

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Theory and Kinetics of Specific Oxidation. IV. The Cerate 2,3-Butanediol Reactions in Perchlorate Solutions¹

BY FREDERICK R. DUKE AND ROBERT F. BREMER

Tetravalent cerium is capable of coordinating glycol to form both the mono- and diglycolated complexes. The formation of the triglycolated species is not ruled out but no evidence of its presence is indicated. Cerium(IV) in perchlorate solutions coordinates only hydroxyl ions or water. The perchlorate ion appears to be incapable of forming a complex with tetravalent cerium. That butanediol is oxidized by cerium only after complex formation is offered as further proof of the theory of intermediate complex formation.

It has been shown that specific oxidations of 1,2-oxygenated organic compounds proceed through the disproportionation of intermediate coordination complexes.²

The present work was undertaken to add to our knowledge of the nature of tetravalent cerium in perchlorate solutions. Thus, when the glycol coordinates with tetravalent cerium, only water, hydroxyl ion, or perchlorate ion can be displaced. Studies of rate constants and equilibrium constants determined from kinetic data permit the determination of whether hydroxyl ion, perchlorate ion, or both are being displaced from cerium.

Theory

Tetravalent cerium has, as indicated by its complexes which have been isolated, a coordination number of six. If it is also assumed that each glycol occupies two coordination positions, the following equilibria are possible



where G is 2,3-butanediol, Ce is tetravalent cerium, and X may be perchlorate ion, hydroxyl ion or water. The kinetics expressed as the rate of disappearance of total cerium(IV), T_{Ce} , is^{2a}

$$\frac{dT_{\text{Ce}}}{dt} = \left[\frac{k_1 K_1 G + k_2 K_1 K_2 G^2 + k_3 K_1 K_2 K_3 G^3}{1 + K_1 G + K_1 K_2 G^2 + K_1 K_2 K_3 G^3} \right] T_{\text{Ce}} \quad (4)$$

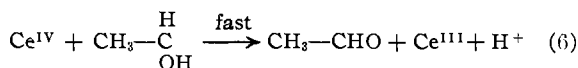
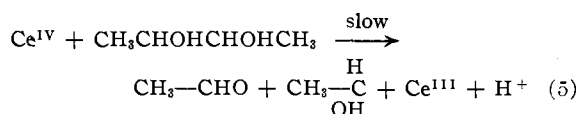
where k_1 , k_2 and k_3 are the rates of disproportionation of the complexes formed in (1), (2) and (3); K_1 , K_2 and K_3 being the respective equilibrium constants. If the glycol concentration is kept sufficiently high in comparison with the total cerium(IV) concentration such that it may be considered constant, the term within the brackets of equation (4) becomes a pseudo first order rate constant, k' , for the disappearance of cerium(IV). A plot of $-\ln T_{\text{Ce}}$ vs. t at a given glycol concentration should give a straight line of slope k' .

The second order rate constant may be determined if both cerium(IV) and glycol concentrations are kept very small and if the equilibrium constant, K_1 , is of the right order of magnitude, as it is in this case. The stoichiometric relationship of this reaction involves two cerium(IV) and one glycol.

(1) Contribution No. 156 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. This work was performed in the Ames Laboratory of the AEC.

(2) (a) F. R. Duke, *THIS JOURNAL*, **69**, 2885 (1947); **69**, 3054 (1947); (b) H. Taube, *ibid.*, **69**, 1418 (1947); **70**, 1216 (1948); (c) F. R. Duke and A. A. Forist, *ibid.*, **71**, 2790 (1949).

However, it is found that the probable slow reaction involves one cerium(IV) and one glycol, the second and probable fast step involves a cerium(IV) and a fragment of the butanediol formed in the first step. The two steps may be thus represented



The kinetics may be expressed as

$$dx/dt = k_{11}(a - x)(b - y) \quad (7)$$

where x is the amount of cerium reacted at time t ; a is the initial concentration of cerium(IV), b the initial concentration of glycol and y is the concentration of glycol at time t . If the glycol and cerium concentrations are made equivalent, $b = a/2$ and $y = x/2$. Under these conditions, the rate equation becomes

$$dx/dt = k_{11}/2(a - x)^2 \quad (8)$$

Integration of equation (8) yields the expression

$$\frac{ak_{11}}{2} t = \frac{x}{(a - x)} \quad (9)$$

It is now possible to evaluate k_{11} by plotting experimental values of $x/a - x$ vs. t , the resulting slope being equal to $ak_{11}/2$.

If K_2 and K_3 are small compared with K_1 , there exists a glycol concentration where equation (4) may be applied assuming insignificant amounts of the di- and triglycolated species. Under these conditions equation (4) reduces to

$$-\frac{dT_{\text{Ce}}}{dt} = \frac{k_1 K_1 G T_{\text{Ce}}}{1 + K_1 G} \quad (10)$$

$$k' = \frac{k_1 K_1 G}{1 + K_1 G} \quad (11)$$

From equations (10) and (8), it is evident that

$$k_{11} = \frac{k_1 K_1}{1 + K_1 G} \quad (12)$$

and if k_{11} is determined at very low glycol concentrations (*ca.* 0.005), the term $K_1 G$ becomes very small compared to 1 and may be neglected. Then

$$k_{11} = k_1 K_1 \quad (13)$$

Equations (13) and (11) permit the evaluation of both k_1 and K_1 , when a value of k' has been determined. The constants k_2 , k_3 , K_2 and K_3 can then be obtained by fitting experimental data at higher glycol concentrations.

TABLE I

Part A		Part B		Part C		Part D		Part E	
H ⁺ , N = 0.1	G, M = 0.01	H ⁺ , N = 1.0	G, M = 1.0	G, M = 0.1	G, M = 0.05	G, M = 0.005	G, M = 0.005	G, M = 0.005	G, M = 0.005
ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0	H ⁺ , N = 1.0	ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0	ClO ₄ ⁻ , N = 1.0
Na ⁺ , N = 0.9	Ce ^{IV} , N = 0.01	Ce ^{IV} , N = 0.01	Ce ^{IV} , N = 0.01	Ce ^{IV} , N = 0.01	Ce ^{IV} , N = 0.01	H ⁺ , N = 1.0	Ce ^{IV} , N = 0.01	Ce ^{IV} , N = 0.01	Ce ^{IV} , N = 0.01
Ce ^{IV} , N = 0.01	G	G	k' × 10 ³	H ⁺	k' × 10 ³	ClO ₄ ⁻	H ⁺	k' × 10 ³	k ₁₁ × 10 ³
0.04	5.09	0.04	7.61	0.1	10.45	1.0	9.5	0.1	15.73
.06	7.26	.06	10.31	.2	11.88	2.0	15.1	0.5	27.21
.08	9.24	.08	12.05	.3	12.55	3.0	19.4	1.0	29.80
.10	10.41	.10	12.90	.4	12.63	4.0	24.6		
.12	11.66	.12	13.82	.5	12.58	5.0	34.8		
.14	12.20	.14	14.09	.6	12.73				
.16	13.32	.16	14.58	.7	12.71				
.18	13.76	.18	14.99	.8	12.82				
.20	14.30	.20	15.11	.9	12.73				
.24	14.71	.24	15.54	1.0	12.71				
.28	14.90	.28	15.76						
.32	15.28	.32	16.10						
.36	16.09	.36	15.71						
.40	15.81	.40	15.94						

Experimental

Specially prepared reagents were used throughout. The tetravalent cerium was prepared by the electrolytic oxidation of pure cerous perchlorate. The cerous perchlorate was obtained by boiling pure cerous oxalate in 72% perchloric acid.

Sodium perchlorate solution was prepared by neutralizing 72% C.P. perchloric acid with C.P. sodium hydroxide.

meso-2,3-Butanediol was obtained by triple vacuum distillation of a mixture of D-, L- and *meso*-butanediol.

Experimental temperature was maintained at 0° in a melting ice-bath. Fifty-ml. volumetric flasks with an additional 48-ml. mark were used as reaction vessels. Glycol, perchloric acid and sodium perchlorate were mixed in the flasks to give the desired concentration and diluted to 48 ml. This mixture was placed in the ice-bath for 45 minutes. Two ml. of 0.25 N Ce^{IV} at the bath temperature were added to make [Ce^{IV}] = 0.01 N.

The reaction rate was followed by removing 5-ml. samples at as rapid intervals as possible. These samples were quenched in KI solution and the liberated iodine titrated with standard thiosulfate. The time of sampling was recorded uniformly to the nearest second.

MIXTURES STUDIED

Mixture	Ce ^{IV} , N	H ⁺ , N	ClO ₄ ⁻ , N	G, M
A	0.01	0.1	1.0	0.04-0.40
B	.01	1.0	1.0	0.04-0.40
C	.01	0.1-1.0	1.0	.10
D	.01	1.0	1.0-5.0	.05
E	.01	0.1, 0.5, 1.0	1.0	.005

Data and Calculations

Pseudo first order rate constants were determined for parts A, B, C and D. The listed values are averages of three or more trials. The maximum deviation was 3%. The second order rate constants were determined for part E. These values are listed in Table I.

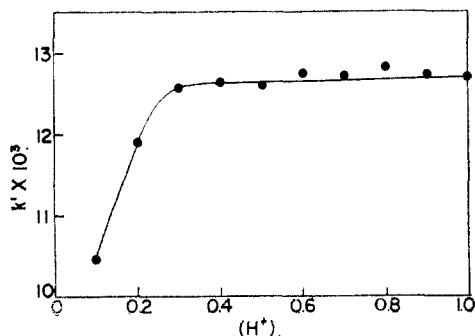


Fig. 1.

The results from part D may be interpreted as an indication that no perchlorate is coordinated by cerium(IV). If the glycol were displacing perchlorate, it could be expected that an increase in perchlorate ion would cause a decrease in reaction rate. In contrast, it is found that the rate increases very rapidly, probably due to increased activity of reactants which accompany the decrease in water activity.³ It is therefore concluded that tetravalent cerium does not coordinate perchlorate ion.

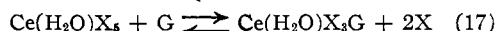
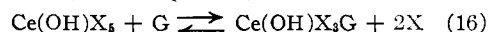
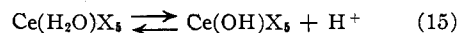
The data obtained from part C, shown graphically in Fig. 1, are sufficient to indicate that the reaction is not hydrogen ion-independent. Further it may be concluded that at low hydrogen ion concentration, the dependency is a linear function of [H⁺].

In view of this evidence, a further equilibrium may be proposed



which leads to the conclusion that there can be additional cerium(IV)-glycol complexes which disproportionate and that equation (4) is no longer the correct representation of the kinetics.

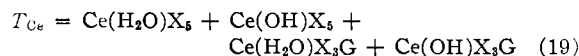
If only low glycol concentrations (*ca.* 0.05 M) are considered, di- and triglycolated complexes need not be considered. Then the three equilibria that need be considered are



where K_8 is the equilibrium constant of equation (15), K_{11} for equation (16) and K_{12} for equation (17). The double subscripts are to be interpreted as follows. The first of the two numbers represent the number of glycol molecules contained in the cerium-glycol complex. The second figure represents the species of cerium, (1) hydroxylated and (2) hydrated. k_{11} and k_{12} are the rate constants for the disproportionation, respectively, of complexes formed in equations (16) and (17). Then

$$-dT_{\text{Ce}}/dt = k_{11}\text{Ce}(\text{OH})\text{X}_5\text{G} + k_{12}\text{Ce}(\text{H}_2\text{O})\text{X}_5\text{G} \quad (18)$$

and



From expressions (15), (16), (17) and (19), both $\text{Ce}(\text{OH})\text{X}_5\text{G}$ and $\text{Ce}(\text{H}_2\text{O})\text{X}_5\text{G}$ may be found in terms of total cerium. Then equation (18) can be rewritten as

$$-\frac{dT_{\text{Ce}}}{dt} = \left[\frac{k_{11}K_{11}K_8/[\text{H}^+] + k_{12}K_{12}}{1 + K_8/[\text{H}^+] + (K_{11}K_8/[\text{H}^+] + K_{12})\text{G}} \right] GT_{\text{Ce}} \quad (20)$$

which is a modified form of equation (10). Therefore, k_{11} is equal to the bracketed portion of equation (20). Again, the

(3) J. N. Pearce and A. P. Nelson, *THIS JOURNAL*, **55**, 3075 (1933).

term $[K_{11}K_a/[H^+] + K_{12}[G]]$ may be considered small and neglected. Since three values of k_{11} are available from part E, three equations may be formed in three unknowns; $[k_{11} \cdot K_{11}K_a]$, $[k_{12}K_{12}]$, and K_a . Solving these equations it is found that $K_a = 0.09$, $k_{12}K_{12} = 0.3285$ and the term $k_{11}K_{11} \cdot K_a$ is very nearly zero (*ca.* 0.0001). Therefore either k_{11} or K_{11} is negligible. The fact that the rate is independent of $[H^+]$ at higher glycol concentration indicates that K_{11} is negligible and no appreciable $Ce(OH)X_3G$ is formed. Since very little $Ce(OH)X_3G$ is formed, it is assumed that the di- and triglycolated species of the hydroxylated cerium can also be neglected. Under these assumptions, equation (4) becomes

$$-\frac{d[C_0]}{dt} = \frac{k_{12}K_{12}[G] + k_{22}K_{12}K_{22}[G]^2 + k_{32}K_{12}K_{22}K_{32}[G]^3}{1 + K_a/[H^+] + K_{12}[G] + K_{12}K_{22}[G]^2 + K_{12}K_{22}K_{32}[G]^3} T_{Ce} \quad (21)$$

which is of the same form as equation (4) except for the modified subscripts and addition of the hydrogen dependency term.

Again at low glycol concentrations ($[G] = 0.05$), the diglycolated complex concentrations may be considered negligible. Using the value of k' from Part A, and the values of K_a , $k_{12}K_{12}$, and $[H^+]$, $K_{12} = 15$ and $k_{12} = 0.0225 \text{ sec.}^{-1}$.

These values, when used to calculate values of k' are found to fit the experimental data only at the lower glycol concentration. Evaluation of equilibrium constants for the di- and triglycolated species is accomplished by trial and error. It was found unnecessary to include the cubed power of glycol to fit experimental data. Selecting two higher values of k' at higher glycol concentrations and using the equation

$$k' = \frac{k_{12}K_{12}[G] + k_{22}K_{12}K_{22}[G]^2}{1 + K_a/[H^+] + K_{12}[G] + K_{12}K_{22}[G]^2} \quad (22)$$

it was found that $K_{22} = 2.3$ and $k_{22} = 0.0117 \text{ sec.}^{-1}$. In view of the uncertainties encountered in the experimental determination of pseudo rate constants, the values of rate constants and equilibrium constants are assigned the limits of error in Table II.

TABLE II

K_a	0.09 ± 0.02
K_{12}	15 ± 1
K_{22}	2.3 ± 0.4
k_{12}	$0.0225 \pm 0.0010 \text{ sec.}^{-1}$
k_{22}	$0.0117 \pm 0.0020 \text{ sec.}^{-1}$

AMES, IOWA

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Kinetics of Catalytic Hydrogenation of Naphthyl-1-cyclopentenes and Naphthyl-1-cyclohexenes¹

BY L. H. KLEMM AND WILLIAM HODES

Kinetic studies of catalytic hydrogenation of the four parent naphthyl-1-cyclopentenes and naphthyl-1-cyclohexenes showed that addition of hydrogen to the olefinic double bond occurs simultaneously with the slower hydrogenation of the aromatic nucleus. 1-(1'-Naphthyl)-1-cyclohexene was found to differ from the other olefins in reacting at a considerably slower rate. A theory is proposed to explain this difference of reactivity in terms of requisite coplanarity of the olefins when adsorbed on the catalyst.

Two major instances have been recorded in the literature on the lower reactivity of 1-(1'-naphthyl)-1-cyclohexene (I) as compared to 1-(1'-naphthyl)-1-cyclopentene (II). Thus Cook and Lawrence² reported very great resistance to catalytic hydrogenation of I while Bachmann and Klemm³ found that II added hydrogen readily under the same conditions. Bachmann and Kloetzel⁴ successfully condensed II as well as 1-(2'-naphthyl)-1-cyclopentene (III) with maleic anhydride by fusion of the reactants on a steam-bath, but Bergmann and Bergmann⁵ could not accomplish this reaction with I under the same conditions though they did find that 1-(2'-naphthyl)-1-cyclohexene (IV) reacted readily. Later Bergmann and Szmuszkowicz⁶ succeeded in condensing I with maleic anhydride at a considerably higher temperature to yield an impure adduct and thereby to indicate that the inertness of I was a matter of degree rather than of type.

(1) (a) Abstracted from a thesis submitted by William Hodes to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree Master of Arts, June, 1950. A detailed description of the construction and manipulation of the apparatus used in this research may be found in the dissertation, available from the Chemistry Library, Indiana University. (b) Part of this material was presented at the Cleveland meeting of the American Chemical Society, April, 1951.

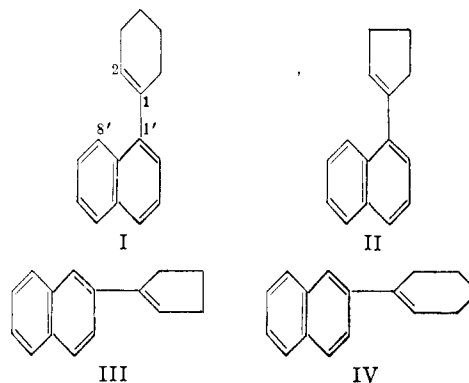
(2) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 1431 (1936).

(3) W. E. Bachmann and L. H. Klemm, *THIS JOURNAL*, **72**, 4911 (1950).

(4) W. E. Bachmann and M. C. Kloetzel, *ibid.*, **60**, 2204 (1938).

(5) F. Bergmann and E. Bergmann, *ibid.*, **62**, 1699 (1940).

(6) F. Bergmann and J. Szmuszkowicz, *ibid.*, **69**, 1367 (1947).



Cook and Lawrence² attributed the chemical inertness of I to a "mutual saturation of the free affinities of the carbon atoms 2 and 8', which can come within atomic distances of each other" and supported their hypothesis by showing that 1-(5'-tetralyl)-1-cyclohexene (V) behaved nor-

