gel, and eluting with methylene chloride gave 48 mg (98%) of phenyl dithiocarbonate (**11**), mp 39–41° (lit.[29] mp 41°).

Control Experiment. All of the ethylenes **4** were shown to be photostable in the absence of sensitizer, except the yellow ylide **9** which served as its own sensitizer. Furthermore, none of the ethylenes reacted with molecular oxygen in the dark. Photooxygenation at −78° and slow warming of the solutions to room temperature in the dark were not accompanied by luminescence. In fact, treatment of tetrakis(benzylthio)ethylene (**4c**) with an excess of the triphenyl phosphite–ozone complex[15] at −20° in the dark produced benzyl dithiooxalate (**6c**) and benzyl disulfide (**7c**) in appreciable amounts, as evidenced by tlc analysis of the product mixture, but again no luminescence was observed.

Acknowledgments. We are grateful for financial support by the National Science Foundation, the Petroleum Research Fund, and the A. P. Sloan Foundation. Particular thanks goes to Dr. D. Seebach of the University of Giessen (Germany), who generously supplied several starting materials. Also, we appreciate a gift sample of benzyl mercaptan from the Evans Chemical Co.

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One-Electron *vs.* Two-Electron Oxidations. Cerium(IV) and Cyclobutanol[1]

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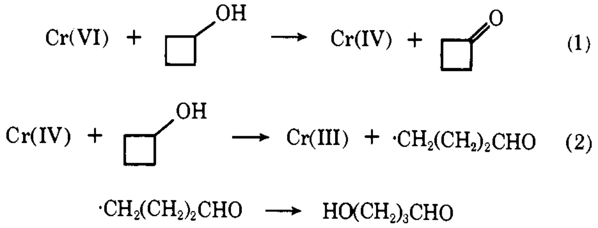
Abstract: Cyclobutanol reacts with cerium(IV) 10^3–10^5 times faster than cyclopentanol to yield products derived only from the ring-opened free-radical intermediate, $\cdot CH_2(CH_2)_2CHO$ (I). Nearly all of the cyclobutanol oxidation products in water or aqueous perchloric acid solution arise from radical dimerization or disproportionation. In aqueous sulfuric acid or in acetonitrile the intermediate, I, is further oxidized through direct electron transfer or by ligand transfer from the oxidant. In the presence of molecular oxygen the ligand transfer reaction is suppressed and succinaldehyde is the only isolable product. Products from the cerium(IV) oxidation of 1-methylcyclobutanol are analogous to those from the cyclobutanol oxidation. The results of this study support the contention that oxidation of cyclobutanol by one-electron oxidants proceeds selectively with ring cleavage. These results are discussed in terms of the unique reactivity of cyclobutanol toward one-electron oxidants and the utility of cyclobutanol in classifying one- and two-electron transfer oxidations.

We have recently found that cyclobutanol reacts with chromic acid to give a mixture of two products, cyclobutanone and γ-hydroxybutyraldehyde.[2] Chromium(VI) reacts with cleavage of the carbon–hydrogen bond to give the cyclic ketone, whereas chromium(IV) yields the acyclic hydroxyaldehyde by cleavage of the carbon–carbon bond (Scheme I).

Scheme I



With these results it was tempting to speculate that cyclobutanol could serve as a useful probe for distinguishing between one- and two-electron oxidizing agents. For this purpose it would be necessary for cyclobutanol to react generally with carbon–carbon bond cleavage in one-electron oxidations and with carbon–hydrogen bond cleavage in two-electron reactions. We were encouraged by the finding that both Mn(III) and V(V), known to be one-electron oxidizing agents, easily convert cyclobutanol to γ-hydroxybutyraldehyde in high yield.[2b] In order to further test the general usefulness of cyclobutanol as a classifying agent for one- and two-electron oxidants of alcohols, we undertook this study of the Ce(IV) oxidation of cyclobutanol.

Experimental Section

Materials. All ceric solutions were prepared from ceric ammonium nitrate (CAN) (G. F. Smith Chemical Co., analyzed reagent) which was used without further purification.

Cyclobutanol was prepared from cyclopropylcarbinol,[3] and 1-methylcyclobutanol from 5-bromo-2-pentanone and magnesium.[4] Commercially available cyclopentanol (Aldrich) was used. All alcohols were purified by preparative glpc.

All carbonyl compounds, except those described below, were obtained from commercial sources. γ-Nitrobutyraldehyde was prepared from acrolein and nitromethane using Shechter's procedure.[5] γ-Hydroxybutyraldehyde was prepared *in situ* by the hydrolysis of 2,3-dihydrofuran.[6] These carbonyl compounds were

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[1] This investigation was supported by the Petroleum Research Fund (Grant No. 1529-4A), administered by the American Chemical Society.

[2] (a) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, 90, 2986 (1968); (b) A. E. Radkowsky, Ph.D. Thesis, The Catholic University of America, Washington, D.C., 1966.

[3] M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, 11, 171 (1960).

[4] G. W. Cannon, R. C. Ellis, and J. R. Leal, *Org. Syn.*, 31, 74 (1951); Y. Leroux, *Bull. Soc. Chim. Fr.*, 359 (1968).

[5] H. Shechter, D. E. Ley, and L. Zeldin, *J. Amer. Chem. Soc.*, 74, 3664 (1952).

[6] R. Paul, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. Fr.*, 668 (1950).

converted to the 2,4-dinitrophenylhydrazones by conventional methods and used as standards in the product analyses.

γ-Nitratobutyraldehyde 2,4-dinitrophenylhydrazone was prepared by a modified method of W. D. Emmons.[7] A mixture of 140 mg of concentrated HNO_3 and 200 mg of concentrated H_2SO_4 was added to a solution of 100 mg (0.37 mmol) of γ-hydroxybutyraldehyde 2,4-dinitrophenylhydrazone in 10 ml of methylene chloride at 0°. After 30 sec the reaction mixture was poured on 20 g of ice, extracted four times with 20-ml portions of methylene chloride, washed with a 1 *M* solution of sodium bicarbonate, dried ($MgSO_4$), and concentrated. The crude product (90.5 mg, 78%, mp 112–115°) was recrystallized from ethanol to give the pure compound: mp 125°; nmr ($CDCl_3$) δ 4.6 (t, 2, J = 5 Hz), 2.7–2.4 (m, 2), 2.3–2.0 (m, 2).[8]

Anal. Calcd for $C_{10}H_{11}N_5O_7$: C, 38.3; H, 3.52; N, 22.3. Found: C, 38.15; H, 3.49; N, 22.34.

Kinetic Measurements. The reaction rates were determined spectrophotometrically on a Cary 15 spectrophotometer by following the decrease in absorbance of cerium(IV). The wavelength used depended on the initial Ce(IV) concentration and was chosen to give a reasonably large initial absorbance. The wavelengths most frequently used were 310 nm for initial cerium(IV) concentrations of 5×10^{-6} *M*, 350 nm for 10^{-4} *M* cerium(IV) in aqueous solutions, and 430 nm for 10^{-3} *M* cerium(IV) in acetonitrile. The CAN solutions were prepared immediately before use, since it was observed that CAN solutions in perchloric acid and acetonitrile slowly decompose. However, this reaction was too slow to affect any of the kinetic measurements.

An excess of the organic substrate (10–50-fold for cyclobutanol, 500–1000-fold for cyclopentanol) was used in all kinetic measurements. Pseudo-first-order rate constants were calculated from the slopes of plots of the logarithm of the absorbance *vs.* time. The rate constants given are the average of at least two determinations. In aqueous solutions the reactions obeyed good pseudo-first-order kinetics and deviations in the rate constants from multiple determinations were small (less than 3%), with the exception of the high oxidation rates in 1 and 0.1 *M* perchloric acid where the reproducibility was lower (10%). In acetonitrile the plots were curved indicating a decrease or increase in rate with time for cyclobutanol and cyclopentanol, respectively. In these reactions rate constants were calculated from the initial slope of the logarithmic plot.

It is known that at high alcohol concentrations a substantial part of cerium is converted into a cerium–alcohol complex.[9,10] This results in a deviation from first-order dependence on the alcohol at higher alcohol concentration; however, as the equilibrium constants for complex formation are generally low, deviations from second-order rate dependence set in only at alcohol concentrations above 10^{-1} *M*. In our rate studies, alcohol concentrations were generally kept below this limit: the concentrations of cyclobutanol were 10^{-5}–10^{-2} *M*, for cyclopentanol 10^{-4}–10^{-1} *M*.

Isolation of Oxidation Products. Oxidation of Cyclobutanol in Aqueous Solution or in 1 *M* Perchloric Acid. In a typical experiment, 5 ml of an aqueous solution containing 620 mg (1.13 mmol) of CAN[11] was added in about 500 10-μl portions over a period of 40 min to 5 ml of a well-stirred aqueous solution of 200 mg (2.82 mmol) of cyclobutanol. The reaction was practically instantaneous. The yellow color of cerium(IV) could be observed only in the immediate vicinity of the syringe despite the vigorous stirring.

After the addition of cerium(IV) was completed, a saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* hydrochloric acid (60 ml) was added to the reaction mixture and stirred at room temperature for at least 24 hr.[12] The resulting reaction mixture was extracted five times with 50-ml portions of methylene chloride. The organic layers were combined, dried ($MgSO_4$), and concentrated. The crude product mixture was separated by column chromatography with a 50-fold excess of silica gel (0.05–0.2 mm, Merck), using a methylene chloride as solvent, into three components. The fastest moving compound was identified as a mixture of crotonaldehyde and butyraldehyde 2,4-dinitrophenylhydrazones by comparison of the nmr and ir spectrum with the spectra of authentic samples. The ratio of the two compounds was obtained from integration of the nmr spectrum, comparing the areas under the methyl triplet of the butyraldehyde derivative with the olefinic protons of the crotonaldehyde derivative. The results were further checked against the aromatic hydrogen in the 3 position of the ring (δ 9.0, d) which has the same chemical shift for both the butyraldehyde and crotonaldehyde 2,4-dinitrophenylhydrazones. The agreement between the two estimates of the product composition was very good. The absence of the triplet signal at δ 2.9 ppm from the protons α to the carbon–nitrogen double bond was taken as evidence that less than 1% cyclobutanone, if any, was formed.[13]

The second compound was identified as suberaldehyde bis-2,4-dinitrophenylhydrazone: mp 183° (lit. 175, 220°);[14,15] nmr ($CDCl_3$) δ 2.5 (m, 4), 1.6 (m, 8).

Anal. Calcd for $C_{20}H_{22}N_8O_8$: C, 47.81; H, 4.41; N, 22.30. Found: C, 47.76; H, 4.38; N, 22.14.

The last component was identified as γ-hydroxybutyraldehyde 2,4-dinitrophenylhydrazone by comparison of the nmr and ir spectrum with the spectra of an authentic sample. A satisfactory elemental analysis was also obtained.

Oxidation of 1-Methylcyclobutanol in Aqueous Solution. The same reaction and work-up procedure as above was employed. The crude product mixture was separated by column chromatography into two fractions. The faster moving fraction was identified as a mixture of 3-penten-2-one and 2-pentanone 2,4-dinitrophenylhydrazones by comparison of the nmr and ir spectra with those of authentic samples. The ratio of the two compounds was obtained from integration of the nmr spectra.

The slower moving fraction was identified as 2,9-decadione bis-2,4-dinitrophenylhydrazone: mp 183–185° (lit. 185°);[16] nmr ($CDCl_3$) δ 2.5 (m, 4), 2.0 (s, 6), 1.6 (m, 8).

Anal. Calcd for $C_{22}H_{26}N_8O_8$: C, 49.80; H, 4.91; N, 21.15. Found: C, 49.59; H, 4.95; N, 21.40.

Oxidation of Cyclobutanol in 1 *M* Sulfuric Acid. A solution of ceric ammonium nitrate (3.1 g, 5.66 mmol) in 10 ml of 1 *M* sulfuric acid was added dropwise over a period of 2 min to 1.0 g (13.9 mmol) of cyclobutanol in 10 ml of 1 *M* sulfuric acid. The crude product was separated by column chromatography into three components. The fastest moving component was identified as a mixture of crotonaldehyde and γ-nitratobutyraldehyde 2,4-dinitrophenylhydrazone by comparison of the nmr and ir spectra with those of authentic samples. The ratio of the two compounds was obtained from the integration of the nmr spectrum, comparing the areas under the multiplet signal of the olefinic protons in the former compound with the area under the triplet signal of the methylene group adjacent to the nitrate function in the latter one. The absence of a methyl triplet at 1 ppm was taken as evidence that less than 3% butyraldehyde, if any, was formed.

The second component was identified as γ-hydroxybutyraldehyde 2,4-dinitrophenylhydrazone by comparison of the nmr and ir spectra with the spectra of an authentic sample.

The last compound was eluted with methanol and identified as succinaldehyde bis-2,4-dinitrophenylhydrazone: mp 257° (lit. 257°).[17]

Anal. Calcd for $C_{16}H_{14}N_8O_8$: C, 43.14; H, 3.14; N, 25.10. Found: C, 43.10; H, 3.24; N, 24.81.

Oxidation of Cyclobutanol in Acetonitrile. A solution of ceric ammonium nitrate (1.55 g, 2.83 mmol) in 30 ml of acetonitrile was added dropwise over a period of 40 min to 0.5 g (6.95 mmol) of cyclobutanol in 10 ml of acetonitrile. The crude dinitrophenylhydrazones were separated by column chromatography into three components. The fastest moving component (mp 121–123°) was identified as γ-nitratobutyraldehyde 2,4-dinitrophenylhydrazone by comparison of the nmr and ir spectra with those of an authentic sample (see above). A satisfactory elementary analysis was also obtained.

The second component was identified as γ-nitrobutyraldehyde 2,4-dinitrophenylhydrazone: mp 135° (lit. 136°);[5] nmr ($CDCl_3$) δ 4.5 (t, 2, J = 5 Hz), 2.5 (m, 4).

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[7] W. D. Emmons, K. S. McCallum, and J. P. Freeman, *J. Org. Chem.*, **19**, 1472 (1954).

[8] Signals for aldehydic and aromatic protons are not given.

[9] W. H. Richardson in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter IV.

[10] L. B. Young and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **91**, 5060 (1969).

[11] The pH of this solution was about 0.

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

[13] Preliminary experiments with known amounts of crotonaldehyde, butyraldehyde and cyclobutanone indicated that yields between 95 and 98% could be obtained using this procedure.

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[15] H. Schildknecht and W. Föttinger, *Justus Liebigs Ann. Chem.*, **659**, 20 (1962).

[16] G. Soussan and P. Freon, *C.R. Acad. Sci. (Paris), Ser. C*, **262**, 933 (1966).

[17] K. Kahr and C. Berther, *Chem. Ber.*, **93**, 132 (1960).

Table I. Second-Order Rate Constants (k_2, M^{-1} sec^{-1}) for CAN Oxidations of Cyclobutanol and Cyclopentanol at 23°

Solvent	k_2, cyclobutanol	k_2, cyclopentanol	k_2, cyclobutanol/k_2, cyclopentanol
0.010 M $HClO_4$	14	8.8×10^{-3}	1.6×10^3
0.10 M $HClO_4$	2×10^2	7.5×10^{-2}	2.7×10^3
1.0 M $HClO_4$	3.3×10^3	7.5×10^{-1}	4.4×10^3
1.0 M H_2SO_4	1.1	2.7×10^{-4}	4.1×10^3
CH_3CN	6.2	2.2×10^{-5}	2.8×10^5

Table II. Reaction Products in the Oxidation of Cyclobutanol and 1-Methylcyclobutanol with CAN[a]

Expt	Solvent	Volume, ml	Amount, mmol Alcohol	Amount, mmol CAN	R–R[b,c]	$CH_3CH{=}CHC(-X){=}O$[c]	HR[b]:$CH_3CH{=}CHC(-X){=}O$	O_2NOR[b,c]	$O_2N{-}R$[b,c]	HOR[b,c]	$(-CH_2CHO)_2$[c]	Total[c]
				Cyclobutanol[d]								
1	H_2O	6	0.714	0.283	70	18	1.0			5		93
2[e]	H_2O	20	2.82	1.13	56	17	1.0			3		76
3	H_2O	10	2.82	1.13	60	25	1.0			2		87
4	H_2O	4	2.82	1.13	53	34	0.75	5		2		94
5	H_2O	1	2.82	1.13	10	40	0.46	12		5		67
6	$HClO_4$, 1 M	60	2.78	1.13	50	23	1.0			2		75
7	$HClO_4$, 1 M	20	6.95	2.83	48	24	0.85	4		3		79
8	H_2SO_4, 1 M	20	13.9	5.65		59	0.00	11		4	3	77
9	CH_3CN	40	6.95	2.83				61	20	5		86
10[f]	CH_3CN	25	13.9	5.65							84	84
				1-Methylcyclobutanol[g]								
11	H_2O	20	3.50	2.05	48	25	1.0					73

[a] Isolated as 2,4-dinitrophenylhydrazones. [b] R = $(CH_2)_3C(-X){=}O$. [c] Yields, in %, based on Ce(IV) available. [d] X = H. [e] Cyclobutanol added to CAN at once. [f] Oxygen bubbled through oxidation mixture. [g] X = $-CH_3$.

Anal. Calcd for $C_{10}H_{11}N_5O_6$: C, 40.43; H, 3.70; N, 23.55. Found: C, 40.31; H, 3.65; N, 23.69.

The last component was identified as γ-hydroxybutyraldehyde 2,4-dinitrophenylhydrazone by comparison of the nmr and ir spectra with those of an authentic sample.

Reduction of the Crude Oxidation Mixture. Cyclobutanol (5 g, 69 mmol) was oxidized in aqueous solution with 15.5 g (28.2 mmol) of CAN as described above; the oxidant was added dropwise over a 5-min period. The solution was neutralized with potassium carbonate and reduced by the addition of 1.5 g of sodium borohydride (solid) to the stirred reaction mixture. After 15 hr the reaction mixture was extracted 10 times with 20-ml portions of ether. The combined extracts were concentrated to 2 ml by distillation using a 30-cm Vigreux distillation column. The residue was purified by preparative glpc on a $^3/_8 \times 80$ in. Carbowax 20M column at 95°. The alcohol was identified as 3-buten-1-ol by the nmr spectrum: nmr (CCl_4) 6.2–5.6 (m, 1), 5.3–4.9 (m, 2), 3.6 (t, 3, J = 6 Hz), 2.3 (q, 2, J = 6 Hz). Glpc analysis showed the absence of 2-buten-1-ol.

Stability of γ-Hydroxybutyraldehyde under Reaction Conditions. A CAN solution in 1 M sulfuric acid was reduced with ethanol and when the red color of cerium(IV) disappeared, γ-hydroxybutyraldehyde was added. After 1 hr, the 2,4-dinitrophenylhydrazone was prepared in the usual fashion. Analysis of the crude product by tlc using a methylene chloride–ethanol (200:1) solvent system showed the absence of crotonaldehyde 2,4-dinitrophenylhydrazone.

Results and Discussion

Oxidation Rates. Cyclobutanol exhibits an unusually high reactivity toward cerium. Table I gives a comparison of the oxidation rate of cyclobutanol with that of cyclopentanol under a number of conditions under which the oxidation rates of each of the alcohols varied by more than three orders of magnitude. In each case, the cyclobutanol was found to be at least a thousand times more reactive than cyclopentanol.

The high relative reactivity of cyclobutanol toward cerium(IV) is in line with the general high reactivity of this alcohol toward one electron oxidants. Cyclobutanol reacts with chromium(IV) about 20 times faster than isopropyl alcohol[18] and is about 35 times more reactive than cyclohexanol[2] toward vanadium(V). It has also been observed that cyclobutanol is rather reactive toward manganese(III) under conditions under which ordinary alcohols are not oxidized.[2] Cerium(IV) thus shares the unusually high reactivity toward cyclobutanol with other one-electron oxidants, but exhibits it to a larger degree than any other oxidant investigated so far.

On the other hand, the two-electron oxidation of cyclobutanol to cyclobutanone is not particularly fast: cyclobutanol reacts with chromium(VI) only 1.08 times faster than cyclopentanol (in 0.25 M perchloric acid).[19]

The high reactivity of cyclobutanol toward one-electron oxidants in general and in cerium(IV) in particular must be due to the fact that these reactions can proceed with the cleavage of a carbon–carbon bond instead of a carbon–hydrogen bond, and that this reaction is strongly assisted by the relief of strain accompanying the opening of the four-membered ring. *All one-electron oxidants investigated so far do indeed react with cyclobutanol to yield open-chain products.*

Oxidation Products. The products of the oxidation of cyclobutanol by ceric ammonium nitrate were determined in aqueous solution, in aqueous sulfuric or perchloric acid, and in anhydrous acetonitrile. The product analysis for oxidation in these solvents is given in Table II. No cyclobutanone was observed in any of our oxidations under conditions where we could have detected at least 1% of this product.

In the oxidations of cyclobutanol with other one-electron oxidizing agents,[2] γ-hydroxybutyraldehyde was the main oxidation product. However, this prod-

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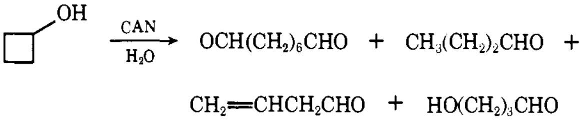
[18] M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455 (1971).

[19] H. G. Kuivila and W. J. Becker, III, *ibid.*, **74**, 5329 (1952).

uct is formed only in very low yield in the cerium(IV) oxidations and never exceeded 5% (Table II). We have been able to show that γ-hydroxybutyraldehyde would survive the reaction conditions and work-up procedures; we can thus safely conclude that the hydroxyaldehyde is only a minor product of the oxidation.

The highest overall yields and probably the most interesting results were obtained in aqueous solution without the addition of mineral acid and under conditions where the solution of the cerium(IV) salt was added very slowly in order to keep the concentration of the oxidant very low at any given time.[20] In addition to the small amounts of γ-hydroxybutyraldehyde, the main products were suberaldehyde and an equimolar mixture of crotonaldehyde and butyraldehyde.

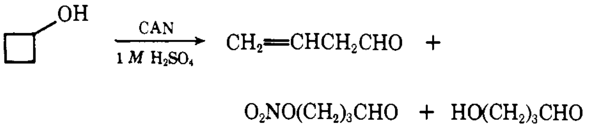
The formation of crotonaldehyde was surprising. We suspected that it was not a direct oxidation product and subsequently determined that the nonconjugated 3-buten-1-al was unstable under our usual work-up conditions and reacted with 2,4-dinitrophenylhydrazine in 2 *M* hydrochloric acid to yield the 2,4-dinitrophenylhydrazone of crotonaldehyde. When the dinitrophenylhydrazones were separated after only 0.5–1.0 hr after the addition of the reagent, a mixture of the conjugated and unconjugated aldehyde-2,4-dinitrophenylhydrazones was found, as under these conditions only a partial rearrangement of the 3-buten-1-al to crotonaldehyde has taken place. When the reaction solution was reduced with sodium borohydride after the oxidation, and the products extracted, only 3-buten-1-ol and no 2-buten-1-ol were found. It is therefore safe to conclude that the main oxidation products are suberaldehyde, 3-buten-1-al, and butyraldehyde formed together with a lesser amount of γ-hydroxybutyraldehyde (eq 3).



(3)

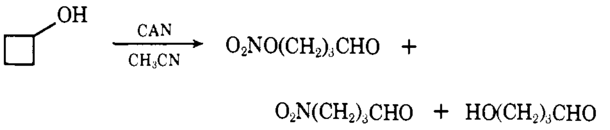
The 1:1 ratio of the unsaturated and saturated aldehyde is preserved even when a higher concentration of ceric ammonium nitrate is used (Table II, expt 3) or when the oxidant and the substrate are mixed at once (Table II, expt 2). Only in experiments 4 and 5, where a very large concentration of ceric ammonium nitrate was employed, does one observe an increase in the yield of the unsaturated aldehyde and the appearance of a new product, a nitrate ester of the hydroxyaldehyde. In 1 *M* perchloric acid the reaction products are the same, although the cerium(IV) concentration has to be kept lower in order to obtain a 1:1 ratio for the unsaturated and saturated aldehydes.

The composition of the reaction products is considerably different if the reaction is carried out in a 1 *M* sulfuric acid solution. Under these conditions no dialdehyde or saturated aldehyde was formed, and main reaction products were the unsaturated aldehyde and nitrate ester (eq 4).

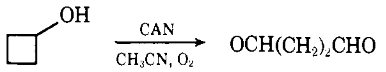


(4)

In acetonitrile γ-nitratobutyraldehyde is the main reaction product together with a sizable amount of γ-nitrobutyraldehyde. Suberaldehyde, butanal, and butenal were absent (eq 5). However, when the reaction was carried out in a stream of oxygen, the only product which could be isolated after treatment with 2,4-dinitrophenylhydrazine was succinaldehyde bis-2,4-dinitrophenylhydrazone, which was formed in high yield (eq 6).

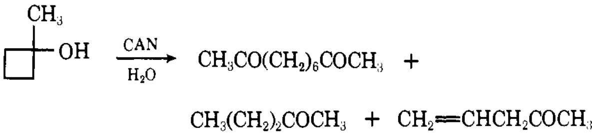


(5)



(6)

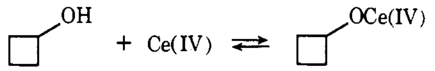
The oxidation products resulting from the reaction of 1-methylcyclobutanol with aqueous ceric ammonium nitrate are quite analogous to those obtained for cyclobutanol (eq 7). The yield of dimerization products is somewhat lower and a proportionately higher amount of disproportionation products is formed with 1-methylcyclobutanol than with cyclobutanol.



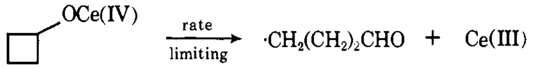
(7)

Mechanism

Both the high reaction rate of the cerium(IV) oxidation of cyclobutanol and the formation of the products which we were able to isolate are in agreement with the mechanism given below (eq 8, 9). The rate-limiting step of the reaction involves the cleavage of the carbon–carbon bond of the strained four-membered ring and leads to a primary free-radical product.[21]



(8)



(9)

In aqueous solution and at low concentration of the oxidant a high enough steady state of the free radical is reached to make bimolecular processes involving two free radicals by far the most important reactions leading to the final products. The radicals either dimerize to suberaldehyde (eq 10) or disproportionate to an equi-

$$2\cdot CH_2(CH_2)_2CHO \longrightarrow OCH(CH_2)_6CHO \qquad (10)$$

molar ratio of 3-buten-1-al and butyraldehyde (eq 11).

$$2\cdot CH_2(CH_2)_2CHO \longrightarrow CH_2{=}CHCH_2CHO + CH_3(CH_2)_2CHO \qquad (11)$$

Only a small fraction of the intermediate reacts with the oxidant to yield γ-hydroxybutyraldehyde (eq 12).

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[20] Because of this technique, it was difficult to estimate the real concentration of cerium ammonium nitrate in the solution.

[21] We have no evidence to support the assumption that the rate-limiting step is preceded by a reversible formation of a cerium–alcohol complex. However, complex formation in the oxidation of alcohols by cerium seems to be generally involved[9,10] and we, therefore, assume that it will occur also with cyclobutanol. The very high rate of reaction of cyclobutanol makes an experimental test for complex formation very difficult.

$$\cdot CH_2(CH_2)_2CHO + Ce(IV) + H_2O \longrightarrow HOCH_2(CH_2)_2CHO + Ce(III) + H^+ \quad (12)$$

At high concentrations of cerium ammonium nitrate the amount of dimerization product decreases sharply and is substituted by products originating from further oxidation of the free radical by ceric ammonium nitrate. One of these products is γ-nitratobutyraldehyde which one can assume to be formed by direct ligand transfer from a molecule of the oxidant to the free radical (eq 13).[22] Another product which now appears in a larger

$$R\cdot + ONO_2Ce(IV) \longrightarrow RONO_2 + Ce(III) \quad (13)$$

amount than would correspond to its formation *via* a disproportionation reaction only is the unsaturated aldehyde. The additional 3-buten-1-al is probably formed directly from the radical by hydrogen abstraction (eq 14). Its formation *via* a carbonium ion by an

$$\cdot CH_2CH_2CH_2CHO + Ce(IV) \longrightarrow CH_2{=}CHCH_2CHO + Ce(III) + H^+ \quad (14)$$

electron-transfer oxidation step (eq 15)[23] is less likely,

$$\cdot CH_2CH_2CH_2CHO + Ce(IV) \longrightarrow \overset{+}{C}H_2CH_2CH_2CHO + Ce(III) \quad (15)$$

as the carbonium ion intermediate would be expected to yield additional amounts of the hydroxyaldehyde together with an increased yield of the olefinic product (eq 16). The products isolated in sulfuric acid solution

$$\overset{+}{C}H_2CH_2CH_2CHO \xrightarrow{H_2O} CH_2{=}CHCH_2CHO + HO(CH_2)_3CHO \quad (16)$$

indicate that reactions 14 and 13 are most important. The formation of the hydroxyaldehyde can be rationalized in terms of reaction 12 or the sequence of reactions 15 and 16.

In acetonitrile, reaction 13 becomes predominant and a new product, γ-nitrobutyraldehyde, appears. Both principal products are obviously derived from a reaction of the free radical with the oxidant. Because we could not isolate any rearranged product, we consider a ligand transfer reaction the most likely pathway.[24] The formation of nitro compound in cerium ammonium nitrate oxidations has been previously observed by T. J. de Boer and coworkers[25] and can be visualized by eq 17.

$$R\cdot + ONO_2Ce(IV) \longrightarrow RNO_2 + OCe(III) \quad (17)$$

The absence of dimerization and disproportionation products in sulfuric acid and acetonitrile solutions raises a question whether one is justified to extend the mechanism given in eq 9 to these systems. A satisfactory conformation of the validity of the free-radical mechanism in acetonitrile was obtained from a successful trapping experiment in which the oxidation was carried out while oxygen was bubbled through the solution. In this experiment no nitrate or nitro compound was formed. The only product isolated in a high yield was succinaldehyde. Obviously, molecular oxygen is more reactive toward the radical than cerium ammonium nitrate. The reaction of the radical with oxygen probably leads to a alkylperoxy radical (eq 18) which then

$$RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot \quad (18)$$

undergoes further oxidation to yield the dialdehyde (eq 19).

$$RCH_2OO\cdot + Ce(IV) \longrightarrow RCHO + Ce(III) \quad (19)$$

Oxidation of the Free-Radical Intermediate. It has been known from the work of Kochi and coworkers that different metal-containing oxidants exhibit rather different reactivities toward free radicals. While some, notably cupric ions,[23] are extremely reactive, other oxidants, *e.g.*, lead tetraacetate,[24,26] react with free radicals slowly enough to allow other reactions, like hydrogen transfer, to take place. Sheldon and Kochi, however, did not observe dimerization of free radicals in the presence of cerium(IV) ions.[27] No dimerization or disproportionation reactions of free radicals in the presence of cerium(IV) salts have been observed by Trahanovsky and coworkers[28] who have carried out a large number of studies concerning cerium(IV) oxidations. The only recorded case of dimer formation in the presence of cerium(IV) seems to be the observation of Schaafsma and coworkers[29] that adipaldehyde is formed in the ceric sulfate oxidation of cyclopropanol. It is clear that the cyclobutanol and the cyclopropanol or cyclopropanone hydrate or hemiacetal systems are closely related through the large ring strain.

The problem of whether the radical will undergo further oxidation or whether dimerization and disproportionation products will occur seems to be determined by the reactivity of both the oxidant and the substrate. In perchloric acid solution and in aqueous solutions of cerium ammonim nitrate cerium is present in a very reactive form. It is therefore understandable that it will react preferentially with the highly reactive cyclobutanol which is present in a very large excess compared with the free radical. Hence, cyclobutanol will successfully compete with the free radical for the oxidant, leading thus to an accumulation of the free radical. The free-radical intermediate can then reach high enough concentrations to yield dimerization or disproportionation products in bimolecular free-radical reactions. On the other hand, cerium(IV) in sulfuric acid or in acetonitrile is much less reactive at least as far as can be judged from the oxidation potentials.[9,30] It will, therefore, react more selectively, attacking the free radical in preference to cyclobutanol despite the much higher concentration of the latter. Under these conditions no products derived from free-radical dimerization or disproportionation are observed. It is interesting to note that dimerization products can be formed even in cerium sulfate oxidations if an even more reactive alcohol competes with the free-radical intermediate. This explains the observation of Schaafsma and coworkers[29] who found mostly dimerization product in

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[22] *Cf.* W. S. Trahanovsky and J. Cramer (*J. Org. Chem.*, **36**, 1890 (1971)) for a recent discussion of this reaction.

[23] J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, **90**, 4616 (1968); J. K. Kochi and J. D. Bacha, *J. Org. Chem.*, **33**, 2746 (1968).

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[30] G. Rao and R. A. V. Moorthy, *J. Phys. Chem.*, **68**, 1573 (1964).

the ceric sulfate oxidation of cyclopropanols and cyclopropanone hemiacetal.[31]

Conclusion

The results of this study confirm that cyclobutanol is uniquely reactive toward one-electron oxidants and reacts with carbon–carbon bond cleavage involving the formation of a free-radical intermediate.

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(31) This interpretation is based on the assumption that cyclopropanol and its derivatives are considerably more reactive to cerium(IV) than even the highly reactive cyclobutanol. While no rate data are reported, the assumption seems at least plausible.

Chromyl Chloride Oxidations. VI. Nature of the Activated Complex in the Electrophilic Addition to Styrenes[1,2]

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Abstract: The kinetics of the rapid chromyl chloride addition to (oxidation of) styrene (**4**) and substituted styrenes, to give the 1:1 chromyl chloride–styrene adducts, have been measured using a spectrophotometric stopped flow system. The rates of addition are increased by electron releasing groups on the benzene ring. α-Methylstyrene is more reactive than *cis*-β-methylstyrene. *cis*-β-Methylstyrene is oxidized at a slower rate than the corresponding trans isomer while *cis*-stilbene reacts almost twice as fast as *trans*-stilbene. 1,1-Diphenylethene is almost twice as reactive as α-methylstyrene and approximately 13 times as reactive as styrene (**4**). The kinetic data suggest an unsymmetrically charged benzylic type carbonium ion like activated complex in the rate-determining step for the chromyl chloride addition to styrenes. The relative rates of oxidation of **4** in carbon disulfide, carbon tetrachloride, chloroform, and CH_2Cl_2 are 1.0:1.1:1.7:5.3. A negligible secondary deuterium kinetic isotope effect of 0.98 is observed in the oxidation of α-deuteriostyrene, and an inverse secondary deuterium kinetic isotope effect ($k_H/k_D = 0.88$) is obtained in the oxidation of β,β-dideuteriostyrene. Large negative entropies of activation ($\Delta S^{\ddagger} = -23.8$ to -42.4 eu) and low enthalpies of activation ($\Delta H^{\ddagger} = 2.0$–$9.0$ kcal/mol) are characteristic of the oxidations. The kinetic data, including the previously observed ρ^+ of -1.99, suggest a rate-determining step involving a partially positive charged benzylic carbon atom in a cyclic epoxide like three-membered ring activated complex or in a partly bridged resonance-stabilized five-membered ring-activated complex. Comparisons of product yields from the chromyl chloride, chromyl acetate, and chromic acid oxidations of unsaturated hydrocarbons suggest that chromyl chloride is the preferred oxidant for a one-step high-yield conversion of 2,2-disubstituted alkenes to aldehydes and ketones. A comparison of the postulated activated complexes for the oxidation of carbon–carbon double bonds by chromic acid, chromyl acetate, and chromyl chloride is also presented.

The chromyl chloride oxidation of unsaturated hydrocarbons is of particular interest because preliminary studies indicate that it might become the most synthetically useful of the readily available and versatile chromium(VI) oxidizing agents for the oxidation of carbon–carbon double bonds to aldehydes and ketones. Oxidation of carbon–carbon double bonds with chromyl acetate and chromic acid can lead to formation of a large variety of compounds, including epoxides, glycols, aldehydes, ketones, acids, and cleavage products. In contrast, chromyl chloride oxidizes unsaturated hydrocarbons to aldehydes and ketones in good to excellent yields without serious side reactions. Table I shows the products from the oxidation of a variety of unsaturated hydrocarbons with chromyl chloride, chromyl acetate, and chromic acid.

Styrenes, which have been postulated as intermediates in the chromyl chloride oxidation of aryl alkanes (Étard reaction),[4,5] react with chromyl chloride to give adducts consisting of one part oxidant and one part reductant.[6,7] Hydrolyses of these adducts under reducing conditions give aldehydes and ketones which result from structural rearrangements (Scheme I).[4,8,9] The yields range from fair to excellent.[1,4,5] Kinetic studies of the electrophilic addition of chromyl chloride to carbon–carbon double bonds have shown that there are several reasonable mechanistic pathways available for reaction. The first kinetic study of the chromyl chloride oxidation of styrene[9] revealed that the reaction is first order in

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