to mixtures of the more stable cyclized allylic ions.[3,4] The high acidity of this solvent also allows one to stablize and observe the intermediate ions in these cyclizations so that step by step detailed mechanisms may be elucidated.

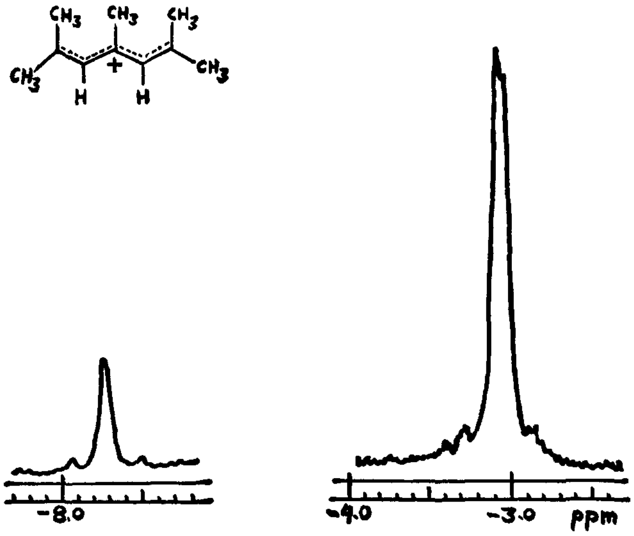


Figure 2.

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Rates of Proton Exchange between Dimethyl Sulfoxide and Its Conjugate Base

Sir:

The chemistry of dimethyl sulfoxide (DMSO) has been studied extensively. DMSO has proved to be an exceptional solvent for base-catalyzed reactions,[1] and its conjugate base (CH$_3$SOCH$_2^-$) has been used synthetically[2] as well as in quantitative measurements.[3,4] Protons adjacent to sulfoxide are known to exchange with base, and studies have been made in a number of systems.[5] Because of the great interest in the DMSO system, we have undertaken some quantitative rate

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