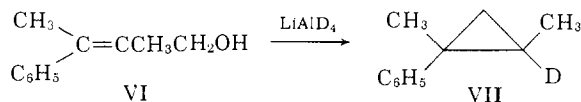


Consistent with the proposed scheme is the observed course of reduction with lithium aluminum deuteride. An isomeric mixture of alcohol VI yields deuterated cyclopropane VII both on water or deuterium oxide work-up. The n.m.r. spectrum of VII, in contrast to that of IVb, is normal, exhibiting the following absorption: a sharp three-proton singlet at τ 8.65, a broad three-proton singlet at τ 8.80, and two broad one-proton doublets centered at τ 8.98 and 9.72 ($J = 4.5$ c.p.s.).



We are investigating in detail the mechanistic course of these reactions and are elucidating the structural features favorable for cyclopropane formation.

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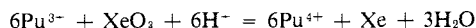
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Oxidation of Plutonium(III) by Xenon Trioxide¹

Sir:

The oxidizing properties of aqueous solutions of xenon trioxide have been described by Williamson and Koch,² and by Appelman and Malm,³ who estimated the xenon-xenon(VI) potential to be -1.8 v. in acid solution. Xenon trioxide is, therefore, one of the most powerful oxidizing agents in acidic aqueous solution, and it has the advantage that its reduced form, xenon, is a relatively insoluble gas and does not contaminate the solution. Despite these advantages, the reactions of xenon trioxide have received little study; the kinetics of only two reactions—the oxidation of bromide and iodide—have been reported.⁴

The xenon-xenon(VI) potential suggests that xenon trioxide should be capable of oxidizing plutonium(III) to plutonium(IV)



We have found this reaction to proceed at a measurable rate, and this communication reports the preliminary results of a study of its kinetics.

The oxidation reaction was studied at $30.0 \pm 0.2^\circ$ in perchlorate solutions with a constant ionic strength ($I = 2.0 M$); the extent of reaction was followed by measurement of the intensity of the plutonium(III) absorption peak at 6000 \AA . with a Cary Model 14 recording spectrophotometer. Runs were made at different plutonium(III), xenon trioxide, and hydrogen

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. M. Williamson and C. W. Koch, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, pp. 158-166.

(3) E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

(4) C. W. Koch and S. M. Williamson, ref. 2, pp. 181-184.

ion initial concentrations, and the data were analyzed using the integrated second-order rate expression. The second-order constants did not vary appreciably as the initial concentrations of the reactants were changed, and second-order plots of the individual runs were straight lines with very little scatter. (Generally the reaction was followed to 50% completion.) The results, shown in Table I, further indicate that the rate

Table I. Second-Order Rate Constants for the Oxidation of Pu^{3+} by XeO_3 (30° , $I = 2.0 M$)

| $[\text{Pu(III)}]_0$, M | $[\text{XeO}_3]_0$, M | $[\text{H}^+]$, M | $k \times 10^2$, $\text{l. mole}^{-1} \text{ sec.}^{-1}$ |
|-------------------------------|-----------------------------|-------------------------|--|
| 0.0117 | 0.00097 | 2.0 | 1.6 |
| 0.0230 | 0.00097 | 2.0 | 1.9 |
| 0.0225 | 0.00194 | 2.0 | 1.5 |
| 0.0459 | 0.00194 | 2.0 | 1.6 |
| 0.0452 | 0.00388 | 2.0 | 1.5 |
| 0.0433 | 0.00388 | 0.5 | 1.6 |

is apparently independent of acidity in the 0.5-2.0 M perchloric acid range. The reaction is therefore second order, and is described by the rate expression

$$-\frac{d[\text{Pu}^{3+}]}{dt} = k[\text{Pu}^{3+}][\text{XeO}_3]$$

with k having an average value of $1.6 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at 30° . It may therefore be concluded that the rate-controlling step is the reaction of xenon trioxide with plutonium(III) to form an unstable species of xenon in an intermediate oxidation state. Subsequent steps, involving oxidation by transitory lower-valent species of xenon, are all rapid compared to the initial step.

Xenon trioxide also oxidizes plutonium(IV) to plutonyl(VI), but significant competition from this reaction was avoided in the present study by selecting conditions such that the concentration of plutonium(IV) was always much less than that of plutonium(III). Nevertheless, there was a slight drift in values of k toward the end of the reaction in 0.5 M perchloric acid, apparently due to plutonium(IV)-plutonyl(VI) oxidation. Investigation of the oxidation of plutonium(III) and plutonium(IV) by xenon trioxide is continuing and will be described in greater detail later.

Acknowledgments. The xenon trioxide solution used in this study was very kindly supplied by Mr. J. G. Malm of the Chemistry Division, Argonne National Laboratory. The author expresses his appreciation to Mr. P. G. Hagan for experimental assistance and to Mr. G. J. Werkema for aid in the computer analysis of the data. The helpful suggestions of Professor Edward L. King of the University of Colorado Chemistry Department are also acknowledged.

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4-Methyl-4-trichloromethyl-2,5-cyclohexadienylidene

Sir:

We wish to report a new thermal reaction of tosyl-hydrazone¹ salts. Pyrolysis of the sodium salt of 4-