

chloride, an oily, sharp-smelling product separated during the reaction. This water-insoluble product was (undoubtedly) a mixture of aliphatic (allylic) bromides¹¹ formed by the addition of bromine atoms, generated by oxidation

(11) Products of this type will be described in a forthcoming paper in this series.

of bromine ions with amino radicals, to butadiene. The molar ratio of titanium(III) chloride consumed to hydroxylamine consumed was 1.64, indicating that about 36% of the bromine atoms generated reacted with butadiene and 64% with titanium(III) ions.

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[CONTRIBUTION FROM THE AMERICAN CYANAMID CO., RESEARCH DIVISION]

The Oxidation of Pinacol by Ceric Sulfate

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The oxidation of pinacol (2,3-dimethylbutandiol-2,3) by ceric sulfate was studied at 25°. The reaction is first order with respect to ceric ion and pinacol. No evidence of complexing between the sulfatocerate species and the glycol was found. The data show that one molecule of acetone is formed per ceric ion consumed. In the presence of acrylamide one molecule of acetone is formed per two ceric ions consumed. To explain the data a mechanism is proposed whereby the primary radicals are captured by the acrylamide, the efficiency of capture being of the order of 100%, and the polymer radicals are terminated by ceric ion. The data also show that the carbon-to-carbon bond of the 1,2-glycol is split before the free radical is captured. The activation energy for the over-all reaction was found to be 22.5 kcal./mole.

Introduction

It has been shown that the oxidation of 1,2-glycols by ceric salts^{1,2} proceeds through the disproportionation of coordination complexes. During the disproportionation of these complexes, free radicals are formed which initiate vinyl polymerization.³

The purpose of this work was to study the oxidation of 1,2-glycols by ceric ion in the presence of a free radical scavenger. It was thought that the stoichiometry of the reaction, determined in the presence or in the absence of a free radical scavenger, would yield useful information about the capture of the free radicals by the monomer and about the oxidation of the free radicals by ceric ion.

Pinacol (2,3-dimethylbutandiol-2,3) was used because upon oxidation it produces acetone, which is very resistant to further oxidation by ceric ion.

Ceric sulfate was chosen because it oxidizes pinacol at a measurable rate at room temperature, while ceric nitrate oxidizes it almost instantaneously even at 0°.

Experimental

1. **Material Used.**—Commercial pinacol was distilled at atmospheric pressure, b.p. 172°.

Anal. Found: C, 61.19; H, 11.64; O, 27.25. Calcd.: C, 60.98; H, 11.94; O, 27.07.

The ceric ammonium sulfate, (NH₄)₂[Ce(SO₄)₆]·2H₂O, reagent grade, from G. Frederick Smith Chemical Co., was dissolved in 1 *N* sulfuric acid and the stock solution, 0.1 *M* in ceric sulfate, was used to prepare the recipes.

Commercial acrylamide, from American Cyanamid Co., was sublimed at 60° under reduced pressure (0.05 mm.).

2. **Determination of the Rate of Reaction.**—Ten ml. of water was added to a 100-ml. volumetric flask followed by 10 ml. of *M* sodium sulfate, 20 ml. of *N* sulfuric acid and the required amount of pinacol solution, to give the desired final concentration and a total volume of 90 ml. The flask was thermostated at 25 ± 0.05° for 0.5 hour; 10 ml. of ceric sulfate solution, 0.1 *M* in *N* sulfuric acid, kept at 25°, was then added. Ten-ml. samples were withdrawn at recorded times, quenched in an excess of 0.01 *N* ferrous ammonium sulfate in 0.5 *N* sulfuric acid, and the excess ferrous salt was back titrated with 0.01 *M* ceric sulfate, using *o*-phenanthroline as an indicator. All other experiments were

carried out in a similar manner, varying the concentration of the reactants as required. Rate determinations in the presence of acrylamide were carried out in screw-capped bottles, under nitrogen.

3. **Determination of the Acetone Formed.**—Acetone was identified as the reaction product by isolation of its 2,4-dinitrophenylhydrazone and determined spectrophotometrically by the method of Behre and Benedict.⁴ Ten-ml. samples were withdrawn from the reaction flask and quenched with 0.5 ml. of saturated aqueous KOH. The hydroxides of cerium were filtered off and 2 ml. of the filtrate added to 1 ml. of salicylic aldehyde in 100-ml. volumetric flasks. After adding 15 ml. of saturated aqueous KOH, the samples were allowed to stand for 20 minutes and then brought to volume. If the red color developed was too intense, the samples were diluted further with distilled water. The optical densities of the solutions were determined at 520 m μ on a G. E. spectrophotometer, using a 1-cm. cell.

The concentration of acetone in the samples was read from a calibration curve obtained by plotting the optical densities of reference solutions, containing known amounts of acetone *vs.* the concentration. The reference solutions contained the same amounts of pinacol, cerous salts, sodium sulfate and sulfuric acid as the samples under examination. When acrylamide was used as a free radical scavenger (see Table V), a new calibration curve was prepared from reference solutions containing the same amount of acrylamide as the samples to be analyzed.

Data and Discussion

The oxidation of pinacol was studied at 25°. At constant *pH* and in the presence of an excess of glycol, the rate of the reaction is first order with respect to the concentration of total ceric ion (Ce^{IV}) and can, therefore, be represented by

$$-d(\text{Ce}^{\text{IV}})/dt = K'(\text{Ce}^{\text{IV}})$$

The rate of the reaction was found to be the same in nitrogen and in air. The values of *K'*, the overall first-order constant, reported in the tables, were calculated from the slopes of the plots log (Ce^{IV}) *vs.* time.

The dependence of *K'* on the pinacol concentration was studied at one hydrogen ion and sulfate ion concentration only (*pH* 0.97, (SO₄⁼)_T = 0.29 mole per liter). Figure 1 shows that *K'* varies linearly with the pinacol concentration. From the slopes of this plot the value of the second-order

(1) F. R. Duke and A. A. Forist, *THIS JOURNAL*, **71**, 2790 (1949).

(2) F. R. Duke and R. P. Bremer, *ibid.*, **73**, 5179 (1951).

(3) G. Mino and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).

(4) P. B. Hawk, B. L. Oser and W. H. Summerson, "Practical Physiological Chemistry," The Blakiston Co., Philadelphia, Pa., 1947, p. 875.

TABLE I
EFFECT OF THE SULFATE ION CONCENTRATION ON K' (PINACOL) = 0.110

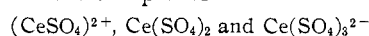
$(\text{SO}_4^{2-})_T$	pH	$(\text{Ce}^{IV}) \times 10^4$	$K' \times 10^3$, min. ⁻¹
0.19	0.85	100	40.78
.29	0.97	100	22.88
.17	..	50	46.30
19	..	50	39.58

TABLE II
EFFECT OF THE CERIC ION CONCENTRATION ON K'
pH 0.97, $(\text{SO}_4^{2-})_T = 0.19$, (pinacol) = 0.110

$\text{Ce}^{IV} \times 10^4$	$K' \times 10^3$, min. ⁻¹
100	40.78
50	39.58
20	39.50

rate constant K was found to be 0.21 liter/mole/minute.

The data of Table I show, at least qualitatively because the pH was not kept strictly constant, that the rate of reaction is decreased when the concentration of total sulfate ion is increased. (In this and subsequent tables, concentrations are expressed in moles per liter; $(\text{SO}_4^{2-})_T$ represents the combined concentration of HSO_4^- and SO_4^{2-}). For the system ceric nitrate-butandiol, Duke and Forist¹ found that plots of $1/K'$ vs. the reciprocal of the glycol concentration are linear. This suggested the formation of intermediate complexes which decompose unimolecularly. Ardon⁵ demonstrated the presence of ceric-ethanol complexes in the system ceric perchlorate-ethyl alcohol. Our data do not show evidence of complexing between ceric sulfate and pinacol. This means that either the concentration of the intermediate glycol complex is extremely small or that the sulfatocerate complexes oxidize the glycol directly. The same dependence of K' on the concentration of the reducing agent was found by Hargreaves and Sutcliffe⁶ for the systems ceric perchlorate-formaldehyde and ceric sulfate-formaldehyde. Hardwick and Robertson⁷ found that these complexes



are present in a ceric sulfate solution and that their relative concentration is a function of the pH and sulfate ion concentration. Under the conditions of this study, the solutions contain mostly $\text{Ce}(\text{SO}_4)_3^{2-}$ with a small proportion of $\text{Ce}(\text{SO}_4)_2$.

TABLE III
INFLUENCE OF TEMPERATURE ON K'
 $(\text{Ce}^{IV}) = 0.01$, (pinacol) = 0.110, $(\text{SO}_4^{2-})_T = 0.29$, pH 0.97

$T, ^\circ\text{C}$.	20	25	30
$K' \times 10^{-3}$, min. ⁻¹	11.80	22.88	42.16

The absence of polynuclear complexes in ceric sulfate solutions, demonstrated by Hardwick and Robertson, is further confirmed by the constancy of K' with dilution (Table II).

The stoichiometry of the reaction was established by determining the concentration of the total ceric

(5) M. Ardon, *J. Chem. Soc.*, 1811 (1957).

(6) G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 1105 (1955).

(7) T. J. Hardwick and R. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

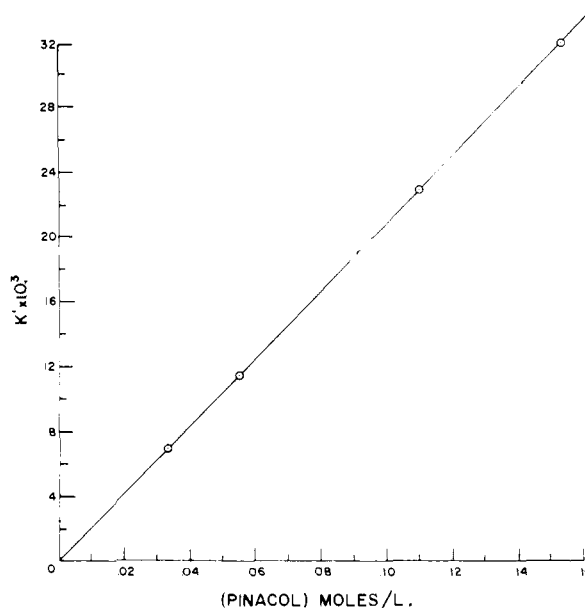
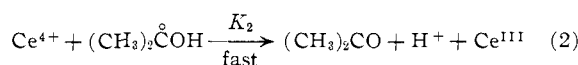
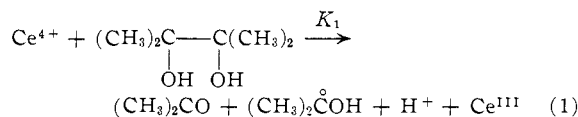


Fig. 1.—Dependence of rate constant on pinacol concentration ($[\text{Ce}^{IV}] = 0.01$, $[\text{SO}_4^{2-}] = 0.29$, pH 0.97).

ion and acetone in the system at different times. The data of Table IV show that one molecule of acetone is formed per ceric ion consumed.

In accordance with these facts, if Ce^{4+} represents the sulfatocerate complexes involved in the oxidation, a general scheme for the reaction can be written as



the first step being rate determining.

It should be pointed out that although the stoichiometry of the reaction excludes the disproportionation of the primary radicals it does not exclude coupling of these radicals to produce pinacol. In this study, however, since the concentration of total ceric ion used was large (0.01 mole/liter), only reaction 2 will be considered.

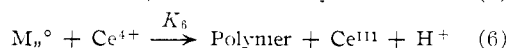
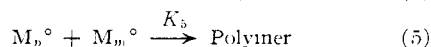
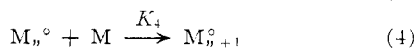
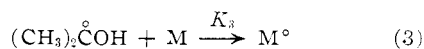
TABLE IV
STOICHIOMETRY OF THE CERIC SULFATE-PINACOL REACTION
 $(\text{SO}_4^{2-})_T = 0.29$, pinacol = 0.105, pH 0.97

Time, min.	$\text{Ce}^{IV} \times 10^4$	Acetone $\times 10^4$	$\frac{(\Delta\text{Ce}^{IV})^a}{(\text{Acetone})}$	$K' \times 10^3$, min. ⁻¹
0	102.0	0	..	22.88
11.17	79.0	24	0.96	
20.69	63.1	41	0.95	
35.13	45.6	57	0.99	
55.12	28.9	72	1.01	

$$^a \Delta\text{Ce}^{IV} = \text{Ce}^{IV}(0) - \text{Ce}^{IV}$$

The absolute rate constant of the rate-determining step K_1 cannot be calculated from the overall rate constant K without a knowledge of the sulfatocerate species responsible for the oxidation. From the data of Table III an over-all activation energy of 22.5 kcal. was obtained.

When the oxidation reaction is carried out in the presence of a vinyl monomer, the free radicals produced in the first step are captured and a chain reaction takes place as



where M represents the acrylamide monomer, and M° the radical formed by the reaction of the primary radical with a molecule of monomer; M_n° and M_m° represent growing polymer chains.

The oxidation of acrylamide by ceric sulfate was found to be negligible at 25°.

TABLE V

STOICHIOMETRY OF THE CERIC SULFATE-PINACOL REACTION IN THE PRESENCE OF ACRYLAMIDE

$(\text{SO}_4^{2-})_T = 0.29$, (pinacol) = 0.105, (acrylamide) = 1.40, $\rho\text{H} = 0.97$

Time, min.	$(\text{Ce}^{IV}) \times 10^4$	(Acetone) $\times 10^4$	$\frac{(\Delta\text{Ce}^{IV})}{(\text{Acetone})}$	$K' \times 10^3$, min. ⁻¹
0	100.0	0	..	
3.04	97.8	1.1	2.00	8.13
12.93	90.0	5.2	1.92	
20.20	85.2	6.6	2.20	
35.35	74.8	13.0	1.94	
48.75	66.8	18.0	1.84	

A kinetic study on the polymerization of acrylamide initiated by ceric ion oxidation-reduction systems showed that, under the conditions of this work, termination occurs exclusively by oxidation of the polymer free radicals by ceric ion, as in step 6, rather than by coupling or disproportionation.⁸ This offers the interesting possibility of determining the efficiency of the capture reaction. According to the proposed scheme if all the radicals are captured by the monomer and termination occurs exclusively by oxidation of the radicals (step 6), one molecule of acetone is formed per two

(8) G. Mino, S. Kaizerman and E. Rasmussen, *J. Polymer Sci.*, in press.

of ceric ion consumed. The data of Table V show this to be true when the pinacol oxidation is carried out in the presence of an excess of acrylamide (1.4 moles/liter). From the rate expressions $d(\Delta\text{Ce}^{IV})/dt$ and $d(\text{Acetone})/dt$ the relationship

$$\rho = \frac{d[\Delta\text{Ce}^{IV}]}{d[\text{acetone}]} = \frac{2 + f' - f}{2 - f} \quad (7)$$

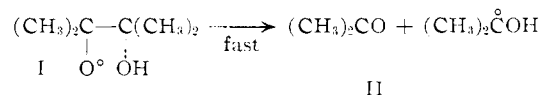
can be derived if it is assumed that the free radical R° and M° attain a steady state concentration. In equation 7, f and f' represent the efficiency of capture and oxidative termination defined as

$$f = \frac{K_3(\text{R}^\circ)(\text{M})}{K_3(\text{R}^\circ)(\text{M}) + K_3(\text{R}^\circ)(\text{Ce}^{IV})}$$

$$f' = \frac{K_6(\text{M}^\circ)(\text{Ce}^{IV})}{K_6(\text{M}^\circ)(\text{Ce}^{IV}) + K_5(\text{M}^\circ)^2}$$

and $(\Delta\text{Ce}^{IV})/(\text{acetone})$ represents the ratio of ceric ion consumed to acetone formed. From equation 7, it is clear that ρ can only be equal to two if both f and f' are equal to one. The value of ρ , obtained from the data of Table V, is 1.94.

The data show, therefore, that the primary radicals are about 100% effective in starting polymerization, and confirm that the termination occurs by an oxidative process involving ceric ion, and they also show that the carbon-to-carbon bond of the 1,2-glycol is split before the radical is captured. If splitting did not occur, no acetone would be formed in the presence of the monomer. On the basis of the data, it is concluded that if the free radical I is formed, it must rearrange very rapidly to give acetone and free radical II.



Inspection of the data of Tables IV and V shows that the rate of reaction is much lower in the presence of acrylamide. A decrease in rate also was noticed during the oxidation of 3-chloro-1-propanol by ceric nitrate in the presence of acrylamide.⁸ The retardation probably is due to the formation of stable complexes between acrylamide and the ceric ion.

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