Oxidation of Organic Compounds with Cerium(IV). VII. Formation Constants for 1:1 Cerium(IV)–Alcohol Complexes[1a–c]

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Abstract: Formation constants for several 1:1 cerium(IV)–alcohol complexes formed between ceric ammonium nitrate and benzyl alcohols, primary, secondary, and tertiary aliphatic alcohols, glycols and glycol monoalkyl ethers, β-substituted ethanols, and some other functionalized alcohols were measured spectrophotometrically in 70% aqueous acetonitrile containing 0.02 *M* ceric ammonium nitrate and 0.5 *M* nitric acid at 21.0°. A few formation constants were measured in 70% aqueous acetic acid, water, and water with added salts, all solutions containing 0.02 *M* ceric ammonium nitrate and 0.5 *M* nitric acid at 21.0°. From these measurements it is concluded that the formation constants of the cerium(IV)–alcohol complexes are not very sensitive to changes in the electronic nature of the hydroxy group of the alcohols that form the complexes. In solvents such as 70% aqueous acetonitrile, the steric requirements of solvation seem to be greater than those of complexation since the formation constants of the cerium(IV)–alcohol complexes increase as the hydroxy group of a series of alcohols becomes more sterically crowded if other factors remain more or less constant. Finally, under the conditions of our study, no evidence for any strong interactions between the cerium(IV) and a second functional group, either near or far from the hydroxy group, was found. Small changes in the equilibrium constants were noted, however, when a second functional group was added to an alcohol, but all of these changes could have resulted from small electronic or steric differences or relatively weak interactions such as hydrogen bonding or dipole–dipole attractions of the second functional group with cerium or its ligands. Formation constants for complexes of cerium(IV) with *cis*- and *trans*-4-*t*-butylcyclohexanols in 70% aqueous acetonitrile containing 0.01 *M* ceric ammonium nitrate and 0.5 *M* nitric acid at 21.0° were measured. Under these conditions, it is found that the equilibrium constant for the *cis* (axial) alcohol is ten times greater than that of the *trans* (equatorial) alcohol. From these results and analysis of existing rate data for chromic acid oxidation of stereoisomeric pairs of alcohols, it is concluded that steric hindrance to solvation of alcohols must be considered as well as relief of steric strain as an explanation for the more rapid rate of metal ion oxidations of the more sterically hindered alcohol of a pair of stereoisomeric alcohols.

The use of cerium(IV) as a qualitative colorimetric reagent for the detection of alcohols has been known for a long time[2] and even quantitative methods for the analysis of alcohols based on the red color of the cerium(IV)–alcohol complexes have been developed.[3] It has been demonstrated that these complexes are 1:1 complexes that involve one molecule of alcohol and one cerium(IV) species and that a rapidly attained equilibrium exists between the complex and its components.[4]

$$\mathrm{Ce^{IV}} + \mathrm{ROH} \overset{K}{\rightleftharpoons} \text{complex}$$

The formation constant for a cerium(IV)–alcohol complex can be readily measured since the complex is more highly colored than the other cerium(IV) species present in solution. Numerous formation constants for cerium(IV) complexes for simple alcohols and glycols have been reported[4–6] but no systematic study of cerium(IV) complex formation with a large number of alcohols has been published. The purpose of this study was to determine the effects of structural variations of alcohols on the position of equilibrium between a 1:1 complex and its components and to investigate solvent effects and the effect of added nitrate ion on these equilibria.

Most of the equilibrium constants were measured at 21.0° in 70% aqueous acetonitrile containing 0.02 *M* ceric ammonium nitrate (CAN) and 0.5 *M* nitric acid. These conditions were chosen mainly because they led to homogeneous and relatively stable solutions with positions of equilibria that could be easily measured.

It is anticipated that the equilibrium constants derived in this study will be useful not only for understanding results obtained from cerium(IV) studies but also in predicting and rationalizing results obtained in other metal ion–alcohol studies where it is impossible or very difficult to measure the magnitude of any metal ion–alcohol interaction. Chromium(VI) and lead(IV) oxidations of alcohols are two cases where metal ion–alcohol complexes have been postulated[7] but where little direct evidence for either the existence of a complex or the amount of complexation has been obtained. Only a few formation constants for chromium(VI)–alcohol complexes have been reported.[8]

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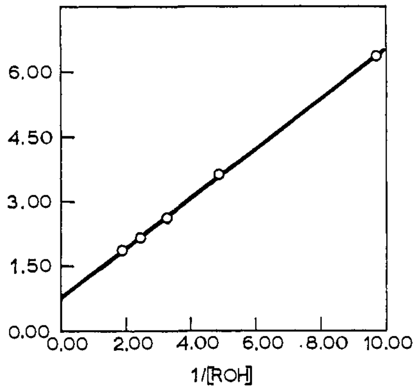

Figure 1. Plot of spectrophotometric data for 2-methoxyethanol assuming 1:1 complex formation.

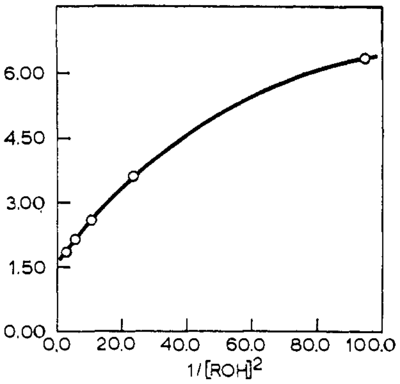

Figure 2. Plot of spectrophotometric data for 2-methoxyethanol assuming 2:1 complex formation.

Results

For the general equilibrium given by eq 1 between two metal species, M and MS_n, that have different extinction coefficients, Ardon[4a] has derived eq 2 for the situation where $[S]_{total}$ is approximately equal to $[S]_{uncomplexed}$. K is the equilibrium constant, $\Delta\epsilon$ is the difference in extinction coefficients between the two

$$M + nS \overset{K}{\rightleftharpoons} (MS_n) \qquad (1)$$

metal species, $[M]_{total}$ is the total concentration of

$$\frac{1}{\Delta A} = \frac{1}{[S]^n}\frac{1}{\Delta\epsilon[M]_{total}K} + \frac{1}{\Delta\epsilon[M]_{total}} \qquad (2)$$

metal species, and ΔA is the difference in absorbance of a solution containing no S and one that contains a certain concentration of S which is represented by [S]. For a 1:1 cerium(IV)–alcohol complex, eq 2 can be written as eq 3. From eq 3 it is easy to see that a plot

$$\frac{1}{\Delta A} = \left(\frac{1}{[ROH]}\right)\left(\frac{1}{\Delta\epsilon[Ce^{IV}]_{total}K}\right) + \frac{1}{\Delta\epsilon[Ce^{IV}]_{total}} \qquad (3)$$

of $1/\Delta A$ *vs.* 1/[ROH] for a series of solutions that contain different concentrations of alcohol but the same total concentrations of cerium(IV) should give a straight line provided that [ROH] is so much greater than $[Ce^{IV}]_{total}$ that the amount of alcohol tied up in the complex is negligible or the amount of alcohol tied up in the complex is subtracted from the initial alcohol concentration. The intercept divided by the slope of this straight line gives K.

The absorbances of five or six 70% aqueous acetonitrile solutions at 21.0° containing 0.02 *M* CAN, 0.5 *M* nitric acid, and 0.0 to 1.0 *M* alcohol were measured for each alcohol. From these absorbances and alcohol concentrations, a K for the formation of the complex between cerium(IV) and the alcohol was calculated using a computer program, RAWDAT, based on eq 3. Although the ratios of alcohol concentrations to cerium(IV) concentrations were high, in most cases the amount of alcohol tied up in the complex was not negligible and was corrected for by an iterative procedure that calculated a K based on the initial alcohol concentration, corrected the free concentration of alcohol based on this K, then calculated a new K, and continued until the difference between the old and new K was 0.01 or less.

Many workers[4a,c,d,6c,e,h,i,7] have substantiated the fact that cerium(IV)–alcohol complexes are 1:1 complexes and further confirmation of this is obtained by comparison of Figures 1 and 2. Figure 1 was plotted using a typical set of data, that for 2-methoxyethanol, and assuming a 1:1 complex, and Figure 2 was plotted using the same data but assuming a 1:2 cerium(IV)–alcohol complex. It can be seen that the 1:1 complex plot of the data is a straight line, while the 1:2 complex plot is a curved line. It has been assumed that 1:1 complexes are formed for all alcohols since treatment of the data assuming a 1:1 complex yielded plots comparable to the one shown in Figure 1.

It should be noted that the equilibrium constants calculated by the above procedures are "apparent" equilibrium constants since they measure the position of the equilibrium of *all* cerium(IV) species with alcohol to form a 1:1 cerium(IV)–alcohol complex. Some authors[4b] have attempted to derive a "true" equilibrium constant which is acid and ligand independent since the nature of the cerium(IV) species in solution is a function of the acidity and added ligands. However, since our system of aqueous acetonitrile with added nitric acid is somewhat complex, we made no attempt to calculate a "true" equilibrium constant. The effects of structural variations of alcohols should still be manifested in our "apparent" equilibrium constants since in most cases everything except the alcohol was kept constant and thus the cerium(IV) species should be the same for all alcohols.

In Table I the equilibrium constants with their standard deviation are presented for various cerium(IV)–alcohol complexes in 70% aqueous acetonitrile containing 0.02 *M* CAN and 0.05 *M* nitric acid at 21.0°. The alcohols are placed in groups that are convenient for discussion. In most cases, the standard deviations are quite low. However, some alcohols were rapidly oxidized, and in these cases it is felt that standard deviations do not accurately reflect the true error and errors have been estimated.

In order to determine the effect of solvent on complex formation, equilibrium constants for various cerium(IV)–alcohol complexes were measured in water, 70% aqueous acetic acid, and 70% aqueous acetonitrile with each mixture containing 0.02 *M* CAN and 0.5 *M* nitric acid at 21.0°. These constants are reported in Table II.

Table I. Formation Constants for Cerium(IV)–Alcohol Complexes in 70% Aqueous Acetonitrile Containing 0.02 *M* CAN and 0.5 *M* Nitric Acid at 21.0°

Alcohol	Equilibrium constant, K, l./mol
Benzyl Alcohols	
Benzyl alcohol	0.75 ± 0.01
p-Methylbenzyl alcohol	0.82 ± 0.01
o-Chlorobenzyl alcohol	0.49 ± 0.02
m-Chlorobenzyl alcohol	0.74 ± 0.01
p-Chlorobenzyl alcohol	0.71 ± 0.01
m-Nitrobenzyl alcohol	0.47 ± 0.03
p-Nitrobenzyl alcohol	0.64 ± 0.01
α-Methylbenzyl alcohol	1.86 ± 0.01
Benzhydrol	1.45 ± 0.01
Primary Alcohols	
Methanol	0.52 ± 0.03
Ethanol	0.74 ± 0.05
Hexanol	1.59 ± 0.03
Nonanol	1.94 ± 0.01
Neopentanol	2.9 ± 0.05
2-Cyclohexylethanol	2.00 ± 0.01
Cyclopropylcarbinol	0.88 ± 0.01
Cyclobutylcarbinol	1.5 ± 0.01
Cyclopentylcarbinol	2.78 ± 0.03
Cyclohexylcarbinol	2.63 ± 0.01
Secondary Alcohols	
Isopropyl alcohol	1.51 ± 0.02
3-Heptanol	4.06 ± 0.01
Cyclopentanol	3.1 ± 0.1[a]
Cyclohexanol	4.73 ± 0.01
Cycloheptanol	5.0 ± 0.3[a]
Cyclooctanol	6.08 ± 0.01
Tertiary Alcohols	
t-Butyl alcohol	2.76 ± 0.02
1-Methylcyclohexanol	10.21 ± 0.01
Glycols and Glycol Monoalkyl Ethers	
Ethylene glycol	3.27 ± 0.01
1,3-Propanediol	4.80 ± 0.01
1,4-Butanediol	2.82 ± 0.02
1,5-Pentanediol	3.54 ± 0.01
2-Methoxyethanol	1.37 ± 0.03
3-Ethoxypropanol	1.13 ± 0.02
β-Substituted Ethanols	
Ethanol	0.74 ± 0.05
3-Buten-1-ol	1.01 ± 0.01
2-Phenylethanol	2.39 ± 0.04
2-Cyclohexylethanol	2.00 ± 0.01
2-Chloroethanol	0.13 ± 0.2[a,b]
Other Functionalized Alcohols	
4-Phenylbutanol	1.68 ± 0.02
5-Hexenol	1.50 ± 0.02

[a] This is not a standard deviation but an estimated error. [b] Because of small Δ *A* values a small value for the intercept of the plot was obtained which could lead to as much error as ±0.4.

Table II. Formation Constants for Cerium(IV)–Alcohol Complexes in Water, 70% Aqueous Acetic Acid, and 70% Aqueous Acetonitrile with Each Mixture Containing 0.02 *M* CAN and 0.5 Nitric Acid at 21.0°

	Equilibrium constant, K, l./mol		
Alcohol	Water	70% aqueous acetic acid	70% aqueous acetonitrile
Ethyl	1.2 ± 0.01	0.15 ± 0.08	0.74 ± 0.05
n-Butyl	1.7 ± 0.04	0.40 ± 0.05	1.1[a]
Isopropyl	0.84 ± 0.04	0.44 ± 0.04	1.51 ± 0.02
t-Butyl	0.54 ± 0.03	0.66 ± 0.06	2.76 ± 0.02

[a] Predicted value based on those of methanol, ethanol, hexanol, and nonanol.

In order to determine the effect of added nitrate ion on complex formation, equilibrium constants for the cerium(IV)–*t*-butyl alcohol complex were also measured in water with added nitric acid and in water with added nitric acid and salts. These constants in water with 0.02 *M* CAN and 0.5 *M* nitric acid, water with 0.02 *M* CAN, 0.5 *M* nitric acid, and 0.2 *M* sodium perchlorate, and water with 0.02 *M* CAN, 0.5 *M* nitric acid, and 0.2 *M* sodium nitrate were found to be 0.54 ± 0.03, 0.50 ± 0.03, and 0.33 ± 0.06, respectively.

The formation constants for the 1:1 cerium(IV)–alcohol complexes of a typical pair of stereoisomeric alcohols, *cis*- and *trans*-4-*t*-butylcyclohexanols, were measured.

The formation constant for the cerium(IV)–*trans*-4-*t*-butylcyclohexanol complex could be readily measured by the usual method under the conditions used to measure formation constants for the other cerium(IV)–alcohol complexes. The formation constant for the complex of the *cis* isomer, however, could not be measured by the usual method under these conditions since the alcohol was too rapidly oxidized. The formation constant for the *cis*-isomer complex was obtained by measuring the over-all constant for a mixture of the two 4-*t*-butylcyclohexanols that contained 73.1% of the *trans* isomer and 26.9% of *cis* isomer under the same conditions except that the solution contained only 0.01 *M* CAN instead of 0.02 *M*.[9]

For a mixture of two alcohols, A and B, an apparent equilibrium constant for complexation of cerium(IV) with the mixture, K_{app}, can be defined by eq 4 where [A] and [B] are the molar concentrations of alcohols A and B, respectively, and K_{A} and K_{B} are the equilibrium constants for the formation of cerium(IV)–alcohol complexes with pure alcohols. Justification for the use of eq 4 is given in the Appendix.

$$K_{\text{app}} = K_{\text{a}}[\text{A}]/([\text{A}] + [\text{B}]) + K_{\text{b}}[\text{B}]/([\text{A}] + [\text{B}]) = K_{\text{a}}(\%\text{A}/100) + K_{\text{b}}(\%\text{B}/100) \quad (4)$$

Confirmation of the validity of this approach is obtained from the close agreement of the experimental and calculated K_{app}'s for mixtures of benzyl alcohol and cyclohexanol given in Table III. The calculated K_{app}'s were determined by use of eq 4 and the known composition of the mixture, and values of 0.73 and 3.2 for the K's for benzyl alcohol and cyclohexanol, respectively, which were measured for the pure alcohols under these conditions.[10]

The equilibrium constant for complex formation for pure *trans*-4-*t*-butylcyclohexanol in 70% aqueous acetonitrile containing 0.01 *M* CAN and 0.5 *M* nitric acid at 21.0° was found to be 3.6 based on two runs. The corresponding equilibrium constant for the *cis* isomer under identical conditions was found to be 36. The constant for the *cis* isomer was calculated from the three determinations of K_{app} for a mixture of 73.1% *trans* and 26.9% *cis* alcohols using eq 4. It can be seen from the data in Table IV that the error involved in the deter-

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(9) Use of the mixture of isomers permits determination of the K_{cis} since the concentration of the complex of the *cis* alcohol is much lower. Determination of the K_{cis} could have been done by using the pure *cis* isomer at lower concentrations with lower cerium(IV) concentrations, but this method was not used since the lower salt concentration would have been a much more drastic change of conditions.

(10) These values differ from those reported in Table I since they are for solutions that contain 0.01 *M* instead of 0.02 *M* CAN.

Table III. Experimental and Calculated Apparent Formation Constants for Cerium(IV)–Alcohol Complexes with Mixtures of Benzyl Alcohol and Cyclohexanol in 70% Aqueous Acetonitrile Containing 0.01 *M* CAN and 0.5 *M* Nitric Acid at 21.0°

Benzyl alcohol, %	Cyclohexanol, %	K_{app}, l./mol	
		Exptl	Calcd[a]
75.9	24.2	1.34	1.33
73.0	27.1	1.23	1.40
52.3	47.7	1.99	1.91

[a] See text.

Table IV. Formation Constant for Cerium(IV)–*cis*-4-*t*-Butylcyclohexanol Complex Derived from Apparent Equilibrium Constants for Complex Formation with a Mixture of 26.9% *cis*- and 73.1% *trans*-4-*t*-Butylcyclohexanols in 70% Aqueous Acetonitrile Containing 0.01 *M* CAN and 0.5 *M* Nitric Acid at 21.0°

K_{app}, l./mol	K_{cis}, l./mol[a]
10.3	28.5
14.7	44.9
11.8	34.1
Average 12.3 ± 1.8	35.8 ± 6.8

[a] A value of 3.6 for the *K* for the *trans* isomer was used to calculate K_{cis}.

minations of *K* for the *cis* alcohol was substantial, no doubt due to the rapid oxidation of the *cis* isomer. Nevertheless, it is quite clear that the *K* for the *cis* (axial) isomer is significantly greater than that for the *trans* (equatorial) isomer.

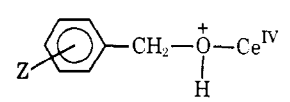
Discussion

Although it is clear that the cerium(IV)–alcohol complex is a 1:1 complex, it is difficult to say much about its structure. Beineke[11] has found using X-ray crystallographic techniques that solid ceric ammonium nitrate has six nitrate ions surrounding each cerium atom with the ammonium ions in the spaces between the cerium–nitrate species. The nitrates are coordinated to the cerium in a bidentate fashion so that the coordination number of cerium is 12. The average cerium–oxygen distance is 2.508 ± 0.007 Å. Larsen and Brown[12] carried out an X-ray diffraction study of an aqueous solution of CAN. They found that there are 12 cerium–oxygen interactions within a distance of 2.85 Å in 1.45 *M* CAN solution. In addition, they found interactions attributable to the nitrogen–oxygen and oxygen–oxygen of the nitrate ion, confirming its proximity to the cerium(IV) ion. The structure of solid state CAN with six bidentate nitrates around the cerium ion is certainly consistent with their findings. From a study of the infrared and Raman attenuated total reflection spectra of CAN solutions of concentrations as low as 0.4 *M*, Miller and Irish[13] found evidence for the existence of cerium–nitrate species and advanced the postulate that the nitrates were coordinated in a bidentate fashion. Karraker[14] has recently reported a Raman and infrared study of CAN that agrees with the conclusions of Miller and Irish. It thus appears that CAN in solution exists mainly as free ammonium ions and highly nitrated cerium species. Although one usually thinks of nitrate ions as weak ligands, bidentate nitrates and the highly symmetrical structure[15] may cause the hexanitratocerate ion to be a relatively stable entity. Thus many of the ligands of the cerium(IV)–alcohol complexes are probably nitrates. The fact that the *K* for cerium(IV)–*t*-butyl alcohol complex formation is lower in the presence of added nitrate but not in the presence of added perchlorate supports the idea that nitrate ions are competing with alcohol molecules for cerium(IV) coordination sites.

It is probable that the bond between the alcohol and cerium(IV) is mainly electrostatic since most authors[16] feel that the amount of covalent bonding between rare earth ions and electronegative atoms is quite small since high energy, diffuse orbitals (4f, 5d, 6s, or 6p) would have to be involved in the bonding. The paucity of stable complexes of rare earth metal ions supports the postulate of weak electrostatic bonding rather than stronger covalent bonding.[16]

Several factors must be considered in attempting to rationalize the changes in the equilibrium constants of cerium(IV)–alcohol complexes with changes in the alcohol structures. These are an electronic effect, a steric effect, size of chelate rings if any exist, and solvation effects.

The electronic effect on stability of the cerium(IV)–alcohol complexes can be seen by comparison of the *K*'s for substituted benzyl alcohols. Comparison of the *K*'s for the first seven alcohols listed in Table I shows that both electron-donating and -withdrawing substituents have very little effect on the stability of the cerium(IV)–alcohol complexes. Although the equilibrium constants increase slightly as the electron-donating power of the substituent increases, the average value of the *K*'s for the benzyl alcohols, excluding the *o*-chloro- or *m*-nitrobenzyl alcohols where direct interactions between the substituent and the cerium could occur, is 0.73 ± 0.058. The standard deviation of 8% clearly indicates that the formation constant of the complex is not very sensitive to electronic effects. This small electronic effect is reasonable in view of the fact that at least five σ bonds must separate the substituent from the metal. The effect of substitution at the α position is greater, leading to an increase in *K* of a factor of 2–3,



but still not very large. Probably the most significant conclusion derived from the fact that the formation constants of the cerium(IV) complexes of α-methylbenzyl alcohol and benzhydrol are greater than that of the benzyl alcohol complex is that no large steric effect that inhibits complex formation exists since the α substituents are located very close to the site of coordination.

In order to attempt to correlate the changes of the *K*'s of the aliphatic alcohols with polar effects, a plot of log *K* *vs.* σ^*[17] was constructed. Figure 3 is such a plot

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(11) T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, **7**, 715 (1968).

(12) R. D. Larsen and G. H. Brown, *J. Phys. Chem.*, **68**, 3060 (1964).

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(16) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

(17) Robert W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

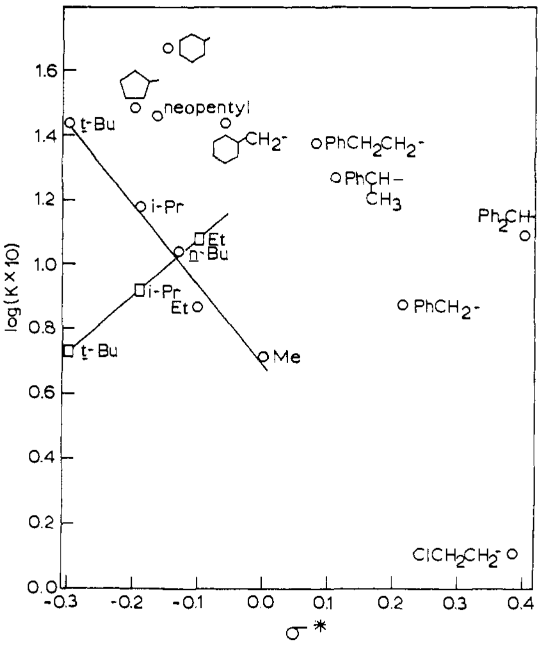

Figure 3. Plot of log K for cerium(IV)-alcohol complexes *vs.* σ^* for the alcohol: ○, data in 70% aqueous acetonitrile; □, data in water.

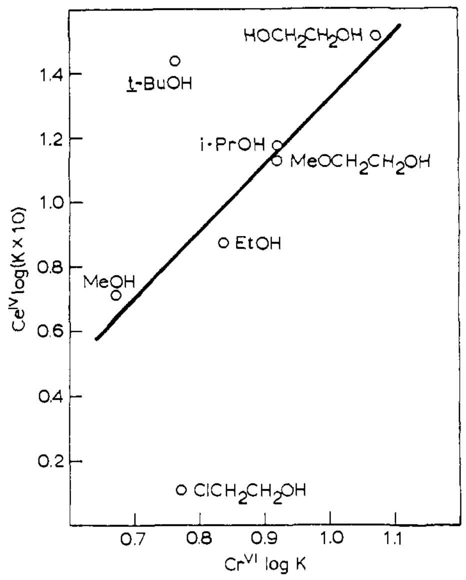

Figure 4. Plot of log ($K \times 10$) for cerium(IV)-alcohol complexes *vs.* log K for chromium(VI)-alcohol complexes.

which uses the log K's for complexes measured in 70% aqueous acetonitrile and water for several alcohols for which a σ^* is available. From Figure 3 it can be seen that although the points for the complexes of simple aliphatic alcohols in 70% aqueous acetonitrile lead to a reasonable ρ^* of -2.4, points for these same complexes in water lead to an unreasonable ρ^* of $+1.7$, and points for complexes of other aliphatic alcohols in 70% aqueous acetonitrile show no reasonable correlation. Figure 3 clearly indicates that no simple relationship exists between the formation constants of cerium(IV)-alcohol complexes and the polar nature of the alcohols that form these complexes. In fact, a trend of the K's of the complexes that does seem to exist is that *the formation constant for the complex of the more sterically hindered alcohol* of a pair of alcohols of comparable polar nature *is greater* than that for the less crowded alcohol. This trend is substantiated by the K's for isopropyl alcohol (1.51) and neopentanol (2.9), hexanol (1.59) and nonanol (1.94), cyclopropylcarbinol (0.88) and cyclobutylcarbinol (1.5), cyclobutylcarbinol and cyclopentylcarbinol (2.78), cyclopentanol (3.1) and cyclohexanol (4.73), and *t*-butyl alcohol (2.76) and 1-methylcyclohexanol (10.2). Most impressively, the K's for a pair of stereoisomeric complexes, those for *trans*-4-*t*-butylcyclohexanol (3.6) and *cis*-4-*t*-butylcyclohexanol (36), clearly show that the K for the more sterically hindered alcohol is greater than that of the less crowded alcohol if the electronic nature of the two alcohols are very similar.

This trend seems to be opposite to that predicted on simple steric arguments. However, if one considers the alcohol as a solvated species, then the trend becomes easy to rationalize as the result of steric requirements of solvation being more demanding than the steric requirements of complexation. The rigid structure of the cerium species and the flexible structure of the solvent make this a reasonable situation even if it is not a predictable one.

In view of this trend, the similarities of equilibrium constants between α-methyl- and α-phenyl-substituted alcohol complexes can be understood. A smaller K for the α-phenyl derivative would be expected based on an electronic effect if one accepts that the phenyl group is electron withdrawing and the methyl group is electron donating as indicated by the σ^*, but the greater steric hindrance of the hydroxy group of the α-phenyl derivative must compensate and lead to a K that is closer to that of the α-methyl derivative. Thus ethanol and benzyl alcohol have K's equal to 0.74 and 0.75, respectively, and α-methylbenzyl alcohol and benzhydrol have K's equal to 1.86 and 1.45, respectively.

That this trend toward larger formation constants with more sterically crowded alcohols in 70% aqueous acetonitrile is a result of solvation is supported by the data reported in Table II. In Table II equilibrium constants for four alcohols in water, 70% aqueous acetic acid, and 70% aqueous acetonitrile with each mixture containing the same amounts of CAN and nitric acid are presented. It is clearly seen that the trend of tertiary > secondary > primary found in 70% aqueous acetonitrile is suppressed in 70% aqueous acetic acid and reversed in water.[18] Thus the solvation of the alcohols which must be a function of the solvent clearly affects the formation constants for complexes with a series of alcohols that possess hydroxy groups with different amounts of steric hindrance.

It is interesting to note that a plot of the log of the K's for cerium(IV)-alcohol complexes against log of the K's for chromium(VI)-alcohol complexes,[8] shown in Figure 4, shows an interesting correlation. Exclusion of the points for *t*-butyl alcohol and 2-chloroethanol leads to a very good linear relationship which supports the use of K's of cerium(IV)-alcohol complexes as models for the K's of other metal-alcohol complexes. Exclusion of the point for 2-chloroethanol is justified since the experimental error for the K for the cerium(IV)

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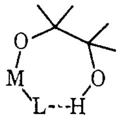
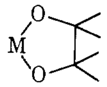
[18] Our observation that the primary K is the largest in water agrees with the results of Offner and Skoog[4c] who measured K's for simple aliphatic alcohols in 1.6 M perchloric acid and 2 M nitric acid.

complex with this alcohol was quite large. It is more difficult to justify neglect of the *t*-butyl alcohol point, but this alcohol is much more sterically hindered than the others. Indeed this correlation may be fortuitous since the solvent systems for the two sets of *K*'s are different and the alcohol concentrations were quite high, 0–5 *M*, in the chromium(VI) measurements which could have resulted in unaccountable medium effects. Nevertheless, the linear correlation does support the use of the behavior of the *K*'s of cerium(IV)–alcohol complexes as models for that of other metal–alcohol complexes.

A series of glycols and glycol monoalkyl ethers were studied to determine the effect of a second hydroxy group and possibly establish evidence for chelation. The question of chelate formation with diols and metal ions has been raised by many authors[7] and indeed several studies exist[4d,6a,b,d,7] involving cerium(IV) and diols. Although many of these studies suggest chelate formation, even the most compelling evidence, which has been reported by Hintz and Johnson,[4d] does not demand chelate formation. These workers measured equilibrium constants for *cis*- and *trans*-1,2-cyclohexanediols, *trans*-2-methoxycyclohexanol, and cyclohexanol with ceric perchlorate in perchloric acid and found values of *K* of 29.3 for *cis*-1,2-cyclohexanediol, 18.6 for *trans*-1,2-cyclohexanediol, 2.9 for *trans*-2-methoxycyclohexanol, and 3.9 for cyclohexanol from spectrophotometric data. These results support bidentate complexation with the diols but not with the monomethyl ether. However, it should be noted that the change in *K*'s in going from the alcohol to the diols amounts to less than 1 kcal difference and might readily be accounted for by a monodentate complex with the second hydroxy hydrogen bonded to a ligand as shown in **1** instead of a true chelate structure as shown in **2**.



1



2

Our data for glycols and glycol monoalkyl ethers presented in Table I offer no support for a true chelate structure for the cerium(IV)–alcohol complex. Comparison of the *K*'s for 1,2- to 1,5-diols shows no particularly stable complexes which one would anticipate if chelate formation were important. Moreover, the difference in the *K* for ethylene glycol and its monomethyl ether is about the factor of 2 that one would expect for statistical reasons. The *K* for the complex of 1,3-propanediol is a little greater than twice that of 3-ethoxypropanol, and the *K* for the complex of ethylene glycol is more than twice that of ethanol, but solvation and electronic effects could account for these slight increases. Another possible explanation for this slight enhancement of stability of the complexes by the presence of a second hydroxy could be hydrogen bonding of the second hydroxy to a ligand of the metal ion as shown by structure **1**.

A series of β-substituted ethanols was investigated in order to ascertain whether bidentate-type complexation occurs in systems other than glycols and the results are given in Table I. Equilibrium constants for complex formation between cerium(IV) and 3-buten-1-ol and 2-phenylethanol were measured in order to ascertain whether a π system can interact with the metal ion in such a fashion as to increase the stability of the complex. The equilibrium constant for butanol in 70% aqueous acetonitrile was not measured, but a value of 1.1 can be arrived at by interpolation between ethanol and hexanol. Using this value of 1.1 for the cerium(IV)–butanol complex, the value of 1.01 for the cerium(IV)–3-buten-l-ol complex shows if anything a slightly destabilizing effect of the olefin. Comparison of the equilibrium constant of 2-phenylethanol (2.39) with that of cyclohexylethanol (2.00) again shows no significant stabilization that would indicate any kind of a strong secondary interaction of the phenyl group and the complex.

The equilibrium constant for 2-chloroethanol (0.13) is sufficiently low that any significant chlorine–cerium(IV) interaction can be ruled out. It should be noted, however, that the experimental error in this measurement was rather large.

Equilibrium constants were measured for 4-phenylbutanol and 5-hexenol to determine whether a π system four carbons removed from the donor atom might interact with the metal ion. Comparison of the equilibrium constant of 5-hexenol (1.50) to that of hexanol (1.59) and comparison of the equilibrium constant of 4-phenylbutanol (1.68) to that of nonanol (1.94) show no stabilization of the cerium(IV)–alcohol complex by a π system four carbons removed from the hydroxy group.

There are three conclusions that can be drawn from these formation constants for cerium(IV)–alcohol complexes. First, the *K*'s for the complexes of the benzyl alcohols show that the stabilities of the complexes are not particularly sensitive to electronic effects. Second, the *K*'s for the complexes of the aliphatic alcohols show that a "reverse steric effect" exists which is most reasonably accounted for by the steric requirements of solvation of the alcohol being greater than those of complexation. Finally, the *K*'s for the complexes of the bifunctional alcohols give no indication that chelation of the metal by these alcohols is important even if the second functional group is a hydroxy group.

The relative rates of chromic acid oxidation of many stereoisomeric pairs of alcohols have been reported[19] and, in general, the more sterically crowded alcohol is oxidized faster. For example, axial cyclohexanols are oxidized 3–34 times more rapidly than equatorial cyclohexanols[19a–c,e] and *endo*-2-bicyclo[2.2.1]heptanols are oxidized 2–150 times faster than the corresponding *exo* isomers.[19a–d,f] Usually the more sterically hindered isomer is oxidized about five times faster than its epimer. This generalization has been so well established that the relative rates of chromic acid oxidation of stereoisomeric alcohols have been used as a means of determining their stereochemistry.[19e,20]

The most widely accepted explanation for this phenomenon is that since the carbon bearing the hydroxy

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(19) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 289; (b) K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965, pp 164–167; (c) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1966, pp 81–84, 271; (d) I. Rothberg and R. V. Russo, *J. Org. Chem.*, 32, 2003 (1967); (e) W. Cocker, A. C. Pratt, and P. V. R. Shannon, *Tetrahedron Letters*, 3919 (1967); (f) A. K. Awasthy, J. Roček, and R. M. Moriarty, *J. Am. Chem. Soc.*, **89**, 5400 (1967), and references cited within these publications.

(20) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 83.

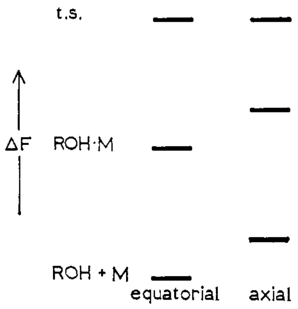

Figure 5. Free energy diagram for formation of metal–alcohol complexes of a pair of axial and equatorial alcohols and decomposition of these complexes with identical formation constants for the complexes of both alcohols.

group goes from sp^3 to sp^2 hybridization during oxidation, steric crowding in the alcohol is partially relieved in going to the carbonyl compound, and therefore the more sterically hindered alcohol is oxidized more rapidly since it has more strain energy to lose.[19,20] The generally accepted mechanism for chromic acid oxidation of alcohols involves the formation of a chromium(VI)–alcohol complex (often referred to as a chromate ester) which exists in equilibrium with its components followed by the rate-determining decomposition of this complex to products.[19,20] The kinetic expression for this type of mechanism is given by eq 5 if

$$\mathrm{Cr^{VI}} + \mathrm{ROH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{(ROH)Cr^{VI}} \xrightarrow[\substack{\text{rate}\\ \text{determining}}]{k_2} \text{products}$$

k_{-1} is much greater than k_2 and K[ROH], where $K = k_1/k_{-1}$, is small so that the concentration of the complex is low. The rates of chromic acid oxidations have usu-

$$\frac{-\mathrm{d(Cr^{VI})}}{\mathrm{d}t} = (k_1/k_{-1})(k_2)[\mathrm{Cr^{VI}}][\mathrm{ROH}] =$$

$$Kk_2[\mathrm{Cr^{VI}}][\mathrm{ROH}] = k_{\mathrm{obsd}}[\mathrm{Cr^{VI}}][\mathrm{ROH}] \quad (5)$$

ally been studied under conditions where the kinetics are given by eq 5. It should be noted that the second-order rate constant, k_{obsd}, is really composed of the equilibrium constant for the formation of the complex, K, times the rate constant for decomposition of the complex to products, k_2. In terms of this mechanism, then, the relief of steric strain argument for the more rapid oxidation of the more sterically hindered alcohol of a stereoisomeric pair of alcohols means that the equilibrium constant for formation of the metal–alcohol complex for both alcohols would be about the same or smaller for the more hindered alcohol,[21] but the rate of decomposition of the complex of the more sterically hindered alcohol to products would be greater. A free energy diagram for this situation is depicted in Figure 5.

Since the behavior of the equilibrium constants for formation of chromium–alcohol complexes might be similar to that of cerium–alcohol complexes (see Figure 4) and most of the chromic acid oxidations have been run in aqueous mixed solvents,[19] it occurred to us that another explanation for the more rapid rate of oxidation of the more sterically hindered alcohol of a stereoisomeric pair of alcohols might be that complex formation occurs to a greater extent with the more hindered alcohol. If this happens, then even if the rates of decomposition of these complexes to products are equal, the more hindered alcohol would be oxidized faster. A free energy diagram for this situation is presented in Figure 6.

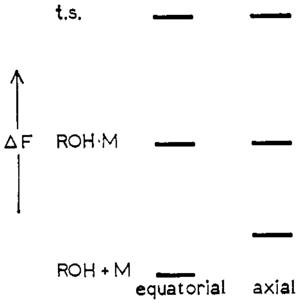

Figure 6. Free energy diagram for formation of metal–alcohol complexes of a pair of axial and equatorial alcohols and decomposition of these complexes with a larger formation constant for the complex of the more hindered alcohol.

Our results that the formation constant for the cerium(IV)–alcohol complex of *cis*-4-*t*-butylcyclohexanol is *ca.* ten times greater than that of the *trans* isomer is in agreement with all the trends that we observed for other types of alcohols which indicate that the more sterically hindered alcohols form complexes to a greater extent. Since it is possible that chromium(VI)–alcohol complexes behave in a similar fashion to cerium(IV)–alcohol complexes, the relief of steric strain argument as the sole explanation of the relative rates of chromic acid oxidations of pairs of stereoisomeric alcohols becomes seriously questionable.[22] The steric hindrance to solvation argument must at least be considered. Support for the importance of steric hindrance to solvation in affecting the equilibrium constants for chromium(VI)–alcohol complexes is given by another comparison in addition to the comparison of the K's of cerium(IV)–alcohol and chromium(VI)–alcohol complexes shown in Figure 4. From Table II it is seen that the ratios of formation constants for a pair of cerium(IV)–alcohol complexes of sterically different alcohols are greater in 70% aqueous acetonitrile than they are in more hydroxylic media. This same trend with rate constants for chromic acid oxidations can be observed in the few cases where comparisons such as this can be made.[19,c,d] For example, the ratio of the rate of chromic acid oxidation of epicholestanol to cholestanol is 8.5 in 90% aqueous acetic acid and increases by almost a factor of 2 in 95% aqueous acetic acid,[25] and the ratio of the rate of the chromic acid oxidation of *endo*- to *exo*-norbornanol has been reported as 2.5 in 30% aqueous acetic acid[21b] and 6.47 in 75% aqueous acetic acid.[19d] Although the strain relief argument can account for these solvent effects by changes in the stabilities of the transition states with solvent, the steric hindrance to solvation argument requires

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[21] (a) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955); (b) H. Kwart and P. S. Francis, *ibid.*, 81, 2116 (1959).

[22] In a manner similar to chromic acid oxidations, the N-bromosuccinimide (NBS) oxidation of the more hindered alcohol of an stereoisomeric pair of alcohols is also faster than that of the less hindered alcohol.[23] However, NBS oxidations seem to be more selective than chromic acid oxidations[23] and in fact the relative rates for several series of alcohols is not the same for chromic acid and NBS.[24] Thus other factors must be important in determining the relative rates of NBS oxidations. Of course, since the NBS oxidations do not involve a metal–alcohol complex, the behavior of the cerium(IV)–alcohol complexes is not directly related to NBS oxidations.

[23] R. Filler, *Chem. Rev.*, **63**, 21 (1963).

[24] J. Kawanami, *Bull. Chem. Soc. Japan*, **34**, 671 (1961).

[25] G. Vavon and B. Jakubowicz, *Bull. Soc. Chim. France*, **53**, 581 (1933).

solvent effects. Moreover, as Awasthy, Roček, and Moriarty point out[26] the rate ratio of 6.47 for the *endo*- to *exo*-norbornanols is close to the maximum of 7 based on strain energy measurements. If only strain relief is important, then one must draw the unlikely conclusion that most of the strain must be released in the transition state. This unlikely conclusion is unnecessary if one considers steric hindrance to solvation to be as important as relief of steric strain.

As can be seen from the free energy diagrams in Figures 5 and 6, both the relief of steric strain and the steric hindrance to solvation arguments involve greater changes in the ground states than the transition states of a pair of alcohols. As Wiberg[19b] points out, the only important energy differences are between the reactants and transition states and species along the way have no bearing on rates. However, the distinction between the two explanations, relief of steric strain and steric hindrance to solvation, is still important since they offer different reasons for the ground state differences of two alcohols which lead to different predictions. In particular, solvent effects on rate ratios and large rate ratios with respect to strain differences are better accounted for by steric hindrance to solvation differences.

In conclusion, we feel that the larger K for cerium(IV)–alcohol complex formation for *cis*-4-*t*-butylcyclohexanol than for the *trans* isomer and the analysis of existing rate data for the chromic acid oxidation of stereoisomeric pairs of alcohols suggest that steric hindrance to solvation must be considered as well as relief of strain energy as an explanation for rate differences of metal ionoxidations of stereoisomeric pairs of alcohols. The magnitude of the ratio of the K's for the cerium(IV)–alcohol complexes with the axial and equatorial alcohols are of the same order of magnitude of most rate ratios for chromic acid oxidation pairs of stereoisomeric alcohols, and thus differences in steric hindrance to solvation alone could account for the rate ratio. However, it is quite possible that both effects, relief of steric strain and steric hindrance to solvation, are important.

Experimental Section

General. Routine equipment and methods have been previously described.[27] Absorption measurements were made with a Beckman Model DU spectrophotometer using Beckman 1-cm matched silica cells. The temperature of the cell holder was kept constant by use of a Haake constant-temperature circulator to circulate water through the cell holder jackets. Most of the calculations were done on the Iowa State University IBM Series 360 Model 50 computer using the least-squares computer program RAWDAT.

Materials. Some materials have been described previously.[28] All other reagents and alcohols except those described below were obtained from commercial sources and purified by distillation or recrystallization when necessary.

Cyclobutylcarbinol. Cyclobutanecarboxylic acid was prepared from diethyl malonate and trimethylene dibromide by the method of Cason and Rapoport.[29] The acid was reduced with lithium aluminum hydride to the alcohol,[30,31] bp 53–55° (7 mm), lit.[31] bp 142–423.5° (760 mm); nmr (CCl_4) δ 3.72 (s, 1, –OH), 3.46 (d, 2, $J = 6$ Hz, $-CH_2O-$), 2.80–1.50 (m, 7).

4-Phenylbutanol was prepared by lithium aluminum hydride reduction of[30] 4-phenylbutyric acid and purified by distillation, bp 105° (1.6 mm), lit.[32] bp 140° (14 mm).

***cis*- and *trans*-4-*t*-Butylcyclohexanols** were obtained as a mixture from Aldrich. The composition of the mixture was found to be 26.9% *cis* and 73.1% *trans* by glpc analysis. Pure *trans* was separated from the mixture by column chromatography as outlined by Winstein and Holness.[21a]

General Procedure for Measurement of the Equilibrium Constants. A quantity of 25 ml of a solution of the alcohol in acetonitrile, usually 1.0 M, was prepared. A quantity of 3.0 ml of a freshly prepared 0.0660 M ceric ammonium nitrate solution in 1.64 M nitric acid was diluted to 10 ml with acetonitrile. The absorbance at 520 mμ was measured as rapidly as possible. A quantity of 3.0 ml of the ceric ammonium nitrate–nitric acid solution was pipetted into a 10-ml volumetric flask, a few milliliters of acetonitrile was added, and 2.0 ml of the alcohol solution was added. The time was noted and the solution was diluted to 10.0 ml with acetonitrile. A portion of the solution was transferred to a cuvette, the cuvette was placed in the spectrometer with the cell holder held at 21.0°, and the absorbance at 520 mμ was measured at 1.0, 1.5, and 2.0 min after the first time noted. This procedure was repeated using 3.0, 4.0, and 5.0 ml of the alcohol solution.

If there was a decrease in absorbance of the cerium(IV)–alcohol solution during the time the absorbance was measured, the absorbance value used in calculating the equilibrium constant was determined by extrapolating absorbance to zero time, usually assuming that absorbance decreased linearly with time. In a few cases the solution faded so rapidly during the absorbance measurement at the highest alcohol concentration that this point could not be used in calculating the equilibrium constant.

Modified Procedures. In addition to 70% aqueous acetonitrile as a solvent for the equilibrium constant measurements, 70% aqueous acetic acid, water, and water with added salts were used. For the measurements in 70% aqueous acetic acid and water, glacial acetic acid and water were substituted for acetonitrile in the general procedure described above. For measurements in water with added salt, the appropriate amount of salt was added to the solid CAN before dissolution and dilution.

Formation constants for cerium(IV)–alcohol complexes with *cis*- and *trans*-4-*t*-butylcyclohexanols were measured in 0.01 M instead of 0.02 M CAN solutions.

Acknowledgment. We thank Gracie L. Brown[33a] and Robert Wayne Shaw[33b] for the preparation of some of the alcohols and Professors T. A. Beineke, J. H. Espenson, and G. A. Russell for helpful discussions.

Appendix

Justification of the Use of Eq 4. Substitution of the expressions for K_a and K_b into eq 4 gives eq 6. From eq 6 it is seen that K_{app} is equal to the sum of the concentrations of the two cerium(IV)–alcohol complexes

$$K_{app} = \left(\frac{[\text{complex a}]}{[A][Ce^{IV}]}\right)\left(\frac{[A]}{[A] + [B]}\right) + \left(\frac{[\text{complex b}]}{[B][Ce^{IV}]}\right)\left(\frac{[B]}{[A] + [B]}\right) = \frac{[\text{complex a} + \text{complex b}]}{[Ce^{IV}]([A] + [B])} \tag{6}$$

divided by the concentration of cerium(IV) times the sum of the concentrations of the two alcohols. Since K_a/K_b must be a constant over a range of alcohol concentrations, it can be seen from eq 7 that the ratio of the

$$K_a/K_b = ([\text{complex a}]/[A][Ce^{IV}])/([\text{complex b}]/[B][Ce^{IV}]) = [\text{complex a}][B]/[\text{complex b}][A] \tag{7}$$

concentrations of complex a to complex b must remain

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(26) Footnote 14 of ref 19f.

(27) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

(28) W. S. Trahanovsky, L. B. Young, and G. L. Brown, *ibid.*, **32**, 3865 (1967).

(29) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(30) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

(31) H. Pines, H. G. Rodenberg, and V. N. Ipatieff, *ibid.*, **75**, 6065 (1953).

(32) J. von Braun, *Ber.*, **44**, 2871 (1911).

(33) (a) National Science Foundation College Teacher Research Participant, Summer, 1966; (b) National Science Foundation Undergraduate Research Participant, Summer, 1967.

constant as long as the ratio of the concentrations of A to B remains constant. Therefore, over a range of alcohol concentrations where the ratio of the two alcohols is constant, the apparent extinction coefficient of the complexes should remain constant and the method used to calculate the K's for the pure alcohols should be applicable for the calculation of the K_{app} for a mixture of alcohols.

Oxidation of Organic Compounds with Cerium(IV). VIII. Oxidation of Bicyclo[2.2.1]-2-heptanols and Bicyclo[2.2.2]-2-octanol[1]

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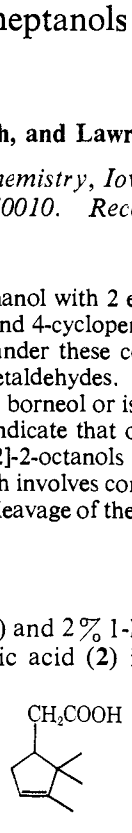
Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. *Received March 4, 1969*

Abstract: It is reported that oxidation of either *exo*- or *endo*-2-norbornanol with 2 equiv of ceric ammonium nitrate in 50% aqueous acetonitrile at 50° gave three major products, 3- and 4-cyclopenteneacetaldehydes and 3-nitratocyclopentaneacetaldehyde. Oxidation of bicyclo[2.2.2]-2-octanol under these conditions was found to give 4-cyclohexeneacetaldehyde, and *cis*- and *trans*-4-nitratocyclohexaneacetaldehydes. Structure proofs for these products are described. The major product from the oxidation of either borneol or isoborneol under these conditions was found to be α-campholenic aldehyde. These results clearly indicate that oxidative cleavage is the preferred mode of oxidation of bicyclo[2.2.1]-2-heptanols and bicyclo[2.2.2]-2-octanols by ceric ammonium nitrate. From these and other experimental results a mechanism is proposed which involves complex formation between the cerium(IV) and alcohol followed by decomposition of this complex with cleavage of the C_1–C_2 bond to give a radical which is then oxidized by another ceric species.

Norcamphor has always been the oxidation product of all previously reported oxidations of either *exo*- or *endo*-2-norbornanol. These oxidations include an Oppenauer oxidation[2] and oxidations by chromium trioxide,[3,4] ammonium vanadate,[5] peroxides in carbon tetrachloride,[6] and nitric acid.[7] No product from oxidative cleavage was reported in these studies.

Most previously reported oxidations of borneol and isoborneol also produced the ketone. Camphor has been obtained from these alcohols by nitric acid oxidation,[7,8] Oppenauer oxidations,[7,9] and oxidation by hypobromite salts.[10] However, oxidation of isoborneol by chromium trioxide is reported to give 2% α-campholenic acid (**1**) and 2% 1-hydroxy-1,2,2-trimethyl-3-cyclopentaneacetic acid (**2**) in addition to 96% camphor.[11]



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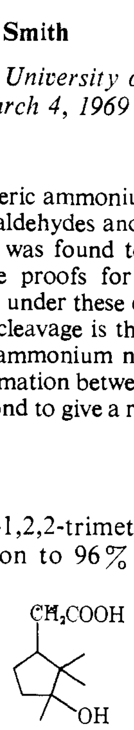
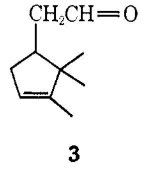


2

The lead tetracetate oxidation of isoborneol at 80° in benzene has been reported to give α-campholenic aldehyde (**3**), 2,2-dimethyl-3-methylenecyclopentaneacetaldehyde (**4**), and camphor in a ratio of 12:8:1, but absolute yields were not reported.[12,13] At 25°, only camphor and camphene were produced.



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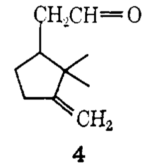

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We have found that unlike previously reported oxidations of these bicyclo[2.2.1]-2-heptanols, the ceric ammonium nitrate (CAN) oxidation of these alcohols leads exclusively to products of oxidative cleavage. In this paper we report a study of the CAN oxidation of these alcohols and bicyclo[2.2.2]-2-octanol.

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[1] (a) Part VII: L. B. Young and W. S. Trahanovsky, *J. Am. Chem. Soc.*, **91**, 5060 (1969). (b) This work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences. The mass spectrometer and Varian Model HA-100 nmr spectrometer were purchased with funds from the National Science Foundation and the Iowa State Alumni Research Foundation. We thank these organizations for their support. (c) Based on work by P. J. F. in partial fulfillment of the requirements for the degree of Master of Science at Iowa State University. (d) Preliminary communication: Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p 166 S.

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[3] H. K. Hall, *J. Am. Chem. Soc.*, **82**, 1209 (1960).

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[5] C. Cohen, U. S. Patent 2,991,308 (July 4, 1961); *Chem. Abstr.*, **49**, 7529 (1955).

[6] W. J. Jackson, *Ind. Eng. Chem. Prod. Res. Develop.*, **3**, 100 (1964).

[7] H. Toivonen, *Soumen Kemistilehti*, **30A**, 130 (1957); *Chem. Abstr.*, **51**, 17832 (1957).

[8] (a) S. Ando, *Nippon Senbai Kosha Chuo Kenkyusho Kenkyu Hokoku*, 41 (1956); *Chem. Abstr.*, **53**, 18975 (1959); (b) B. G. S. Acharya, R. C. Shah, and T. S. Wheeler, *J. Univ. Bombay*, **11A** [5], 113 (1943); *Chem. Abstr.*, **37**, 5957 (1943).

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[10] M. Metayer and S. Roumens, *Compt. Rend.*, **225**, 1324 (1947).

[11] W. A. Mosher and E. O. Langerak, *J. Am. Chem. Soc.*, **73**, 1302 (1951).

[12] R. E. Partch, *J. Org. Chem.*, **28**, 276 (1963).

[13] Professor R. E. Partch has informed me that the absolute yield of products 3 and 4 was 65%.