1.0 and 3.0. *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.42; H, 9.38.

Solvolysis of *trans*-1-Bromo-3-vinylcyclopentane.—To 1.3 g of silver perchlorate in 15 ml of formic acid (97–100%) buffered with an equimolar quantity of sodium formate was added 0.8 g of *trans*-1-bromo-3-vinylcyclopentane and the reaction was stirred for 10 min. A 10% *M* excess of 20% sodium hydroxide solution was added and the solution was stirred 2 hr. The product was extracted with ethyl ether, dried, and concentrated to give 0.29 g of brown oil. The product was isolated and purified by analytical vpc using a 5 ft × 0.25 in. Carbowax column to give 3-vinylcyclopentanol (stereochemistry not determined) as the major product. The product was identified by comparison of its vpc retention time and of its infrared spectrum with an authentic sample.

Solvolysis of *trans*-1-Bromo-3-vinylcyclopentane in 50% Aqueous Ethanol.—The solvolysis was carried out at 69.64 ± 0.01° (temperature calibrated with National Bureau of Standards thermometer and deviation averaged over a period of 3 days) utilizing the conductimetric technique to give absolute rate constants for cyclopentyl bromide as $1.4 \pm 0.2 \times 10^{-3}$ sec^{-1} and for *trans*-1-bromo-3-vinylcyclopentane as $6.2 \pm 0.2 \times 10^{-4}$ sec^{-1}.

Solvolysis of *trans*-1-Bromo-3-vinylcyclopentane in Aqueous Silver Nitrate.—Four grams of *trans*-1-bromo-3-vinylcyclopentane was added dropwise to 6 g of silver nitrate in 100 ml of water and the solution was stirred for 30–45 min and then the silver bromide was filtered. The reaction mixture was extracted twice with 50-ml portions of ethyl ether, dried, and concentrated to give 1.4 g of crude product. The reaction product was isolated and purified by analytical vpc and identified by comparison of its vpc retention time and its infrared spectrum with those of an authentic sample, and the 3,5-dinitrobenzoate was prepared as above. The 3,5-dinitrobenzoate melted at 74.8–75.4° (low melting probably owing to *cis–trans* isomers) and the mixture melting point with the *cis*-3-vinylcyclopentyl benzoate was 76.1–78.8°. *Anal.* Calcd for $C_{14}H_{14}N_2O_6$: C, 54.94; H, 4.61; N, 9.15. Found: C, 55.07; H, 4.49; N, 8.83.

Registry No.—**3,** 5724-61-8; **4,** 7442-41-3; **1,** 7442-42-4; **6,** 7442-43-5; **5,** 7442-44-6; *cis*-3-vinylcyclopentyl 3,5-dinitrobenzoate, 7430-87-7; *cis*-3-vinylcyclopentyl tosylate, 7442-45-7; 3-vinylcyclopentyl acetate, 7442-46-8; *trans*-3-vinylcyclopentyl 3,5-dinitrobenzoate, 7430-88-8; 3-vinylcyclopentanol, 7442-71-9; **7,** 137-43-9.

The Mechanism of Oxidation of Cyclic Alcohols by Cerium(IV)[1]

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Received April 6, 1966

Cerium(IV) oxidations of a series of cyclic alcohols and glycols were studied in 1.0 *M* perchloric acid and in mixed sulfuric and perchloric acids. The results are related to the oxidation phase of the cerium(IV) initiation of graft polymerization onto cellulose. Definite evidence was obtained for formation of cerium(IV) complexes with *cis*- and *trans*-1,2-cyclohexanediols, *trans*-2-methoxycyclohexanol, and cyclohexanol in 1.0 *M* perchloric acid. The magnitudes of the equilibrium constants for complex formation indicated that the 1,2-cyclohexanediols form chelate complexes. In mixtures of sulfuric and perchloric acids there were no large differences in the over-all oxidation rates of *cis*- and *trans*-1,2-cyclohexanediol or of *cis*- and *trans*-1,2-cyclopentanediol. The effect of ring size was considerable, however, with the cyclopentanediols reacting much more rapidly (200–1000-fold) than cyclohexanediols. A study of the effect of sulfate ion concentration indicated that $CeSO_4^{2+}$ is the most reactive of the cerium(IV)–sulfate complexes present in the sulfuric–perchloric acid systems. The relative reactivities of the cellulose model compounds, *trans*-1,2-cyclohexanediol, cyclohexanemethanol, and tetrahydropyran-2-methanol, suggested that cerium(IV) oxidation of cellulose will occur mainly, but not exclusively, at the C_2–C_3 glycol.

The oxidations of alcohols and glycols by cerium(IV) are generally believed to proceed by disproportionation of coordination complexes. Evidence for complex formation has been obtained by kinetic and spectrophotometric methods in cerium(IV) oxidations of many compounds in perchloric and nitric acid media.[4-9] Complex formation has been detected in cerium(IV) oxidations in sulfuric acid media only in a few instances.[10-12] Reactions in sulfuric acid often follow second-order kinetics,[8,13-16] and a direct oxidation mechanism, without complex formation, has been suggested for oxidations in this acid.[14] However, it is also possible that oxidation proceeds through an intermediate complex, but with a small equilibrium constant for complex formation.

The complex formed in the cerium(IV) oxidation of a 1,2-glycol may be either a chelate complex or an acyclic complex in which only one hydroxyl is coordinated with the cerium(IV). Littler and Waters[17] concluded from studies of the relative rates of oxidation of certain glycols and their monomethyl ethers that cerium(IV) oxidations of 1,2 glycols proceed by an acyclic mechanism. On the other hand, Duke and Forist[4] assumed that both hydroxyls of 2,3-butanediol coordinate with cerium(IV), and the spectrophotometric measurements of Offner[18] clearly suggest the possibility of chelate complex formation with cerium(IV). The nature of the complexes formed in the oxidation of 1,2 glycols by

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(1) (a) This paper is a portion of a thesis submitted by H. L. H. in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis., Jan 1966. (b) Presented in part at the Winter Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966.

(2) National Science Foundation Cooperative Graduate Fellow, 1962–1965.

(3) West Virginia Pulp and Paper Co., Charleston, S. C.

(4) F. R. Duke and A. A. Forist, *J. Am. Chem. Soc.*, **71**, 2790 (1949).

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

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

(7) S. S. Muhammad and K. V. Rao, *Bull. Chem. Soc. Japan*, **36**, 943 (1963).

(8) G. G. Guilbault and W. H. McCurdy, Jr., *J. Phys. Chem.*, **67**, 283 (1963).

(9) S. Venkatakrishnan and M. Santappa, *Z. Physik. Chem.* (Frankfurt), **16**, 73 (1958).

(10) K. P. Bhargava, R. Shanker, and S. N. Joshi, *J. Sci. Ind. Res.* (India), **21B**, 573 (1962).

(11) J. S. Littler, *J. Chem. Soc.*, 4135 (1959).

(12) Y. A. El-Tantawy and G. A. Rechnitz, *Anal. Chem.*, **36**, 1774 (1964).

(13) G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).

(14) S. S. Muhammad and K. V. Rao, *Bull. Chem. Soc. Japan*, **36**, 949 (1963).

(15) V. H. Dodson and A. H. Black, *J. Am. Chem. Soc.*, **79**, 3657 (1957).

(16) A. McAuley, *J. Chem. Soc.*, 4054 (1965).

(17) J. S. Littler and W. A. Waters, *ibid.*, 2767 (1960).

(18) H. G. Offner and D. A. Skoog, *Anal. Chem.*, **37**, 1018 (1965).

cerium(IV) was evaluated in this work from studies of the oxidation of cyclic alcohols, glycols, and monomethyl ethers of the glycols.

Experimental Section

Source of Reactants and Products.—Commercial cyclopentanol, cyclohexanemethanol, and tetrahydropyran-2-methanol (Aldrich) and cyclohexanol (Eastman) were purified by fractional distillation. *trans*-1,2-Cyclohexanediol (Aldrich) was purified by recrystallization from benzene. The following compounds were prepared by literature procedures: *cis*-1,2-cyclohexanediol,[19] *cis*-1,2-cyclopentanediol,[20] *trans*-1,2-cyclopentanediol,[20] and *trans*-2-methoxycyclohexanol.[21]

Cyclopentene oxide was prepared by oxidation of cyclopentene (Philips Petroleum) with peroxybenzoic acid[22] and converted to *trans*-2-methoxycyclopentanol with methanol and sulfuric acid by a procedure analogous to the preparation of *trans*-2-methoxycyclohexanol. *cis*-2-Methoxycyclohexanol was prepared according to the procedure of Buck, *et al.*,[23] except that the intermediate mesylate and benzoate esters were not distilled and the final product was purified by preparative gas chromatography using a 10 ft × $^{3}/_{8}$ in. 20% Hyprose on Chromosorb W column (retention times: *cis*, 34 min; *trans*, 41.6 min at 125°; and 100 ml/min He flow rate).

Cyclohexanone, cyclopentanone, 1,2-cyclohexanedione, and glutaraldehyde were purchased from Aldrich Chemical Co. for use as standards in the product analysis experiments. Adipaldehyde was prepared from *trans*-1,2-cyclohexanediol.[24] 2-Methoxycyclohexanone was prepared from *trans*-2-methoxycyclohexanol by chromic acid oxidation[25] using a procedure given by Fieser[26] for the preparation of cyclohexanone from cyclohexanol.

Solutions of the organic substrates were prepared by weighing out samples of the pure compounds, using care to prevent absorption of moisture by the hygroscopic substrates. Triply distilled water was used in these and all other solutions. The kinetic experiments were run in either 1.0 *M* perchloric acid or mixtures of sulfuric and perchloric acids (usually 0.25 *M* sulfuric and 0.75 *M* perchloric acids). For reactions in sulfuric acid media, a stock solution 0.1 *M* in cerium(IV) was prepared by dissolving ceric sulfate [$Ce(HSO_4)_4$, G. Frederick Smith] in 0.5 *M* sulfuric acid. A second stock solution, 0.05 *M* cerium(IV) in 1.0 *M* perchloric acid, was prepared for use in perchloric acid media by appropriate dilution of a 0.5 *M* cerium(IV) in 6 *M* perchloric acid solution (G. Frederick Smith).

Product Analysis.—Qualitative identifications and quantitative determinations of the carbonyl products of cerium(IV) oxidation reactions were made by formation of 2,4-dinitrophenylhydrazone derivatives directly in the reaction mixtures. The experimental procedure used was based on the work of Iddles and Jackson.[27] In a typical determination 10 ml of 0.05 *M* cerium(IV) solution was added to 40 ml of 0.125 *M* substrate solution, and the reaction was allowed to proceed to completion. The reaction mixture was then added slowly with stirring to 50 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* hydrochloric acid. After storing for 1 hr in an ice bath the precipitate was collected in a tared, fine-porosity, fritted-glass crucible, washed with 2 *M* hydrochloric acid and water, and dried in a vacuum desiccator over Drierite. Preliminary experiments with known adipaldehyde, cyclohexanone, cyclopentanone, and glutaraldehyde indicated that yields between 92 and 100% could be obtained with this procedure.

Infrared spectra were obtained of the 2,4-dinitrophenylhydrazone derivatives of the reaction products using the potassium bromide pellet technique and compared with spectra of the derivatives of known aldehydes and ketones. The spectra of the derivatives of the various possible reaction products were sufficiently different to permit reasonably positive identification of the products.

The precipitates were also examined by thin layer chromatography using Eastman Chromatogram Sheets Type K301R. The plates were developed in either 95:5 benzene–ethyl acetate or 95:5 benzene–petroleum ether (bp 60–110°). Qualitative product identifications were made by comparison of the movement of the product 2,4-dinitrophenylhydrazone with that of knowns run on the same plate. The solvent systems were sufficiently sensitive to permit essentially unambiguous identifications of the products.

In an attempt to prepare the 2,4-dinitrophenylhydrazone from a *cis*-1,2-cyclopentanediol reaction mixture, a very low weight of precipitate was obtained. Later it was found that on storage of *cis*-1,2-cyclopentanediol–cerium(IV) reaction mixtures overnight at 0°, a white, crystalline precipitate is formed. Similar treatment of a synthetic mixture of *cis*-1,2-cyclopentanediol and known glutaraldehyde also produced crystals. The crystalline products from the reaction mixtures and the known *cis*-1,2-cyclopentanediol–glutaraldehyde solution were isolated and shown to be identical by comparison of infrared spectra, melting points, and mixture melting points. A larger quantity of this material was prepared from a solution containing 3.6 g of *cis*-1,2-cyclopentanediol and 2.0 ml (0.005 mole) of 25% aqueous glutaraldehyde solution (Aldrich) in 100 ml 0.5 *M* sulfuric acid (yield 1.2 g, 0.0045 mole, 90%). Two recrystallizations from ethanol–water gave white crystals of glutaraldehyde bis(*cis*-1,2-cyclopentanediol acetal), mp 43.7–44.3° cor.

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01; mol wt, 268.4. Found: C, 67.39; H, 8.92; mol wt, 271 (by freezing point lowering).[28]

Rate Determinations.—All kinetic experiments were run with the organic substrate in excess so that the reactions would be pseudo first order with respect to cerium(IV). Reaction rates were determined by following the absorbance of the reaction solution using a Cary Model 15 recording spectrophotometer. After thermostating the reactant solutions for 30 min in a constant-temperature bath, the reaction was initiated using a procedure similar to that described by Dodson and Black.[15] A sample of the reaction mixture was transferred to a 1-cm spectrophotometer cell, and the recording of the absorbance was started. The time lag between initiating the reaction and recording of the absorbance was measured with a stop watch so that initial absorbances could be calculated. The reaction temperature in the spectrophotometer cell was maintained constant by circulating water from the bath through a thermostatable cell jacket. The temperatures reported are the mean of the temperatures measured at the inlet and outlet of the cell jacket. Temperature fluctuations were less than ±0.03°, and the reaction temperatures are conservatively estimated to be accurate to ±0.1°.

The spectrophotometric method was shown to give results equivalent to the titrimetric procedure described by Duke and Forist[4] for the reaction of *cis*-1,2-cyclopentanediol in 0.5 *M* sulfuric acid.

The wavelength at which the absorbance was followed depended on the initial cerium(IV) concentration and was chosen to give a reasonably large initial absorbance. The wavelengths most frequently used were 317.5 and 400 mμ for initial cerium(IV) concentrations of 0.00025 and 0.001 *M*, respectively, in mixed sulfuric and perchloric acids, and 425 mμ for 0.0025 *M* cerium(IV) in 1.0 *M* perchloric acid.

Pseudo-first-order rate constants were calculated from the slopes of plots of the logarithm of the absorbance *vs.* time. Despite the fact that all reactions were run with an excess of the organic substrate, the logarithm plots for some reactions were curved indicating an increase in the rate with time. This autocatalysis is believed to be due to secondary oxidations of the reaction product. In these reactions, initial rate constants were calculated from the initial slope of the logarithm plot. The reactions of *cis*- and *trans*-1,2-cyclohexanediols and *trans*-2-methoxycyclohexanol in 1.0 *M* perchloric acid and of *cis*- and *trans*-1,2-cyclopentanediols and *trans*-2-methoxycyclopentanol in sulfuric acid media gave good pseudo-first-order kinetics. Autocatalysis was observed in the oxidations of cyclohexanol in 1.0 *M* perchloric acid and of cyclopentanol, *cis*- and *trans*-1,2-cyclohexanediols, and *cis*- and *trans*-2-methoxycyclohexanols in mixed 0.25 *M* sulfuric and 0.75 *M* perchloric acids. The rate constants

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[19] M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 315 (1949).

[20] L. N. Owen and P. N. Smith, *ibid.*, 4026 (1952).

[21] S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943).

[22] H. G. Derx, *Rec. Trav. Chim.*, **41**, 312 (1922).

[23] K. W. Buck, A. B. Foster, A. Labib, and J. M. Webber, *J. Chem. Soc.*, 2846 (1964).

[24] W. Rigby, *ibid.*, 1907 (1950).

[25] M. Mousseron and R. Granger, *Compt. Rend.*, **205**, 327 (1937).

[26] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 94.

[27] H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem.* (Anal. Ed.), **6**, 454 (1934).

[28] Determined by Geller Laboratories, Charleston, W. Va.

TABLE I

DETERMINATIONS OF CARBONYL REACTION PRODUCTS

Substrate	Substrate concn, M	Ce(IV) concn, M	Reacn medium	Products	Yield, %
Cyclohexanol	0.1	0.01	1.0 M $HClO_4$	Cyclohexanone	69.3 72.3
Cyclopentanol	0.1	0.01	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Cyclopentanone	57.1 54.8
cis-1,2-Cyclohexanediol	0.1	0.01	1.0 M $HClO_4$	Adipaldehyde	98.5 98.5
trans-1,2-Cyclohexanediol	0.1	0.01	1.0 M $HClO_4$	Adipaldehyde	89.8 91.3
	0.1	0.01	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Adipaldehyde and unknown[a]	24.3[b] 27.7[b]
	3.7	0.005	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Adipaldehyde and unknown[a]	67.4[b]
trans-2-Methoxycyclohexanol	0.1	0.01	1.0 M $HClO_4$	Adipaldehyde and formaldehyde	54.8[b] 55.1[b]
	0.1	0.01	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Adipaldehyde and unknown[a]	17.4[b]
cis-2-Methoxycyclohexanol	0.1	0.01	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Adipaldehyde and unknown[a]	24.9[b]
trans-1,2-Cyclopentanediol	0.1	0.01	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Glutaraldehyde	103.3 103.1
trans-2-Methoxycyclopentanol	0.1	0.01	0.25 M H_2SO_4 and 0.75 M $HClO_4$	Glutaraldehyde	104.5 105.2

[a] The unknown formed in reactions producing adipaldehyde was shown to be a product of the cerium(IV) oxidation of adipaldehyde.
[b] Yields for reactions producing more than one product are based on the primary product and thus are only very approximate.

given are the average of duplicate determinations. The precision of the kinetic experiments depended to a large measure on the type of kinetics observed. For reactions obeying good pseudo-first-order kinetics the average deviation in the rate constants for duplicate runs was usually quite small (less than 3%). On the other hand, the rate constants for the autocatalytic reactions were, in general, less reproducible. Only for cyclopentanol and cyclohexanol, however, was the average deviation significantly greater than 3%.

A very marked effect of dissolved oxygen was observed in the reaction of *trans*-1,2-cyclohexanediol in perchloric acid. The effect was similar to that noted by Shorter in the oxidation of acetone in nitric acid.[29] When the reactant solutions were purged with nitrogen before mixing, good pseudo-first-order kinetics were observed, although at very low initial cerium(IV) concentrations (0.001 and 0.0005 M), a slight initial curvature was found in the logarithm plot. An initial cerium(IV) concentration of 0.0025 M was therefore used in all reactions in perchloric acid, and the reactant solutions were purged with nitrogen before mixing. The presence of dissolved oxygen did not affect the reactions in sulfuric acid media.

Results and Discussion

Product Analysis.—The carbonyl products of the oxidation reaction were characterized by formation of 2,4-dinitrophenylhydrazone derivatives directly from the reaction mixtures. Products were qualitatively identified by comparison of the infrared spectra and thin layer chromatographic behaviors of these derivatives with the derivatives of known carbonyl compounds. The results of product analysis are shown in Table I.

The calculation of the yield of product from the weight of 2,4-dinitrophenylhydrazone formed requires a knowledge of the reaction product and stoichiometry. In all cases it was assumed that 1 mole of carbonyl product is formed per 2 moles of cerium(IV) reduced. Yields approaching 100% indicate that the assumed stoichiometry is correct. For reactions producing more than one product, a rigorous calculation of yield would require determination of the relative amounts of the various products. In these cases approximate yields were calculated based on the major reaction product. In general, reactions in which good pseudo-first-order kinetics were observed gave yields approaching 100%, whereas lower yields were obtained in the autocatalytic reactions. For one of the autocatalytic reactions, the oxidation of *trans*-1,2-cyclohexanediol in mixed 0.25 M sulfuric and 0.75 M perchloric acids, it was shown that a 70-fold increase in the excess of the substrate produced a substantial increase in the yield (from 25 to 67%). This result is evidence that the low yields are caused by secondary oxidation of the initial reaction product.

The oxidations of *cis*- and *trans*-1,2-cyclohexanediols and *cis*- and *trans*-1,2-cyclopentanediols proceed by carbon–carbon bond cleavage to form the corresponding dialdehydes, adipaldehyde and glutaraldehyde. As indicated in the Experimental Section the glutaraldehyde formed in the reaction of *cis*-1,2-cyclopentanediol reacts with the diol to form a bisacetal. *trans*-2-Methoxycyclopentanol also reacted by carbon–carbon bond cleavage to form glutaraldehyde. The reactions of *cis*- and *trans*-2-methoxycyclohexanols produced adipaldehyde as the major reaction product, although low yields were obtained. In the reaction of *trans*-2-methoxycyclohexanol in 1.0 M perchloric acid some formaldehyde was also formed, probably from secondary oxidation of the methanol which must also be formed in the oxidation of the 2-methoxy alcohol to adipaldehyde. An unknown product was detected in the reactions producing adipaldehyde in 0.25 M sulfuric and 0.75 M perchloric acids. This unknown product probably results from secondary oxidation of the adipaldehyde, since it was also found in an oxidation of known adipaldehyde by cerium(IV). The oxidations of cyclohexanol and cyclopentanol produced the corresponding ketones as products.

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(29) J. Shorter, *J. Chem. Soc.*, 1868 (1962).

Search for Complex Formation.—A general theory of specific oxidations of glycols and related compounds was proposed by Duke[30] based on the hypothesis that coordination complexes are necessary for the reaction. It is assumed that a coordination complex (C) is formed between the organic substrate (S) and cerium(IV) in a prior equilibrium step. The intermediate complex then disproportionates unimolecularly in the rate-determining step forming cerous ion and a free radical. The free radical is rapidly oxidized by a second

$$\mathrm{Ce(IV)} + \mathrm{S} \overset{K}{\rightleftarrows} \mathrm{C} \xrightarrow{k} \mathrm{R\cdot} + \mathrm{Ce(III)} + \mathrm{H^+}$$

$$\mathrm{Ce(IV)} + \mathrm{R\cdot} \xrightarrow{\text{fast}} \text{product} + \mathrm{Ce(III)} + \mathrm{H^+}$$

cerium(IV). It is assumed that the coordination equilibrium is rapidly established and that equilibrium is maintained despite the unidirectional disproportionation of the complex. The rate expression corresponding to this mechanism is

$$-d[\mathrm{Ce(IV)}]_T/dt = \{kK[\mathrm{S}]/(1 + K[\mathrm{S}])\}[\mathrm{Ce(IV)}]_T$$

where $[\mathrm{Ce(IV)}]_T$ is the total cerium(IV) concentration. In the presence of excess substrate the rate expression becomes pseudo first order with respect to the total cerium(IV) concentration

$$-d[\mathrm{Ce(IV)}]_T/dt = k'[\mathrm{Ce(IV)}]_T$$

where

$$k' = kK[\mathrm{S}]/(1 + K[\mathrm{S}])$$

The equilibrium constant for complex formation and the rate constant for complex disproportionation can be experimentally evaluated by determining the pseudo-first-order rate constant (k') at a number of reductant concentrations. Then, since

$$1/k' = 1/k + 1/kK[\mathrm{S}]$$

K and k can be calculated from the slope and intercept of a plot of $1/k'$ *vs.* $1/[\mathrm{S}]$.

A second mechanism was proposed by Muhammad and Rao[14] for cerium(IV) oxidations in sulfuric acid media. It was assumed that cerium(IV) and the organic substrate react directly to form a free radical, hydrogen ion, and cerous ion as is shown below.

$$\mathrm{S} + \mathrm{Ce(IV)} \longrightarrow [\mathrm{Ce(IV)}\text{---}\mathrm{S}] \longrightarrow \mathrm{R\cdot} + \mathrm{Ce(III)} + \mathrm{H^+}$$

The above mechanism predicts second-order kinetics.

$$-d[\mathrm{Ce(IV)}]_T/dt = k_{II}[\mathrm{S}][\mathrm{Ce(IV)}]_T$$

In the presence of excess substrate the reaction is again pseudo first order. In this case the pseudo-first-order rate constant will be a linear function of the substrate concentration. However, second-order kinetics may also result for reactions proceeding through an intermediate complex if the equilibrium constant for complex formation is small. When second-order kinetics are experimentally observed it is not possible to distinguish between these two mechanisms.

The reactions of *cis*- and *trans*-1,2-cyclohexanediols, *trans*-2-methoxycyclohexanol, and cyclohexanol were studied in 1.0 *M* perchloric acid at 15.0°. The results are summarized in Table II. The plots of k' *vs.* [S] for these reactions were definite curves indicating complex formation between cerium(IV) and the substrate. The reciprocal plots were linear and equilibrium constants and disproportionation rate constants were calculated from the slopes and intercepts of these plots. In Figures 1 and 2 the results for *trans*-1,2-cyclohexanediol are illustrated, and in Table III the values calculated for k and K are summarized.

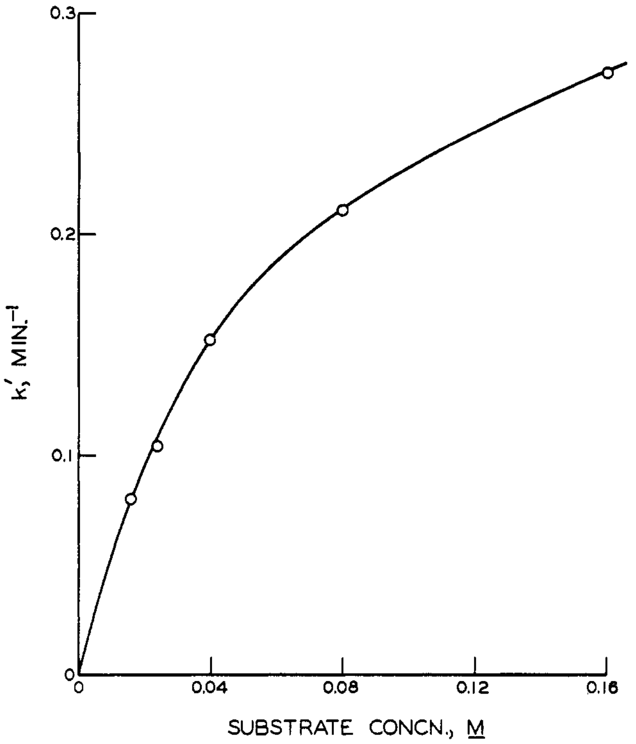

Figure 1.—Effect of substrate concentration on the pseudo-first-order rate constant for the reaction of *trans*-1,2-cyclohexanediol with 0.0025 *M* cerium(IV) in 1.0 *M* perchloric acid at 15.0°.

Table II

Effect of Substrate Concentration for Reactions in 1.0 *M* Perchloric Acid at 15.0°[a]

Substrate	Substrate concn, *M*	k', min⁻¹	$A_0 - A_b$
cis-1,2-Cyclohexanediol	0.016	0.258	0.578
	0.024	0.340	0.748
	0.040	0.459	1.013
	0.080	0.604	1.286
	0.160	0.656	1.545
trans-1,2-Cyclohexanediol	0.016	0.080	0.432
	0.024	0.104	0.600
	0.040	0.152	0.812
	0.080	0.211	1.133
	0.160	0.274	1.473
trans-2-Methoxycyclohexanol	0.016	0.110	0.107
	0.024	0.163	0.155
	0.040	0.262	0.261
	0.080	0.497	0.460
	0.160	0.824	0.713
Cyclohexanol[b]	0.024	0.00862	0.157
	0.036	0.0130	0.225
	0.048	0.0150	0.288
	0.080	0.0250	0.432
	0.160	0.0457	0.712

[a] Reactions with 0.0025 *M* initial cerium(IV) concentration.
[b] Reproducibility in this case was ±5.3%; in all other cases reproducibility was better than ±3%.

When the ceric ion and substrate solutions were mixed for the reactions in 1.0 *M* perchloric acid, the ceric ion solutions, which are normally yellow, became

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[30] F. R. Duke, *J. Am. Chem. Soc.*, **69**, 2885 (1947).

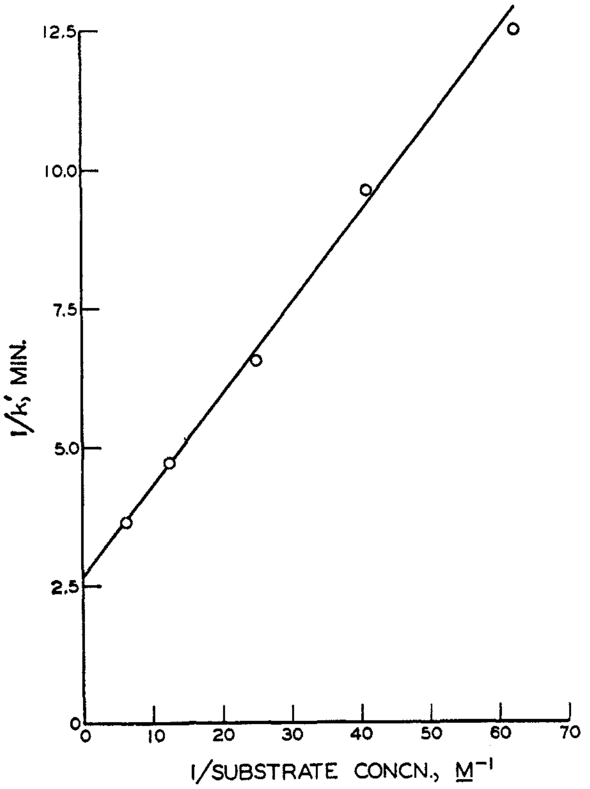

Figure 2.—Reciprocal plot of kinetic data for reactions of *trans*-1,2-cyclohexanediol with 0.0025 *M* cerium(IV) in 1.0 *M* perchloric acid at 15.0°.

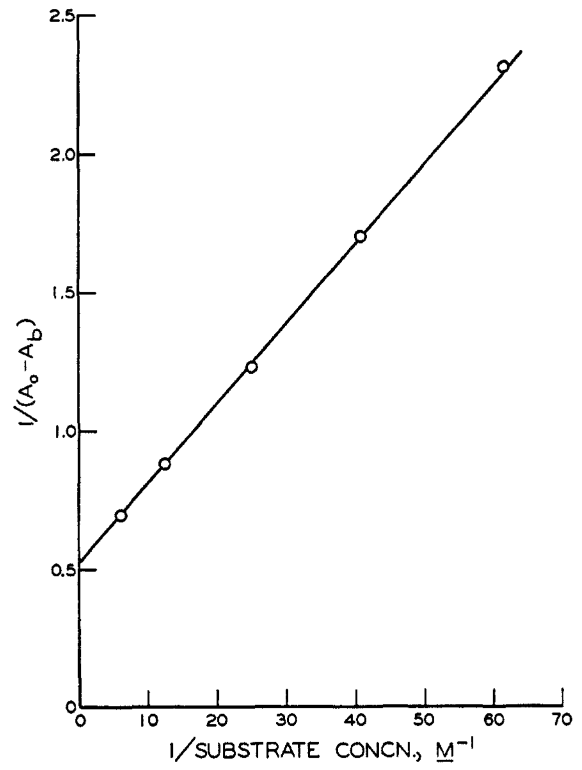

Figure 3.—Reciprocal plot of spectrophotometric data for reactions of *trans*-1,2-cyclohexanediol with 0.0025 *M* cerium(IV) in 1.0 *M* perchloric acid at 15.0°.

TABLE III

EVIDENCE FOR COMPLEX FORMATION IN 1.0 *M* PERCHLORIC ACID. COMPLEX FORMATION CONSTANTS AND RATE CONSTANTS FOR COMPLEX DISPROPORTIONATION AT 15.0°

	Complex formation constant K, M^{-1}		
Substrate	Spectrophotometric data	Kinetic data	Rate constant k, min^{-1}
cis-1,2-Cyclohexanediol	29.3	29.0	0.85
trans-1,2-Cyclohexanediol	18.6	18.0	0.36
trans-2-Methoxycyclohexanol	2.9	2.1	3.3
Cyclohexanol	3.9	2.9	0.13

red-brown. Ardon[6] developed a method for relating this color change to the equilibrium constant for reactions proceeding through a 1:1 complex. It can be shown that the difference between the observed initial absorbance, A_0, and the absorbance that would be observed with a cerium(IV) solution of the same concentration but without the organic substrate, A_b, is given by

$$A_0 - A_b = \Delta\epsilon\{K[S]/(1 + K[S])\}[Ce(IV)]_0$$

where $[Ce(IV)]_0$ is the initial cerium(IV) concentration and $\Delta\epsilon$ is the difference in the molar absorptivities of the complex and cerium(IV).

The equilibrium constants can be calculated from the slope and intercept of a plot of $1/(A_0 - A_b)$ *vs.* $1/[S]$.

$$1/(A_0 - A_b) = 1/\Delta\epsilon[Ce(IV)]_0 + 1/\Delta\epsilon[Ce(IV)]_0K[S]$$

The plot of $1/(A_0 - A_b)$ *vs.* $1/[S]$ for *trans*-1,2-cyclohexanediol shown in Figure 3 is typical of the results obtained for the reactions in 1.0 *M* perchloric acid. The equilibrium constants obtained by this spectrophotometric method are given in Table III. These values agree reasonably well with the equilibrium constants calculated from the kinetic data.

The equilibrium constants for complex formation given in Table III show that the presence of adjacent hydroxyl groups in the organic substrate causes a substantial increase in the stability of the complex compared to compounds with only one hydroxyl. Thus, the equilibrium constants for *cis*- and *trans*-1,2-cyclohexanediols (29.0 and 18.0, respectively) are considerably larger than for the monohydric alcohols cyclohexanol and *trans*-2-methoxycyclohexanol (2.9 and 2.1, respectively). Similarly, literature results indicate that glycerol forms a more stable complex with cerium(IV) than methanol and ethanol (25.0[8] *vs.* 1.5[7] and 4.3,[6] respectively, at 20°). The greater stability of the complexes with the 1,2 glycols indicates that these compounds form a chelate complex with cerium(IV).

The large difference between the equilibrium constants for *trans*-1,2-cyclohexanediol and *trans*-2-methoxycyclohexanol and the similarity of the values for the latter compound to cyclohexanol suggests that substitution of a methyl group for a hydroxyl hydrogen effectively prevents chelate complex formation. While the equilibrium constants for *cis*- and *trans*-1,2-cyclohexanediols are significantly larger than that for *trans*-2-methoxycyclohexanol, the reverse is true for the disproportionation rate constants. The disproportionation rate constant for *trans*-2-methoxycyclohexanol is almost ten times larger than for the *trans*-diol. The over-all rate constants (at low substrate concentrations), kK, are about the same for these two compounds. Thus, chelate formation does not appear to be a necessary requirement of the oxidation reaction.[31]

The equilibrium constants for the *cis*- and *trans*-1,2-cyclohexanediols are consistent with chelate complex formation. In the stable conformations of these compounds the separation of the hydroxyl groups is about the same, and the relatively large cerium(IV) ion can easily bridge this distance. The formation of a five-membered chelate ring fused to the cyclohexane ring results in a relatively rigid system with the *trans* isomer, whereas the complex with the *cis* isomer is relatively flexible since conformation interconversion can occur as readily in the complex as in the uncomplexed diol (see Figure 4). This greater flexibility of the complex with the *cis* isomer thus contributes to its somewhat greater stability (more positive entropy of formation).

The reactions of *cis*- and *trans*-1,2-cyclopentanediols and *trans*-2-methoxycyclopentanol were too rapid in 1.0 *M* perchloric acid for study by ordinary kinetic methods. In an attempt to detect intermediate complex formation, the effect of substrate concentration was determined for these compounds in 0.25 *M* sulfuric and 0.75 *M* perchloric acids The results are given in Table IV and Figure 5. The plots of the pseudo-first-order rate constant *vs.* substrate concentration for these reactions were linear, indicating second-order kinetics. The second-order rate constants calculated from the slopes of these plots are given in Table V.

Table IV

Effect of Substrate Concentration for Reactions in 0.25 *M* Sulfuric and 0.75 *M* Perchloric Acids at 15.0°[a]

Substrate	Substrate concn, *M*	k', min^{-1} [b]
cis-1,2-Cyclopentanediol	0.016	0.0590
	0.040	0.148
	0.080	0.292
	0.120	0.426
	0.160	0.560
trans-1,2-Cyclopentanediol	0.016	0.0990
	0.041	0.247
	0.082	0.495
	0.122	0.729
	0.163	0.940
trans-2-Methoxycyclopentanol	0.015	0.0422
	0.038	0.100
	0.075	0.193
	0.112	0.278
	0.150	0.360

[a] Reactions with 0.00025 *M* initial cerium(IV) concentration. [b] Reproducibility was better than ±3%.

Table V

Second-Order Rate Constants for Reactions in 0.25 *M* Sulfuric and 0.75 *M* Perchloric Acids at 15.0°

Substrate	k_{II}, M^{-1} min^{-1}
cis-1,2-Cyclopentanediol	3.46
trans-1,2-Cyclopentanediol	5.76
trans-2-Methoxycyclopentanol	2.35

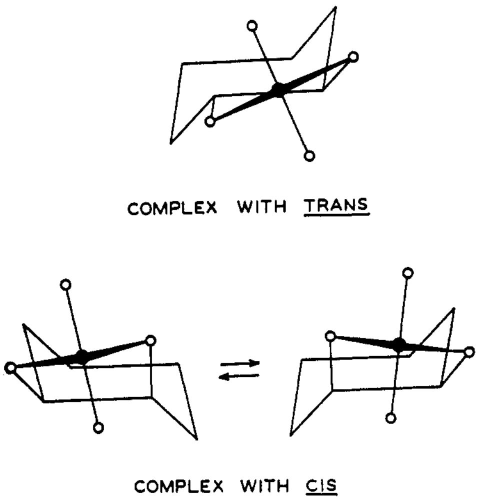

Figure 4.—Cerium(IV) complexes with *cis*- and *trans*-1,2-cyclohexanediols: ○ = oxygen; ● = cerium(IV). Sixfold coordination was assumed for the cerium(IV) although the bonds to two of the ligands are not shown for clarity.

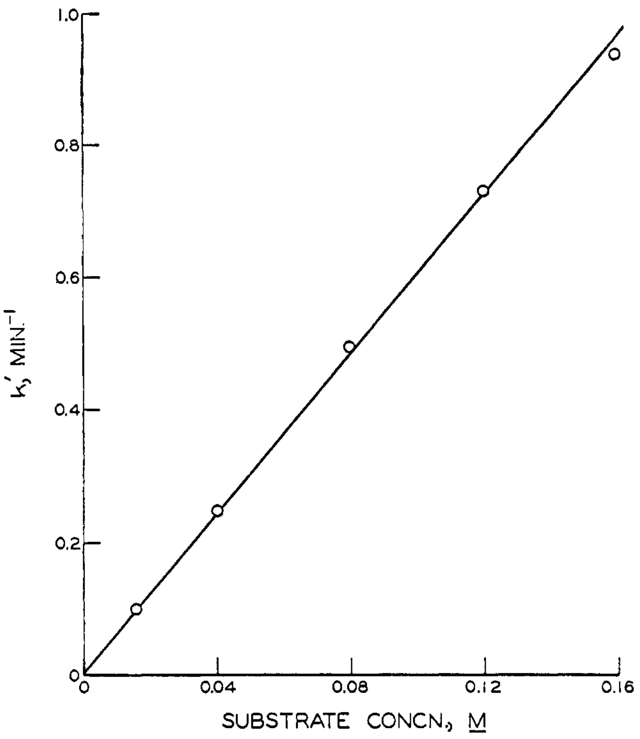

Figure 5.—Effect of substrate concentration on the pseudo-first-order rate constant for reactions of *trans*-1,2-cyclopentanediol in 0.25 *M* sulfuric and 0.75 *M* perchloric acids at 15.0°.

The observation of second-order kinetics in cerium(IV) oxidations is consistent with either a direct oxidation mechanism or with reaction through a complex formed in low concentration. It is not possible to distinguish between these mechanisms on the basis of kinetics, and it is difficult to attach mechanistic significance to the relative rates of reaction observed for the cyclopentane derivatives.

Effect of Sulfate Ion Concentration.—The reactions of *cis*- and *trans*-1,2-cyclopentanediols were studied in a series of solutions with total sulfate ion concentrations varying from 0.25 to 0.75 *M*. (See Table VI and Figure 6.) Hardwick and Robertson[32] found that cerium(IV) solutions in sulfuric acid contain varying amounts of hydrated Ce^{4+}, $CeSO_4^{2+}$, $Ce(SO_4)_2$, and Ce-

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[31] The conclusion of Littler and Waters[17] that cerium(IV) does not oxidize pinacol *via* a chelate intermediate is therefore questionable, since it was based on the similarity of the over-all rates of oxidation of pinacol and pinacol monomethyl ether. Cerium(IV) can apparently oxidize glycols and their monomethyl ethers through cyclic and acyclic complexes, respectively, at about the same over-all rate.

[32] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

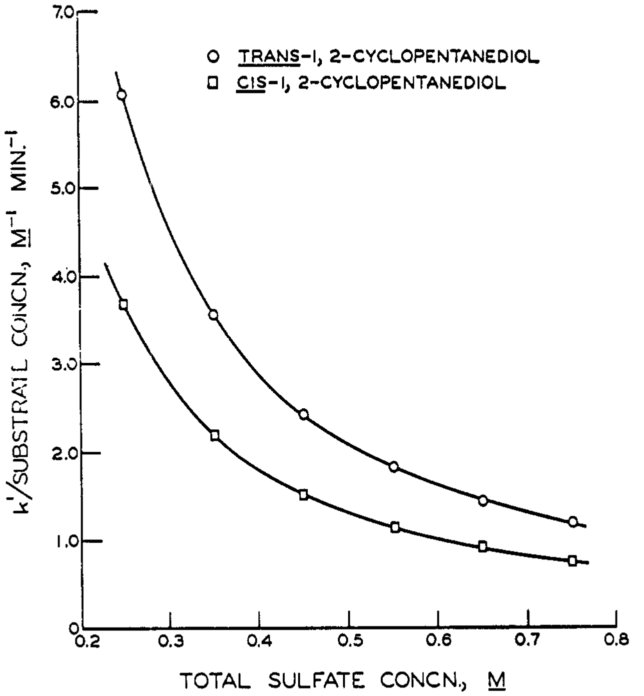

Figure 6.—Effect of total sulfate ion concentration on the reactions of *cis-* and *trans*-1,2-cyclopentanediols at 15°: initial cerium(IV) concentration, 0.00025 *M;* hydrogen ion concentration, 1.0 *N.*

$(SO_4)_3^{2-}$ and determined equilibrium constants for the equilibria

$$Ce^{4+} + HSO_4^- \overset{K_1}{\rightleftarrows} CeSO_4^{2+} + H^+$$

$$CeSO_4^{2+} + HSO_4^- \overset{K_2}{\rightleftarrows} Ce(SO_4)_2 + H^+$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftarrows} Ce(SO_4)_3^{2-} + H^+$$

In the range of concentrations used in this work the di- and trisulfated cerium(IV) complexes predominate. The percentage of the total cerium(IV) present as $CeSO_4^{2+}$ varies from 0.33% at 0.25 *M* to 0.04% at 0.75 *M* sulfuric acid. The concentration of the Cd^{4+} species is negligible in this concentration range (<0.0005%).

TABLE VI

EFFECT OF TOTAL SULFATE ION CONCENTRATION FOR REACTIONS OF *cis-* AND *trans*-1,2-CYCLOPENTANEDIOLS AT 15.0°[a]

Concn, *M*		*k'/S*, min⁻¹ *M*⁻¹	
H_2SO_4	$HClO_4$	*cis*	*trans*
0.25	0.75	3.68	6.07
0.35	0.65	2.18	3.56
0.45	0.55	1.52	2.43
0.55	0.45	1.15	1.83
0.65	0.35	0.916	1.43
0.75	0.25	0.761	1.20

[a] Reactions with 0.00025 *M* initial cerium(IV) concentration and 0.016 *M* substrate concentration.

The observed variation in the rate of oxidation with total sulfate ion concentration could be accounted[33] for by assuming that the cerium(IV)–sulfate complexes $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ participate in the reaction and oxidize the organic substrate through

$$CeSO_4^{2+} + S \overset{K_1'}{\rightleftarrows} C_1 \xrightarrow{k_1} \text{products}$$

$$Ce(SO_4)_2 + S \overset{K_2'}{\rightleftarrows} C_2 \xrightarrow{k_2} \text{products}$$

$$Ce(SO_4)_3^{2-} + S \overset{K_3'}{\rightleftarrows} C_3 \xrightarrow{k_3} \text{products}$$

intermediate complexes. The concentrations of the complexes must be very small since complex formation could not be detected kinetically or spectrophotometrically in sulfate ion containing media. The total cerium(IV) concentration, $[Ce(IV)]_T$, is then

$$[Ce(IV)]_T = [CeSO_4^{2+}] + [Ce(S)_4)_2] + [Ce(SO_4)_3^{2-}]$$

The rate expression for this reaction scheme is

$$\frac{-d[Ce(IV)]_T}{dt} =$$

$$[S][Ce(IV)]_T \left\{ \frac{k_1K_1' + k_2K_2'K_2([HSO_4^-]/[H^+]) + k_3K_3'K_2K_3([HSO_4^-]/[H^+])^2}{1 + K_2([HSO_4^-]/[H^+]) + K_2K_3([HSO_4^-]/[H^+])^2} \right\}$$

The products k_iK_i' represent the over-all rate constants for reaction with the cerium(IV)–sulfate complex containing *i* sulfate ions. These rate constants were calculated from the experimental data using multiple regression techniques and the data of Hardwick and Robertson for K_1, K_2, and K_3. The results of these calculations are given in Table VII. The rate constants increase as the number of sulfate ions in the complex decreases. This result is reasonable since incorporation of sulfate ions in place of water molecules into the coordination sphere of cerium(IV) reduces the effective positive charge of the cerium(IV) and hence its electrophilic attraction for the reductant molecules.[34]

TABLE VII

RATE CONSTANTS FOR REACTION WITH INDIVIDUAL CERIUM(IV)–SULFATE COMPLEXES

	Rate constant, *M*⁻¹ min⁻¹		
Substrate	$CeSO_4^{2+}$	$Ce(SO_4)_2$	$Ce(SO_4)_3^{2-}$
trans-1,2-Cyclopentanediol	1500	5.4	0.24
cis-1,2-Cyclopentanediol	850	4.6	0.12

In the above discussion it was assumed that the reaction proceeds by disproportionation of a complex formed in a prior equilibrium. However, since it was not possible to detect complex formation for the reaction in sulfuric acid media, it is not possible to distinguish between this type of mechanism and a direct bimolecular oxidation. If the latter mechanism is assumed, the same rate expression results except that the product k_iK_i' are replaced by specific second-order rate constants.

Thermodynamic Activation Functions.—The experimentally observed kinetics in sulfuric acid media were consistent with either a direct bimolecular oxidation or disproportionation of a complex with a very small equilibrium concentration. The transition state

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(33) The effect of total sulfate ion concentration on the rate of oxidation could not be accounted for satisfactorily by assuming either that one or any two of the cerium(IV)–sulfate complexes were the active oxidants.

(34) It is interesting to note that the monosulfated species accounts for the major part of the oxidation in spite of its low concentration (below 1% of total ceric ion). Its contribution is estimated to be 78 to 48% of the total reaction over the range of sulfate concentrations examined. The less sulfated ceric ion species also appear to be the more reactive oxidants toward ethylene glycol.[35]

(35) A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, *J. Phys. Chem.*, **68**, 522 (1964).

would be similar for these mechanisms and would involve an interaction between the cerium(IV) and the hydroxyl(s) of the substrate.

In the oxidation of a 1,2 glycol it is possible that the transition state could be acyclic or cyclic depending on whether one or both of the hydroxyls interact with the cerium(IV). For closely related compounds differences in the entropies of activation should reflect differences in the nature of the transition state. Thus, although it was not possible to decide between the direct oxidation and complex formation mechanisms, it should be possible to distinguish between cyclic and acyclic pathways by determination of the entropies of activation for related compounds.

The temperature dependence of the cerium(IV) oxidation was studied for a series of alcohols in 0.25 *M* sulfuric and 0.75 *M* perchloric acids.[36] Three or four temperatures ranging from 10 to 30° or 20 to 40° were employed in each case. Arrhenius temperature dependence was observed for these reactions and the calculated energies and entropies of activation are summarized in Table VIII.

TABLE VIII

RATE CONSTANTS, ARRHENIUS ACTIVATION ENERGIES, AND ENTROPIES OF ACTIVATION FOR REACTIONS IN 0.25 *M* SULFURIC AND 0.75 *M* PERCHLORIC ACIDS

Substrate	$k'/[S]$ at 30°, M^{-1} min^{-1}	E_a, kcal/mole	ΔS^*, cal/deg^{-1} mole^{-1}
cis-1,2-Cyclopentanediol	27.7	23.3	14.7
trans-1,2-Cyclopentanediol	44.4	23.2	15.4
trans-2-Methoxycyclopentanol	20.3	23.0	13.0
Cyclopentanol	0.0693[a]	27.5	16.5
cis-1,2-Cyclohexanediol	0.107	29.2	23.0
trans-1,2-Cyclohexanediol	0.0319	28.0	16.6
cis-2-Methoxycyclohexanol	0.138	28.9	22.8
trans-2-Methoxycyclohexanol	0.0358	30.7	25.8

[a] Reproducibility in this case was ±4.8%; in all other cases reproducibility was better than ±3%.

It was shown in a previous section that several cerium(IV)-sulfate complexes participate in reactions in sulfuric acid media. The thermodynamic functions calculated for these reactions are thus over-all values and would be expected to vary with sulfate ion concentration. However, it is possible to compare the values obtained for related compounds in a single medium since the contribution of the medium will be constant.

The activation energies for the diols and 2-methoxy alcohols are closely related to ring size. Thus, the activation energies for *trans*-2-methoxycyclopentanol and *cis*- and *trans*-1,2-cyclopentanediols vary only from 23.0 to 23.3 kcal/mole. Also, the values for the *cis*- and *trans*-1,2-cyclohexanediols and *cis*- and *trans*-2-methoxycyclohexanols differ only slightly (28.0 to 30.7 kcal/mole). The difference of 5–7 kcal/mole in the activation energies for the 1,2-oxygenated cyclopentane and cyclohexane derivatives probably reflects the greater internal strain in the cyclopentane ring. Because of the lower activation energy for the cyclopentane derivatives, these compounds react 200–1000 times faster at 30° than the corresponding cyclohexane derivatives.

The entropies of activation obtained for the 1,2-cyclohexanediols are consistent with a cyclic pathway for the cerium(IV) oxidation. The significantly less positive entropy of activation for the *trans* isomer is evidence for reaction through a cyclic transition state. If the transition state were acyclic, little difference would be expected in the values for the *cis* and *trans* isomers.

The entropies of activation obtained for the *cis*- and *trans*-2-methoxycyclohexanols suggest an acyclic mechanism for these compounds. If a cyclic transition state were involved, the entropy of activation would be expected to be less positive for the *trans* isomer. However, the value for the *cis* isomer was found to be slightly less positive than for the *trans*. The substitution of a methyl group for a hydroxyl hydrogen thus effectively blocks formation of a cyclic intermediate.

The entropies of activation obtained for the *cis*- and *trans*-1,2-cyclopentanediols and *trans*-2-methoxycyclopentanol are practically identical. This result suggests that these compounds are oxidized *via* a common acyclic mechanism, although the possibility of a cyclic pathway cannot be rigorously excluded for *cis*-1,2-cyclopentanediol.

Oxidations of Cellulose Model Compounds.—The fact that cerium(IV) oxidations of alcohol and glycols involve free radicals as intermediates has been used to develop a technique for producing graft copolymers with cellulose.[37] The most likely sites for the oxidation reaction with cellulose would be the C_6 hydroxyl and C_2–C_3 glycol of the anhydroglucose monomer unit, although there is some possibility of reaction at end groups. The results obtained in this work with *trans*-1,2-cyclohexanediol suggest that reaction of the C_2–C_3 glycol would proceed *via* disproportionation of a chelate complex forming carbon–carbon bond-cleavage products.

The relative reactivities of the C_6 hydroxyl and C_2–C_3 glycol were estimated by comparing tetrahydropyran-2-methanol and cyclohexanemethanol as models for the C_6 hydroxyl with *trans*-1,2-cyclohexanediol. The results given in Table IX suggest that in the ceric ion oxidation of cellulose reaction will occur mainly at the glycol group and to some extent at the primary hydroxyl.

TABLE IX

OXIDATIONS OF CELLULOSE MODEL COMPOUNDS IN 0.25 *M* SULFURIC AND 0.75 *M* PERCHLORIC ACIDS AT 30°

Substrate	Relative rate
trans-1,2-Cyclohexanediol	6.0
Cyclohexanemethanol	1.3
Tetrahydropyran-2-methanol	1.0

Conclusions

Chelate complexes are formed in the oxidations of *cis*- and *trans*-1,2-cyclohexanediol in 1.0 *M* perchloric acid. Evidence for the cyclic complexes was obtained from determinations of the equilibrium constants for complex formation. The thermodynamic activation data in 0.25 *M* sulfuric and 0.75 *M* perchloric acids suggested a cyclic transition state in the oxidation of these diols. The nature of the interaction of cerium-

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(36) In this system the relative contributions of the three cerium(IV)-sulfate complexes are estimated to be mono:di:tri = 78:20:2 from their equilibrium concentrations and the rate constants shown in Table VII.

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

(IV) with *cis*- and *trans*-1,2-cyclopentanediols is less certain since these reactions could not be studied under conditions permitting determination of the equilibrium constant for complex formation. However, the entropies of activation for these compounds suggested that the *trans*-diol is oxidized *via* an acyclic mechanism.

Substitution of a methyl group for a hydroxyl hydrogen apparently prevents chelate complex formation with cerium(IV). However, *trans*-1,2-cyclohexanediol and *trans*-2-methoxycyclohexanol are oxidized by cerium(IV) at approximately the same rate, although the complex formed with these compounds is different. Thus, the nature of the complexes formed in cerium(IV) oxidations cannot be determined from measurements of relative rates of oxidation.

For reaction media containing from 0.25 to 0.75 *M* sulfuric acid, the cerium(IV)–sulfate complexes $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ participate in the oxidation reaction. The reactivities of the various species increase as the number of sulfate ions in the complex decreases, and in the range of sulfate ion concentrations studied the $CeSO_4^{2+}$ species accounts for a major portion of the reaction.

The relative reactivities of certain cellulose model compounds suggest that in the cerium(IV)-initiated graft polymerization onto cellulose, the oxidation reaction of cerium(IV) with cellulose will occur mainly at the C_2–C_3 glycol unit and to a lesser extent at the C_6 primary hydroxyl.

Registry No.—Cyclohexanol, 108-93-0; cyclopentanol, 96-41-3; *cis*-1,2-cyclohexanediol, 1792-81-0; *trans* isomer of **5**, 1460-57-7; *trans*-2-methoxycyclohexanol, 7429-40-5; *cis* isomer of **8**, 7429-41-6; *trans*-1,2-cyclopentanediol, 5057-99-8; *trans*-2-methoxycyclopentanol, 7429-45-0; *cis*-1,2-cyclopentanediol, 5057-98-7; cyclohexanemethanol, 100-49-2; tetrahydropyran-2-methanol, 100-72-1; glutaraldehyde bis(*cis*-1,2-cyclopentanediol acetal, 7616-85-3.

Acknowledgments.—The authors appreciate the comments and suggestions of Drs. J. W. Green and D. G. Williams.

Electrolyses of Mixtures of Carboxylic Acids

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Received May 9, 1966

Formic acid, acetic acid, propionic acid, and trifluoroacetic acid have been electrolyzed competitively in mixtures of pairs. In terms of the products formed in these competitive electrolyses, formic and trifluoroacetic acids are comparable in ease of electrolysis, both are more readily electrolyzed than acetic and propionic acids, and these last two are comparable with each other. These results are not entirely consistent with the conclusions that would be drawn from voltammetric data in the literature, and the deviations are rationalized on the basis of differences in ionization among the acids.

During a continuing study of anodic reactions of carboxylic acids, it became desirable to obtain knowledge of the relative electrochemical behavior of several acids.

In previous work, formic and acetic acids were electrolyzed in the presence of various added substrates, notably hydrocarbons[1] and amides.[2,3] Rates of gas production were measured and both gaseous and liquid products were determined.

In the present study, a number of competitive electrolyses were conducted on mixtures of acids under conditions similar to those previously employed, again measuring rates of gas production and analyzing the gaseous products. The information thus obtained permits a determination of the relative ease of anodic discharge of the various acids. The acids used were formic, acetic, propionic, and trifluoroacetic.

Experimental Section

Apparatus and Gas Analyses.—The electrolysis cell has been described previously.[1] Electrolyses were conducted at 0.40 or 0.20 amp provided by a constant-current power supply. The cell was connected to a gas-measuring apparatus, also described previously,[4] with which the rate of gas production was measured. Samples of the gas were analyzed with a Perkin-Elmer Model 154 vapor fractometer, using a Perkin-Elmer J column (silica gel packing) and a gas-sampling valve for reproducing sample sizes.

Materials.—The glacial acetic acid used was ACS grade from the General Chemical Division of Allied Chemical Co. Formic acid, from the same source, was CP grade 98–100%. Analyzed, reagent grade potassium acetate was obtained from the J. T. Baker Chemical Co. Sodium formate was Fisher Scientific Co. purified grade. Fisher certified reagent grade propionic acid was redistilled and a cut boiling at 49° (14 mm) was used. Trifluoroacetic acid was redistilled and a middle cut boiling at 69° was used. Sodium trifluoroacetate was prepared by neutralization of trifluoroacetic acid. Gases used as standards for vpc analyses were obtained from the Matheson Co. and were of the highest purity available in lecture bottles.

Results

Mixed Formic and Acetic Acids.—When a solution of potassium acetate (5.0 g) in glacial acetic acid (60 ml) is electrolyzed at 20° at 0.40 amp (1 cm^2 platinum electrodes at a separation of 0.6 cm) the rate of total gas production is 100 ± 1% of that demanded by eq 1 and 2 and the gas contains the proper amounts of carbon dioxide and ethane.[1]

$$2H^+ + 2e \longrightarrow H_2 \qquad (1)$$

$$2CH_3COO^- \longrightarrow 2CO_2 + C_2H_6 + 2e \qquad (2)$$

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[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

[2] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 2745 (1964).

[3] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

[4] R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).