

similar compounds where data are available, the atomic polarizability is at least several cubic centimeters.

TABLE III
DIPOLE MOMENT OF 1,1,2-TRICHLOROETHANE CALCULATED USING:

T, °K.	$P_a = 0$	$P_a = 3.0$	$P_a = 4.5$	$P_a = 6.7$
339.7	1.39	1.33	1.30	1.25
354.7	1.39	1.32	1.29	1.24
376.7	1.40	1.33	1.30	1.24
394.9	1.40	1.33	1.29	1.24
427.7	1.43	1.35	1.31	1.25
450.4	1.43	1.35	1.31	1.25
472.7	1.44	1.36	1.31	1.25
516.6	1.46	1.38	1.33	1.25
ΔE , cal./mole	(2100)	2400	3000	≥ 4000
$\mu_0 \times 10^{18}$ e. s. u.	(1.37)	1.30	1.28	1.25

It is impossible to calculate the atomic polarizability, because the shape of the potential barrier to internal rotation is unknown, and internal rotation contributes heavily to the atomic polarizability.¹⁹

Fortunately this alternate interpretation of the data alters our conclusion only slightly. The skew form of 1,1,2-trichloroethane is the low energy form, as before. The energy difference between the two forms is at least 2300 cal./mole, instead of 4000 cal./mole, as before. This affects no other conclusions concerning this molecule.

Since the atomic polarizability of 1,1,2,2-

(19) An over-simplified calculation of the atomic polarization, using only bending force constants, no cross terms, and a force constant for internal rotation of 0.7×10^{-12} ergs/rad.² molecule (a 2500 cal./mole threefold cosine barrier), gives 3 cc. for the atomic polarizability. It is quite conceivable that the minimum in 1,1,2-trichloroethane may be flatter, and internal rotation may contribute much more to atomic polarizability.

tetrachloroethane is only 2.7 cc., there is no alternate interpretation of the data.

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Summary

The dipole moments of gaseous 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and of pentachloroethane have been determined from the slope of the polarizability *vs.* $1/T$ curves to be 1.25×10^{-18} , 1.29×10^{-18} and 0.92×10^{-18} e. s. u., respectively. Within experimental error the dipole moments are independent of temperature. This leads to a high atomic polarizability for 1,1,2-trichloroethane (6.7 cc.). If smaller atomic polarizabilities are assumed, the dipole moment becomes somewhat larger and slightly temperature dependent. From these data and a survey of the C-Cl bond moments for a number of chlorinated compounds it is concluded that the *cis* configuration of 1,1,2-trichloroethane is at least 4000 cal./mole (or at least 2300 cal./mole if a smaller atomic polarizability is assumed) less stable than the skew configuration, while the energy difference between the *trans* and skew configurations of 1,1,2,2-tetrachloroethane is concluded to be 0 ± 200 cal./mole. The dipole moments of these compounds give no information as to the heights of the potential barrier to internal rotation. These results are compared with existing data on 1,2-dichloroethane. It is proposed that in these compounds the steric interactions between chlorine atoms are important factors determining the relative stability of the equilibrium rotational configurations.

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The Theory and Kinetics of Specific Oxidation. III. The Cerate-2,3-Butanediol Reaction in Nitric Acid Solution

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Previous work involving the trivalent manganese-oxalate reaction² and the periodate-glycol reaction³ has supported the theory that specific oxidations of glycols and related compounds proceed through the disproportionation of coordination complexes. To further test this theory, a study of the cerate oxidation of 2,3-butanediol in nitric acid solution was undertaken.⁴ The butanediol was used instead of ordinary

glycol because tetravalent cerium attacks the product (formaldehyde) of ethylene glycol oxidation at a rate comparable to that of the main reaction.

Theory

Since tetravalent cerium is known to have a coordination number of six, the reaction between cerate and 2,3-butanediol presents the possibility of the formation of mono-, di- and tri-glycolated coordination intermediates, as indicated



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(2) (a) Duke, *THIS JOURNAL*, **69**, 2885 (1947); (b) Taube, *ibid.*, **69**, 1418 (1947); **70**, 1216 (1948).

(3) Duke, *ibid.*, **69**, 3054 (1947).

(4) See Smith and Duke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 120 (1943), for a discussion of cerium oxidations of this type.

where G represents 2,3-butanediol and the X's, the groups coordinated with tetravalent cerium in nitric acid solution which may be OH⁻, NO₃⁻ and/or H₂O.

The kinetics according to the theory¹ would be expressed by the equation

$$-\frac{d[A]}{dt} = \left[\frac{k_1 K_1 [G] + k_2 K_1 K_2 [G]^2 + k_3 K_1 K_2 K_3 [G]^3}{1 + K_1 [G] + K_1 K_2 [G]^2 + K_1 K_2 K_3 [G]^3} \right] [A] \quad (4)$$

where [A] is total cerate, [G] is uncomplexed 2,3-butanediol, k_1 , k_2 and k_3 the specific rate constants for the disproportionation of the complexes containing 1, 2 and 3 glycol molecules, respectively, and K_1 , K_2 and K_3 the equilibrium constants for reactions (1), (2) and (3). Assuming that at lower 2,3-butanediol concentrations, only the mono-glycolated complex exists in appreciable quantity, equation (4) becomes

$$-\frac{d[A]}{dt} = \left[\frac{k_1 K_1 [G]}{1 + K_1 [G]} \right] [A] \quad (5)$$

The concentration [X] does not appear in equations (4) or (5) because it has been incorporated into the equilibrium constants. For example

$$K_1 = \frac{[CeG](X)_1}{[Ce(X)_4][G]} = \frac{K_{eq}}{[X][X]} \quad (6)$$

where K_{eq} is the true equilibrium constant for reaction (1). The nature of X may be subjected to experimental investigation by independently varying the hydrogen ion and nitrate ion concentrations and determining the effect upon K_1 . Equation (5) may be subjected to experimental verification by determining the rate of disappearance of cerate from solutions containing sufficient 2,3-butanediol to validate the assumption that [G] remains constant during the portion of the reaction under consideration. Under these conditions a series of first order (in oxidant) pseudo constants may be obtained, the pseudo constant k' being identified with the bracketed portion of equation (5).

Experimental

C. P. reagents were used. The experiments were carried out at the temperature of melting ice, $0 \pm 0.05^\circ$. The constant temperature bath consisted of a 2-liter wide-mouthed Dewar flask containing ice in distilled water and equipped with an electric stirrer.

Fifty-ml. volumetric flasks with an additional 48-ml. calibration line were used as reaction vessels. In Experiments I, the amount of 2.0 M 2,3-butanediol to give the desired final concentration, 12.0 ml. of 2.0 M nitric acid, and 12.5 ml. of 2.0 M sodium nitrate were placed in the 50-ml. volumetric flask and the contents diluted to 48 ml. After half an hour in the constant temperature bath, 2.0 ml. of 0.25 M ammonium hexanitrate cerate in 0.5 M nitric acid at the temperature of the bath were added and the Sargent electric timer started during the mixing. Five-ml. samples were removed at recorded times and quenched in 5 ml. of 0.01 M ferrous ammonium sulfate in 0.2 M sulfuric acid. The excess ferrous ammonium sulfate was titrated with 0.01 M ceric sulfate.

Experiments II were run in the same manner except that 12.5 ml. of 2.0 M sodium perchlorate replaced the sodium nitrate in the reaction mixture.

Experiments III were carried out similarly using 4.5 ml. of 2.0 M nitric acid and 20 ml. of 2.0 M sodium nitrate in the reaction mixture.

Results and Discussion

Pseudo constants obtained with various concentrations of 2,3-butanediol taken from the slope of plots of $\log [A]$ vs. t at different concentrations of hydrogen ion and nitrate ion are recorded in Table I. The value of uncoordinated 2,3-butanediol was obtained by first plotting $1/k'$ vs. the reciprocal of the initial 2,3-butanediol concentration and extrapolating the straight portion of the curve to the $1/k'$ axis. Reference to equation (5) shows that the slope of the straight line obtained is $1/K_1 k_1$ while the intercept is $1/k_1$. From this intercept and slope, a first approximation to K_1 was obtained and used to calculate the amount of uncoordinated 2,3-butanediol, shown in Table I.

TABLE I
PSEUDO-CONSTANTS (TIME IN SECONDS); CONCENTRATIONS IN ML.

Expt. I		Expt. II		Expt. III	
[H ⁺] = 0.5 M		[H ⁺] = 0.5 M		[H ⁺] = 0.2 M	
[Na ⁺] = 0.5 M		[Na ⁺] = 0.5 M		[Na ⁺] = 0.8 M	
[NO ₃ ⁻] = 1.0 M		[ClO ₄ ⁻] = 0.5 M		[NO ₃ ⁻] = 1.0 M	
		[NO ₃ ⁻] = 0.5 M			
[G]	$k' \times 10^3$	[G]	$k' \times 10^3$	[G]	$k' \times 10^3$
0.0407	1.24	0.0406	1.57	0.0422	1.28
.0492	1.39	.0491	1.72	.0507	1.44
.0579	1.49	.0578	1.80	.0594	1.59
.0841	1.72	.0840	2.14	.0856	2.05
.1285	1.93	.1284	2.37	.1298	2.30
.1731	2.04	.1730	2.44	.1840	2.44
.2715	2.07	.2715	2.58	.2715	2.44
.3620	2.14	.3620	2.58	.3620	2.30
.4525	2.19	.4525	2.56	.4525	2.17
.5430	2.26	.5430	2.61	.5430	2.13
		.6335	2.65		
.7240	2.19	.7240	2.50	.7240	2.13
.8145	2.14	.8145	2.50		

Figure 1 shows a plot of $1/k'$ vs. $1/[G]$ for experiments I, II, III. Since at lower 2,3-butanediol concentrations, the curve is a straight line, the assumption that only the mono-glycolated complex exists in appreciable quantity is validated and extrapolation to the $1/k'$ axis allows calculation of K_1 and k_1 .

Increasing the nitrate ion concentration from 0.5 to 1.0 M at constant hydrogen ion concentration produced no change in K_1 (25.5 at 0.5 M [NO₃⁻] and 24.2 at 1.0 M [NO₃⁻] which may be considered constant within experimental error) and it may be concluded therefore that nitrate ion was not displaced from the cerate complex by the 2,3-butanediol in the formation of the intermediate. At the same time the specific rate constant k_1 underwent appreciable change (3.06×10^{-3} sec.⁻¹ at 0.5 M [NO₃⁻] and 2.55×10^{-3} sec.⁻¹ at 1.0 M [NO₃⁻]) indicating that the disproportionating complex under the two

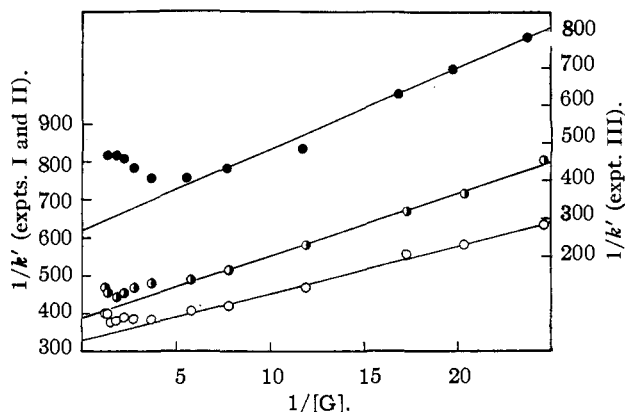
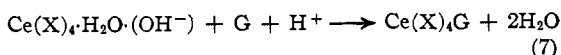


Fig. 1.—Plot of $1/k'$ vs. $1/[G]$: ●, expt. I $[H^+] = 0.5 M$, $[NO_3^-] = 1.0 M$; ○, expt. II $[H^+] = 0.5 M$, $[NO_3^-] = 0.5 M$, $[ClO_4^-] = 0.5 M$; ●, Expt. III, $[H^+] = 0.2 M$, $[NO_3^-] = 1.0 M$.

conditions was not the same. This presents two possibilities: (1) that perchlorate ion was present in the complex in experiments II or (2) that nitrate ion was present in the complexes. On the basis of the potentials⁵ of the $Ce^{+4}-Ce^{+3}$ couples in perchloric and nitric acid solutions and the lower rate of disproportionation at higher nitrate ion concentrations it is concluded that the disproportionating complex contained nitrate ions and thus that the cerate complex is richer in nitrate ions when in solution of higher nitrate ion concentration.

Increasing the hydrogen ion concentration from 0.2 to 0.5 M at constant nitrate ion concentration doubled K_1 (12.4 to 0.2 M $[H^+]$ and 24.2 at 0.5 M $[H^+]$). Since no nitrate ion is displaced, a reaction as follows is indicated



If one (OH^-) were displaced from each molecule of the cerate complex, K_1 would be increased two and one-half times. It is therefore concluded that more than one unglycolated cerate complex may exist and that K_1 represents an average of these complexes with somewhat less than one (OH^-) per molecule being displaced by the 2,3-butane-

(5) Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191-195 (1938).

diol. At the same time, k_1 also exhibited significant change ($3.70 \times 10^{-3} \text{ sec.}^{-1}$ at 0.2 M $[H^+]$ and $2.55 \times 10^{-3} \text{ sec.}^{-1}$ at 0.5 M $[H^+]$). This presents two alternatives: (1) that hydrogen ion was produced upon disproportionation of the complex, or (2) that the disproportionating complex was not the same under the two conditions considered. The first is highly unlikely since it implies reversibility of the reaction. It is therefore concluded that the disproportionating complexes were not the same and hence that the structures of the cerate complexes vary with the hydrogen ion concentration of the solution.

Departure from a straight line curve at the higher 2,3-butanediol concentrations indicates formation of the poly-glycolated complexes. In fact, the complexity of the function above 0.2 M butanediol concentrations probably requires the presence in appreciable concentrations of complexes in which only one hydroxyl of the organic molecule is coordinated (see Fig. 1). However, it is not felt that definite conclusions may be drawn due to significant changes in the dielectric constant of the solution at these high 2,3-butanediol concentrations.

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Summary

The oxidation of 2,3-butanediol by cerate is shown to proceed through the disproportionation of a mono-glycolated coordination intermediate involving the oxidizing and reducing agents. Evidence indicates the formation of poly-glycolated coordination intermediates at high 2,3-butanediol concentrations.

Tetravalent cerium in nitric acid solution is shown to be coordinated with nitrate ions, hydroxyl ions, and water molecules. In addition this complex is shown to vary with the nitrate ion and hydrogen ion concentration of the solution.