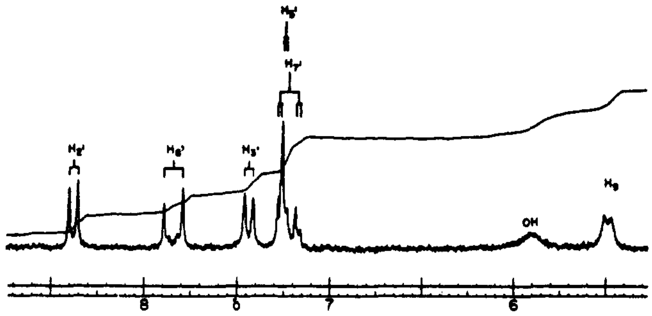


Figure 1. Portion of the 100-MHz spectrum of natural (−)-dihydroquinine, *ca.* 0.36 *M* $CDCl_3$ solution.

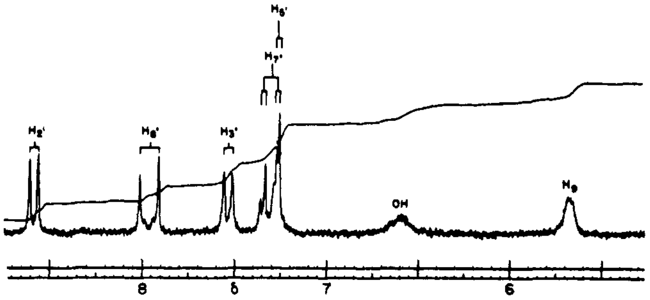
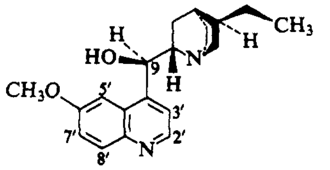


Figure 2. Portion of the 100-MHz spectrum of racemic dihydroquinine, *ca.* 0.35 *M* $CDCl_3$ solution.

concentration in deuteriochloroform. Furthermore, if the ratio of (−)- and (+)-dihydroquinines[2] in a mixture differs from 1:1, two sets of peaks for some protons are observed, and the peak areas are proportional to the relative amount of each enantiomer.



I

The differences are best illustrated in the chemical shifts of the protons $H_{2'}$, $H_{3'}$, $H_{8'}$, and H_9. Thus, the 100-MHz spectrum[3] of a 0.36 *M* solution of (−)-dihydroquinine (I) in deuteriochloroform (Figure 1) shows $H_{2'}$ at δ 8.38 (d, $J = 4.5$ Hz), $H_{3'}$ at 7.44 (d, $J = 4.5$ Hz), $H_{8'}$ at 7.85 ($J = 10$ Hz), and H_9 at 5.48, whereas the spectrum of racemic dihydroquinine (Figure 2) exhibits $H_{2'}$ at δ 8.58 (d, $J = 4.5$ Hz), $H_{3'}$ at 7.54 (d, $J = 4.5$ Hz), $H_{8'}$ at 7.95 ($J = 10$ Hz), and H_9 at 5.68.

In the spectrum of a mixture of (−)- and *rac*-dihydroquinines in a ratio of 1:1 (Figure 3) the above mentioned protons give rise to two sets of peaks with areas in a ratio of 3:1 and with the following chemical shifts: $H_{2'}$ at δ 8.46 (d, $J = 4.5$ Hz) and 8.58 (d, $J = 4.5$ Hz), $H_{3'}$ at 7.47 (d, $J = 4.5$ Hz) and 7.55 (d, $J = 4.5$ Hz), $H_{8'}$ at 7.88 ($J = 10$ Hz) and 7.96 ($J = 10$ Hz), and H_9 at 5.57 and 5.77.

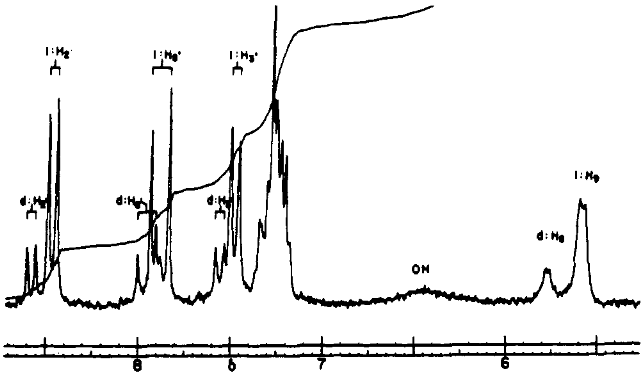


Figure 3. Portion of the 100-MHz spectrum of an artificial 1:1 mixture of racemic and natural (−)-dihydroquinine, *ca.* 0.27 *M* $CDCl_3$ solution.

Concentration[4] studies revealed that the nmr spectra of the pure enantiomers, the racemate, and various mixtures[5] thereof on high dilution tend to become identical. The chemical shifts of the aromatic protons are most susceptible to change in concentration, whereas those of protons H_9 are mainly dependent upon the relative concentration of the enantiomers.

The spectral differences are greatly reduced when deuterated methanol is used as a solvent. The nmr spectra of the acetates of optically active and racemic dihydroquinine, recorded in deuteriochloroform solution, show significantly smaller differences than those observed with dihydroquinine.

These facts can be rationalized by consideration of solute–solute interactions of the enantiomers. In solutions of the pure enantiomers, the racemate, and mixtures thereof, the molecules of each individual enantiomer reside in environments which are by intrasolution comparison identical, enantiomeric, and diastereomeric, respectively. By intersolution comparison the environments experienced by the molecules of individual enantiomers are diastereomeric when solutions of different, nonreciprocal compositions are considered.

The above-illustrated effects were also observed in the spectra of other compounds in the same class and will be found for other types of compounds. One practical application of these effects would be the determination of optical purity.

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(3) Nmr spectra were recorded on a Varian HA-100 spectrometer using tetramethylsilane as an internal reference.

(4) Solutions ranging from 0.54 to 0.01 *M* in deuteriochloroform.

(5) (−)-Dihydroquinone:(+)-dihydroquinone: 87.5:12.5, 75:25, 62.5:37.5.

T. Williams, R. G. Pitcher, P. Bommer
J. Gutzwiller, M. Uskoković
Chemical Research Department
Hoffmann-La Roche Inc., Nutley, New Jersey 07110

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Kinetics and Mechanism of the Reaction of the Thianthrene Cation Radical with Water

Sir:

The reactions of organic cation radicals are not at all clearly defined. For the most part these radical ions are prepared in solution by anodic or chemical oxidation for correlation of their esr spectra with structure and unpaired electron density. The environment in which chemical oxidation is carried out, *e.g.*, concentrated sulfuric acid, aluminum chloride–nitromethane solution, is usually itself too reactive to encourage *in situ* studies of the cation-radical reactions. Quite a number of reactions are described in the literature which are interpreted as involving cation radicals, and in these a cation-radical intermediate is usually inferred from the nature of the reactants and the type of products formed.[1-5]

Knowledge about the reactions of cation radicals with water is particularly obscure. The reaction is important since it is likely to be encountered in all reaction systems involving cation radicals unless scrupulously dried solvents are used. This proviso applies particularly to reactions studied at an anode. Cauquis[6] has stressed this fact and has noted that sometimes a cation radical reacts with water to give a new compound (*e.g.*, the phenoxathiin cation radical forms phenoxathiin 5-oxide) and sometimes oxidizes the water (*e.g.*, the dibenzodioxin cation radical is said to react with water to form dibenzodioxin and hydrogen peroxide). Recently, the formation of 9-anthranol in the anodic oxidation of anthracene has been reported,[7,8] and in this reaction the cation radical is thought to undergo nucleophilic attack by a water molecule.[7] The pouring of a solution of the perylene cation radical in sulfuric acid into water regenerated perylene,[9] while similar experiments with the thianthrene cation radical gave both thianthrene and thianthrene 5-oxide.[10] Thus, it would appear that several courses of reaction are available between a cation radical and water, but it is not clear whether the mechanisms proposed for them are more speculation than fact.

In order to reach a better understanding of cation-radical reactions we have begun studying certain radicals after isolating them as salts. We are now able to describe the reaction of thianthrenium perchlorate ($Th^{\cdot +}ClO_4^-$, **1**) with water and to settle on a mechanism.

Crystalline $Th^{\cdot +}ClO_4^-$ was prepared by two methods: the disproportionation of thianthrene and thianthrene 5-oxide in perchloric acid,[11] and the oxidation of thianthrene by perchloric acid in carbon tetrachloride.[12] The latter method was found to be more convenient. **1** was stable for long periods (sometimes indefinitely) in solvents dried with phosphorus pentoxide and/or calcium hydride followed by a molecular sieve. The presence of water in the solvent caused the rapid formation of thianthrene (Th) and thianthrene 5-oxide (ThO) in equal amounts (determined spectrophotometrically after separation by tlc). Two mechanisms (paths A and B) may be considered for the formation of these products. Kinetic studies have been carried out, and the results fit path B rather than path A.

Path A

$$Th^{\cdot +} + H_2O \rightarrow Th + H^+ + 0.5H_2O_2 \tag{1}$$

$$Th + H_2O_2 \rightarrow ThO + H_2O \tag{2}$$

Path B

$$2Th^{\cdot +} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Th + Th^{2+} \tag{3}$$

$$Th^{2+} + H_2O \xrightarrow{k_2} ThO + 2H^+ \tag{4}$$

A solution of **1** was made in molecular sieve dried acetonitrile and evaporated in a quartz cuvette so as to leave a thin, readily soluble film of **1** on the cuvette walls. A solution of thianthrene and water was made in a known volume of molecular sieve dried acetonitrile and transferred to the cuvette containing solid **1**. All of the solvent transfers were carried out by distillation on a vacuum-line system, and the final pouring of the thianthrene–water solution into the cuvette was made after the apparatus had been sealed and removed from the vacuum line. **1** dissolved very quickly, and its disappearance by reaction with the water was followed spectrophotometrically at 546 mμ.

The disappearance of **1** was too rapid to measure unless some Th was first introduced, a fact which itself supports path B. It was also necessary to keep the concentration of water reasonably low for the disappearance of the $Th^{\cdot +}$ to be slow enough to measure.

The disappearance of $Th^{\cdot +}$ is first order in $Th^{\cdot +}$ according to path A and second order according to path B. If a steady-state concentration of Th^{2+} is assumed, the rate expression in eq 5 can be derived. If, on the other hand, the equilibrium in eq 3 is rapidly reached, the rate expression in eq 6 can be derived. In either case, by using a ratio of $[H_2O]_0/[Th]_0$ in which the $[H_2O]_0$ and $[Th]_0$ are several fold greater than $[Th^{\cdot +}]_0$, it is possible to treat the disappearance of the $Th^{\cdot +}$ spectroscopically easily according to eq 7, in which k_a is, for example, $k_2K[H_2O]/[Th]\varepsilon$, and ε is the extinction coefficient of $Th^{\cdot +}ClO_4^-$ in acetonitrile.

$$-\,d[Th^{\cdot +}]/dt = \frac{k_1[Th^{\cdot +}]^2}{(k_{-1}[Th]/k_2[H_2O]) + 1} \tag{5}$$

$$-\,d[Th^{\cdot +}]/dt = k_2K[H_2O][Th^{\cdot +}]^2/[Th] \tag{6}$$

$$\frac{1}{A_t} - \frac{1}{A_0} = k_at \tag{7}$$

Experiments were performed in which $[\mathbf{1}]_0$ was 1.03×10^{-3} *M*, $[H_2O]_0$ was 1.24, 1.55, and 1.24×10^{-2} *M*, and $[Th]_0$ was 2.12, 2.10, and 1.06×10^{-4} *M*. Plots of $1/A$ against time were linear. By assuming that equilibrium in eq 3 is reached rapidly we calculated from these plots k_2K to be 11.4, 11.5, and 17.1 M^{-1} min^{-1} for the three cases studied. The inhibitory effect of Th on the disappearance of $Th^{\cdot +}$ and the reasonable agreement among the values of k_2K are strong support for path B. Our result is not necessarily applicable to other aromatic cation radicals, but it suggests that the role of the disproportionation reaction (eq 3) in cation-radical reactions must be considered, even in electrochemical systems in which the

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dication could be present in very low concentration.

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Henry J. Shine, Yuzuru Murata
Department of Chemistry, Texas Technological College
Lubbock, Texas 79409
Received January 24, 1969

Preparation and Properties of Alkali Fluoroxenates, $M_x(FXeO_3)_x$

Sir:

The preparation of $CsF \cdot XeO_3$ by atmospheric hydrolysis of $CsF \cdot XeOF_4$ and $CsXeF_7$ was reported by Selig.[1] A similar salt containing cesium fluoride and xenon trioxide was prepared by precipitation from aqueous solutions and was reported by us.[2] In contrast to the explosive nature of xenon trioxide, this salt appeared to be as stable toward shock and heat as the most stable of the perxenates. In fact, the alkali fluoroxenates are the most stable solid oxygenated compounds of xenon(VI) reported to date. In this note we report the preparation and properties of cesium, rubidium, and potassium fluoroxenates.

Alkali fluoroxenate salts were prepared from aqueous solutions by either of two methods. (1) Aqueous xenon trioxide, 0.5 *M*, containing HF from the hydrolysis of xenon hexafluoride, was neutralized with 2 *M* rubidium or cesium hydroxide to pH 4. This solution was allowed to evaporate slowly until a good yield of crystalline salt was formed. Crystals were filtered, washed with ice-cold water, and stored in a desiccator. (The presence of atmospheric moisture apparently had no effect on the stability of these salts.) This procedure was successfully used with the cesium and rubidium salts.[2] Potassium fluoroxenate was prepared by taking approximately equal volumes of 0.5 *M* aqueous xenon trioxide and 1 *M* potassium fluoride. This solution was acidified with a few drops of 1 *M* HF and was slowly evaporated until the precipitate formed. High-purity cesium, rubidium, and potassium fluoroxenates were prepared by this procedure. However, all attempted preparations of sodium fluoroxenate contained impurities of sodium fluoride or xenon trioxide depending on the procedure used. This difficulty in preparing pure sodium fluoroxenate can be attributed to the relative solubilities of alkali fluoroxenates and alkali fluorides in water. Solubility of alkali fluoroxenates decreases with increasing atomic weight of alkali, and that of alkali fluorides increases. The potassium fluoroxenate is approximately three times more soluble than rubidium fluoroxenate, which yields saturated solutions of 0.22 *M* at 20°.

Formula weights were obtained from the oxidation equivalent and alkali and fluoride[3] analyses. Formula weights derived from these analyses for cesium, rubidium, and potassium fluoroxenates are 334 ± 3, 287 ± 3, and 236 ± 3, respectively. These values compare well with the calculated formula weights of $CsFXeO_3$ (283.8) and $KFXeO_3$ (237.4).

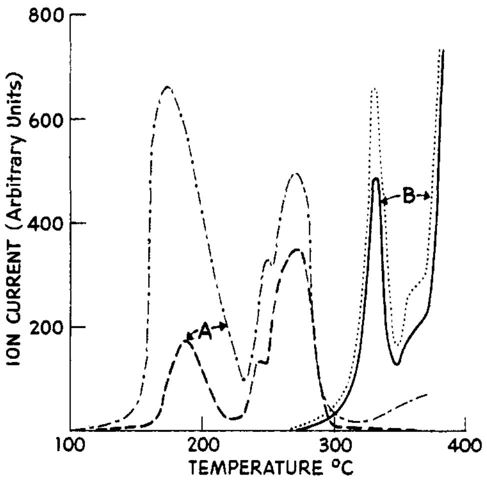

Figure 1. Thermal decomposition of Na_4XeO_6 (curve A) and $Rb_x(FXeO_3)_x$ (curve B): heating rates ~4°/min; mass spectrometer sensitivities for Xe and O_2 calibrated by decomposing $XeO_3 \rightarrow Xe + 1.5O_2$. (Evolution of O_2 is represented by dashed lighter lines and that of Xe by heavier lines.)

Infrared studies carried out in a silver chloride matrix showed four bands at 812 (s), 761 (m), 380 (w), and 333(w) cm^{-1}, the exact position of these bands depending on the alkali metal. No bands were observed in the usual Xe–F stretching region, 500–600 cm^{-1}.[4] Hydroxyl or water bands were completely absent.

Thermal stability of the alkali fluoroxenates was investigated by mass spectrometric, thermogravimetric, and differential thermal analysis methods. All showed that alkali fluoroxenates underwent no decomposition whatsoever up to 200°. Appreciable decomposition to oxygen and xenon began above 260° and became substantial around 300°. Some samples ultimately underwent explosive decomposition when heated above 300°, leaving alkali fluoride residues. Thermal decomposition characteristics of sodium perxenate and that of rubidium fluoroxenate are shown in Figure 1. Qualitative mass spectrometric examination of gases evolved during thermal decomposition of fluoroxenates confirmed the unhydrous nature of the compounds and showed only xenon and oxygen with a small amount of CO_2. We have shown that the fluoroxenates are thermally more stable than sodium perxenate, in the sense of being able to withstand higher temperatures without decomposition.

The high stability of fluoroxenates has allowed small samples to be ground and subjected to shock without explosion. Caution: in the presence of basic xenates or of xenon trioxide fluoroxenate samples so treated can explode. In addition, solid fluoroxenates do not react with normal alcohols, while basic xenate salts[5] or xenon trioxide react explosively. The unusual stability of alkali fluoroxenates may be due to the pseudo-octahedral coordination of the xenon atom in these compounds. A recent X-ray diffraction study of crystalline potassium

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