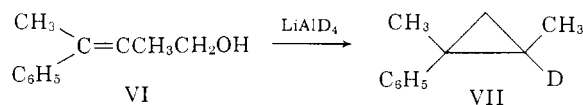


Consistent with the proposed scheme is the observed course of reduction with lithium aluminum deuteride. An isomeric mixture of alcohol VI yields deuterated cyclopropane VII both on water or deuterium oxide work-up. The n.m.r. spectrum of VII, in contrast to that of IVb, is normal, exhibiting the following 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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Margaret J. Jorgenson, Anne W. Friend

Department of Chemistry, University of California
Berkeley 4, California

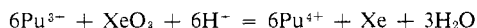
Received December 28, 1964

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

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	$k \times 10^2$, l. mole ⁻¹ 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 1.6×10^{-2} l. mole⁻¹ 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.

J. M. Cleveland

The Dow Chemical Company, Rocky Flats Division
Golden, Colorado 80402

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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-

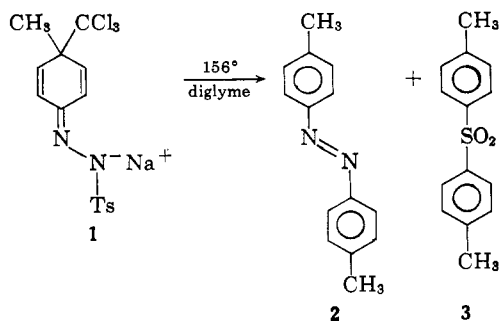
(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(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).

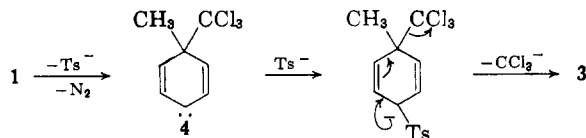
(4) C. W. Koch and S. M. Williamson, ref. 2, pp. 181–184.

methyl-4-trichloromethyl-2,5-cyclohexadienone tosylhydrazone (1) in refluxing diglyme afforded, as the major products, *p*-azotoluene² (2) and *di-p*-tolyl sulfone³ (3), in 48 and 38% yields, respectively. The reaction products were identified by spectral evidence



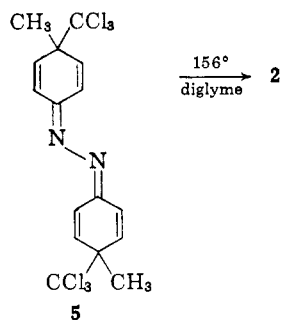
(infrared, ultraviolet, and n.m.r.) and by comparison of physical properties with those in the literature.

We suggest that sulfone 3 is formed by reaction of 4-methyl-4-trichloromethyl-2,5-cyclohexadienylidene⁴ (4) with *p*-toluenesulfonate ion, followed by aromatization of the initial adduct by ejection of trichloromethyl anion. Sulfone formation has been noted in another



aprotic tosylhydrazone decomposition.⁵ Under our reaction conditions trichloromethyl anion is undoubtedly converted to dichlorocarbene. This may account for the complexity of the reaction mixture, which contains at least eleven products.

Our finding that 4-methyl-4-trichloromethyl-2,5-cyclohexadienone azine (5) is converted to azotoluene 2 in 82% yield under the original reaction conditions,



coupled with the well-documented formation of azines in the decomposition of diazo compounds,⁶ suggests that the azine 5 may be an intermediate in the conversion of 1 to 2.

Tosylhydrazone⁷ 1, m.p. 150–151°, was prepared in 81% yield by condensation of 4-methyl-4-trichloro-

methyl-2,5-cyclohexadienone⁸ with tosylhydrazine in pyridine. Condensation of the dienone with hydrazine hydrate in refluxing methanol afforded the orange azine⁷ 5, m.p. 202.5–203.5° dec. (78% yield).

We are investigating the mechanisms of the thermal transformations reported herein, and are extending our studies to other cyclohexadienylidenes.

Acknowledgments. Dr. Robert S. H. Liu, of the Central Research Department, E. I. duPont de Nemours and Company, kindly obtained the n.m.r. spectra of the compounds studied in this work. This research was supported from a National Science Foundation Institutional Grant to Wesleyan University.

(8) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

Albert J. Fry

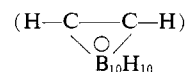
Hall Laboratory of Chemistry, Wesleyan University
Middletown, Connecticut 06457

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Complexes of Bisphosphinocarboranes with Nickel(II) Chloride

Sir:

Considerable interest has been aroused by recent reports on the synthesis and reactions of *o*-carborane¹



which consists of an icosahedron, the apices of which are ten boron and two carbon atoms, the latter being in nearest proximity and *ortho* to each other.² Of particular interest are the bisphosphino derivatives^{3,4} which should be structurally analogous to the *cis* forms of ethylenediamines and ethylenediphosphines and to the *o*-phenylenediphosphines and -diarsines. They lend themselves to a detailed study of ligand-metal bonding since varying the substituents on the borane portion of the molecule should affect the electronic environment of the phosphorus atoms and thus the stability of the complexes.

The reaction of nickel(II) chloride 6-hydrate with bisdiphenylphosphino-*o*-carborane³ as well as with the corresponding derivatives containing one, two, and three bromine atoms attached to the carborane nucleus⁴ in methanol and/or ethyl acetate produced complexes containing two molecules of bisphosphine and one of nickel(II) chloride. *Anal.* [Ni(B₁₀C₂H₃₀P₂)₂]Cl₂ as red crystals. Calcd. for C₅₂H₆₀B₂₀Cl₂NiP₄: C, 54.1; H, 5.20; Cl, 6.10; P, 10.7. Found: C, 53.1; H, 5.26; Cl, 6.14; P, 10.0. [Ni(B₁₀C₂H₂₉BrP₂)₂]Cl₂ as red crystals. Calcd. for C₅₂H₅₈B₂₀Br₂Cl₂NiP₄: C, 47.5; H, 4.41; Br, 12.16; Cl, 5.42. Found: C, 46.7; H, 4.42; Br, 12.15; Cl, 5.07. [Ni(B₁₀C₂H₂₈Br₂P₂)₂]Cl₂ as orange crystals. Calcd. for C₅₂H₅₆B₂₀Br₄Cl₂NiP₄: Br, 21.40; Cl, 4.80. Found: Br, 21.4; Cl, 4.88. [Ni(B₁₀C₂H₂₇Br₃P₂)₂]Cl₂ as orange crystals. Calcd. for C₅₂H₅₄B₂₀Br₆Cl₂NiP₄: Br, 27.30; Cl, 4.04. Found: Br, 28.30; Cl, 4.07.

(1) A comprehensive listing of relevant references appears as ref. 1 of F. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

(2) J. A. Potenza and W. N. Lipscomb, *ibid.*, **86**, 1874 (1964).

(3) R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

(4) H. D. Smith, T. A. Knowles, and H. Schroeder, *ibid.*, **4**, 107 (1965).

(1) Tosyl = Ts = *p*-toluenesulfonyl.

(2) D. Vorländer and F. Meyer, *Ann.*, **320**, 122 (1902).

(3) H. Meyer, *ibid.*, **433**, 327 (1923).

(4) A large body of evidence suggests that carbenes are generated in the pyrolysis of tosylhydrazone salts in aprotic media. See, e.g., L. Friedman and H. Schecter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(5) D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964).

(6) E.g., P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, **84**, 879 (1962).

(7) Satisfactory microanalyses have been obtained for all new compounds.