The pattern of behavior of fluorenone triplet may be compared with that of biacetyl.[15,16] The two compounds have similar triplet energies, similar reduction potentials, and similar rates of interaction with triethylamine, 1.7×10^8 and 5.7×10^7 M^{-1} sec^{-1}, respectively.[11] Biacetyl has a low-lying n,π^* triplet and is photoreduced efficiently by alcohols by direct hydrogen transfer, while fluorenone is not photoreduced by alcohols, presumably because of its π,π^* triplet and inefficient intersystem crossing in this solvent. Quenching of biacetyl singlet and triplet by amines follows a pattern similar to that for fluorenone, and biacetyl is photoreduced by primary and secondary aliphatic amines, possibly more efficiently than is fluorenone, but quantum yields were not reported.[15] Biacetyl triplet is quenched by ring-substituted anilines at rates an order of magnitude lower than those of fluorenone but with similar low sensitivity to polar substituents,[16] $\rho = -0.85$. Comparison of aniline NH_2 and ND_2, however, indicated an inverse kinetic isotope effect,[15] $k_H/k_D = 0.52$, apparently arising from the inductive effect of deuterium[12] and indicating no important contribution of H transfer to the quenching interaction. The fairly high rate, apparently without assistance from partial transfer of H, and low sensitivity to substituents in the amine indicate that it is a property of biacetyl to form a stable radical anion. Further, despite the n,π^* character which leads to abstraction of H from alcohols, biacetyl is not photoreduced by N,N-dialkylanilines but is quenched at high rate,[15] $k_q \sim 10^8$–10^9 M^{-1} sec^{-1}, while fluorenone is reduced by these compounds. The

stability of the radical anion of biacetyl is reflected in its low basicity; the pK_a of its ketyl radical is 4.4,[17] compared with 9.2[18,19] for benzophenone and 6.3[19] for fluorenone ketyl. The low basicity, arising from the adjacent, electropositive carbonyl group, leads to low tendency for transfer of a proton from α-C in the CT complex, and charge destruction and quenching dominate. Both the proton-donating power of the α-C of the cationic part and the proton-accepting power of the anionic part of the CT complex affect the quantum yields of photoreduction.

The electron-donating property of the donor, indicated by ionization potential, the electron- and hydrogen-accepting properties of the acceptor, indicated by reduction potential and triplet energy, and the availability of hydrogen for partial transfer from N or α-C in the transition state determine the rates of the initial interaction, k_{ir}.[9,12] In cases where there is much contribution of hydrogen transfer from N or very little from α-C,[20] quenching results, with little photoreduction. Where there is substantial contribution of hydrogen transfer from α-C, photoreduction occurs with good quantum efficiency.

(15) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).
(16) N. J. Turro and T. Lee, *Mol. Photochem.*, **2**, 185 (1970).

(17) J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **70**, 529 (1968).
(18) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961).
(19) E. Hayon, T. Ibata, N. N. Lichtin, and M. Simic, *J. Phys. Chem.*, **76**, 2072 (1972).
(20) J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.*, **38**, 2001 (1973).

Chromic Acid Oxidation of Cyclobutanol[1]

Kenneth B. Wiberg* and Samir K. Mukherjee

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. Received March 1, 1974

Abstract: The chromic acid oxidation of cyclobutanol has been examined in 97% acetic acid. The preoxidation equilibrium steps leading to ester intermediates were characterized by faster rates of esterification and larger ester equilibrium constants than found for isopropyl alcohol. This presumably arises from smaller steric effects with the small cyclic alcohol. The rates of chromium(VI) and chromium(V) oxidations could be determined spectrometrically, and the spectrum of the intermediate chromium(V) species was derived. The oxidation by chromium(IV) was studied by an analysis of the rate of production of cyclobutanone. Both chromium(VI) and -(V) lead to cyclobutanone whereas chromium(IV) leads to cleavage of the four-membered ring.

We have studied the oxidation of isopropyl alcohol by chromium(VI), -(V), and -(IV)[2] and have obtained results which are in good agreement with similar studies by Rahman and Roček[3] using different experimental methods. The oxidation of isopropyl alcohol is relatively simple in that only acetone is formed.

Cleavage products are commonly found in chromic acid oxidation of alcohols, and thus we have applied our experimental approach to one of these compounds, cyclobutanol. This is a particularly useful substrate since Roček and Radkowsky[4] have demonstrated that cyclobutanol gives extensive cleavage to γ-hydroxybutyraldehyde during chromic acid oxidation. The reaction of cyclobutanol with chromium(IV) formed by the chro-

(1) This investigation was supported by a grant from the National Science Foundation.
(2) K. B. Wiberg and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **93**, 2543 (1971); **96**, 1884 (1974).
(3) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455, 5462 (1971).

(4) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **95**, 7123 (1973). *Cf.* W. S. Trahanovsky, *Methods Free-Radical Chem.*, **2**, 133 (1969).
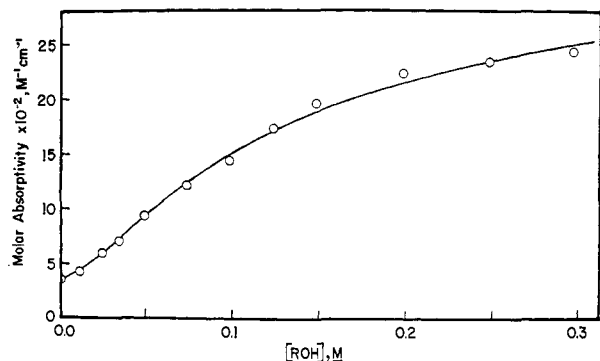
Figure 1. Effect of cyclobutanol concentration on the initial equilibrium molar absorptivity for chromium(VI) in 97% acetic acid. The line represents the calculated values. The conditions were: $[Cr(VI)] = 1.00\text{-}1.15 \times 10^{-3}\ M$, $[H^+] = 0.0125\ M$, $\mu = 0.184\ M$ (NaClO$_4$), $T = 15°$, 385 nm.
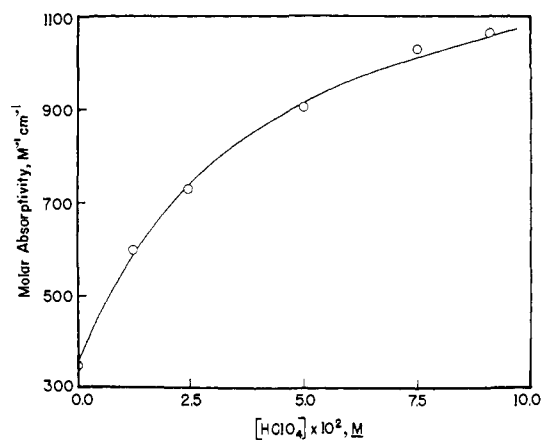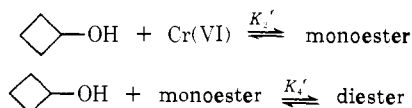

Figure 2. Effect of perchloric acid concentration on the initial equilibrium molar absorptivity for chromium(VI) in 97% acetic acid containing 0.0247 M cyclobutanol. The line represents the calculated values. The conditions were: $[Cr(VI)] = 1.09\text{-}1.18 \times 10^{-3}\ M$, $T = 15°$, 385 nm.
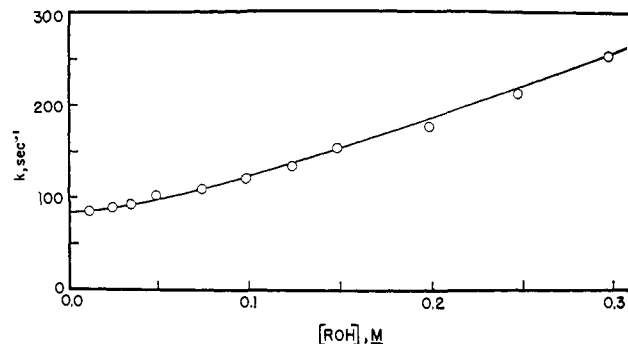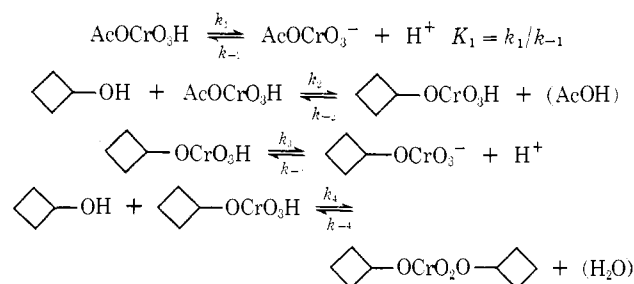

Figure 3. Effect of cyclobutanol concentration on the rate of formation of chromium(VI) esters in 97% acetic acid. The line represents the rate constants calculated using the data given in the text.

A more complete scheme for the preoxidation equilibrium is

The evidence for acetochromic acid as the principal chromium(VI) species as well as for the value of K_1 (0.24 ± 0.02 M) has been presented.[2] In order to separate K_2' into K_2 and K_3, the effect of acid concentration on the preoxidation molar absorptivities was examined using [cyclobutanol] = 0.0247 M. An analysis of these data (Figure 2) gave $K_3 = 0.0108\ M$. The rates of formation of the mono- and diesters were obtained as described previously,[2,5] and a comparison of the calculated and observed rate constants is shown in Figure 3. The final set of constants which describe the preoxidation equilibria are shown in Table I along with the corresponding values for isopropyl alcohol. The con-

mium(VI)–vanadium(IV) reaction leads exclusively to cleavage, suggesting that it is the species responsible for the cleavage.[4]

The oxidation was carried out in 97% acetic acid since in this solvent oxidation of alcohols by chromium(V) is slower than the oxidation by chromium(VI). The several spectrometrically observable steps (ester formation and oxidation by the above chromium species) will be considered separately.

Esterification Equilibria. The initial rapid changes in absorbance on mixing chromic acid and cyclobutanol solutions results from the formation of mono- and diester. The molar absorptivities which are observed just before the onset of the oxidation reaction at 385 nm are shown in Figure 1. The values could be fit to the scheme

using the constants $K_2' = 18.08\ M^{-1}$, $K_4' = 8.10\ M^{-1}$, $\epsilon(Cr(VI)) = 347\ M^{-1}\ cm^{-1}$, $\epsilon(monoester) = 593\ M^{-1}\ cm^{-1}$, and $\epsilon(diester) = 3450\ M^{-1}\ cm^{-1}$ with an rms deviation of 2%. The curve in Figure 1 corresponds to these constants.

Table I. Preoxidation Equilibrium and Rate Constants for the Reaction of Chromium(VI) with Cyclobutanol and Isopropyl Alcohol in 97% Acetic Acid[a]

Constant[b]	Cyclobutanol	Isopropyl alcohol
K_2, M^{-1}	196.3	115.4
K_3, M	0.0108	0.0192
K_4, M^{-1}	15.07	9.21
k_2, $M^{-1}\ sec^{-1}$	58,000	13,200
k_{-2}, sec^{-1}	295	114
k_4, $M^{-1}\ sec^{-1}$	1,340	710
k_{-4}, sec^{-1}	89	77
ϵ_A, $M^{-1}\ cm^{-1}$	529	529
ϵ_{A^-}, $M^{-1}\ cm^{-1}$	306	306
ϵ_M, $M^{-1}\ cm^{-1}$	746	785
ϵ_{M^-}, $M^{-1}\ cm^{-1}$	490	311
ϵ_D, $M^{-1}\ cm^{-1}$	3,450	2,900

[a] 15.0°, 385 nm, $\mu = 0.184\ M$ (NaClO$_4$). [b] A is acetochromic acid, A$^-$ is its anion, M is the monoester, M$^-$ is its anion, and D is the diester.

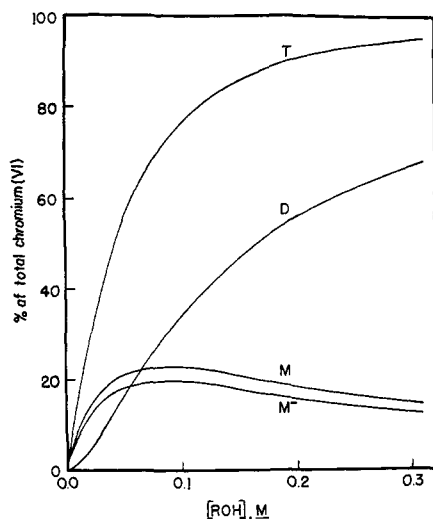(5) K. B. Wiberg and H. Schafer, *J. Amer. Chem. Soc.*, **91**, 927, 933 (1969).

Figure 4. Relative concentrations of monoester (M), monoester anion (M⁻), diester (D), and total esters (T) as a function of cyclobutanol concentration with [H⁺] = 0.0125 M.

centrations of each of the species as a function of cyclobutanol concentration are shown in Figure 4.

The comparison between the two alcohols indicates that cyclobutanol has the larger formation constants for both the mono- and diesters. This results largely from the greater forward rate constants for the esterification steps. The change in rate constants undoubtedly results from steric factors, cyclobutanol being effectively smaller than isopropyl alcohol. It is known that the esterification step is subject to steric effects.

Oxidation Steps. After the initial very rapid change in absorbance on mixing, there follow two successive oxidation steps in which chromium(VI) is converted to chromium(III). The first reaction is easily followed at 385 nm where the absorbance changes are mainly due to the disappearance of chromium(VI). The second may be observed at wavelengths around 540 nm where the absorbance first rises and then decreases to the value characteristic of chromium(III).

In order to fully characterize the reaction, the change in absorbance was observed at 23 wavelengths, and all of the data were fit to the scheme

$$Cr(VI) \xrightarrow{k_a} Cr(V)$$

$$Cr(V) \xrightarrow{k_b} Cr(III)$$
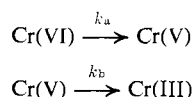
using the method of least squares.[6] A good fit was obtained at all wavelengths using the same values of k_a and k_b. As a result of this calculation, the absorptivities for all of the species were obtained at each wavelength. These data are shown in Figure 5. The curves are very close to those obtained with isopropyl alcohol,[2] indicating that the same species are being observed.

The oxidation steps were studied using 5–6 wavelengths for each set of concentrations, allowing the rate constants k_a and k_b to be determined with little uncertainty. The effect of the cyclobutanol concentration on the rate constants is shown in Table II. It can be seen that the rates of oxidation by chromium(VI) and by chromium(V) first rise rapidly, and then approach a constant value. This is indicated more clearly in

(6) Cf. C. Deutsch, "Computer Programs for Chemistry," Vol. 4, D. F. DeTar, Ed., Academic Press, New York, N. Y., 1972, p 243.
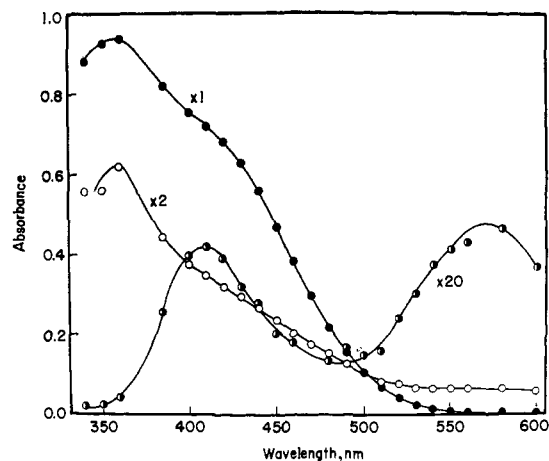

Figure 5. Calculated absorption spectra of chromium(VI) (largely diester (●)) chromium(V) (O) and chromium(III) (◑). The conditions were: [Cr(VI)] = 3.04 × 10⁻³ M, [ROH] = 0.0744 M, [H⁺] = 0.0125 M, μ = 0.184 M, T = 15°.

Table II. Effect of Cyclobutanol Concentration on the Rate of Appearance (k_a) and Disappearance (k_b) of Chromium(V) in 97% Acetic Acid, 15° ᵃ

[Cr(VI)] × 10³, M	[ROH], M	k_a × 10², sec⁻¹	k_b × 10², sec⁻¹
1.11	0.0114	4.4 ± 0.1ᵇ	2.3 ± 0.1ᵇ
1.00	0.0247	6.9 ± 0.1	2.3 ± 0.2
1.14	0.0342	9.6 ± 0.1	3.2 ± 0.1
1.20	0.0494	10.6 ± 0.1	4.6 ± 0.1
1.18	0.0580	13.2 ± 0.1	5.8 ± 0.2
1.08	0.0741	13.5 ± 0.1	6.3 ± 0.4
1.07	0.0988	14.7 ± 0.3	8.6 ± 1.5
1.04	0.1237	15.6 ± 0.1	6.6 ± 0.7
1.16	0.1482	14.9 ± 0.2	7.3 ± 0.4

ᵃ [H⁺] = 0.0125 M, μ = 0.184 M (NaClO₄). The rate constants were obtained using six wavelengths (360–560 nm). ᵇ Average deviation for a set of triplicate runs at each wavelength.

Figure 6. The effect of perchloric acid concentration on the rates of oxidation also was determined giving the data summarized in Table III. Both rate constants

Table III. Effect of Perchloric Acid Concentration on the Rate of Appearance (k_a) and Disappearance (k_b) of Chromium(V) in 97% Acetic Acid, 15.0° ᵃ

[Cr(VI)] × 10³, M	[HClO₄], M	k_a × 10², sec⁻¹	k_b × 10², sec⁻¹
1.00	0.0125	6.9 ± 0.1ᵇ	2.1 ± 0.2ᵇ
1.14	0.0250	11.4 ± 0.1	2.3 ± 0.2
1.18	0.0500	20.8 ± 0.1	3.5 ± 0.1
1.08	0.0750	30.7 ± 0.2	4.7 ± 0.1
1.09	0.0920	36.7 ± 0.4	5.2 ± 0.2

ᵃ [ROH] = 0.0247 M, μ = 0.184 M (NaClO₄). The rate constants were obtained using five wavelengths (360–560 mm). ᵇ Average deviation for a set of duplicate runs at each wavelength.

increased linearly with increasing hydrogen ion concentration (Figure 7).

Since the equilibrium constants for the formation of both mono- and diesters have been obtained, it is possible to obtain the rate constants for the decompositions of each of the chromium(VI) esters from k_a. The values thus obtained were k_M = 0.433 sec⁻¹ and k_D = 0.139 sec⁻¹. The values of k_a which are calculated
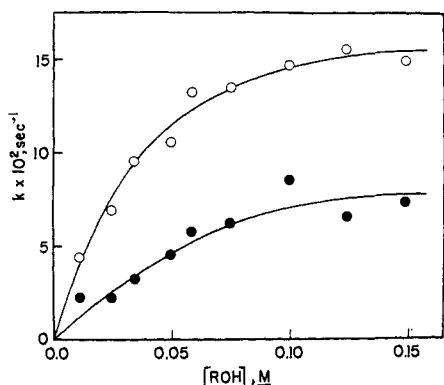
Figure 6. Effect of cyclobutanol concentration on the rate of oxidation by chromium(VI) (O) and chromium(V) (●). The line for chromium(VI) represents the calculated rate constants using $k_M = 0.433\ \mathrm{sec^{-1}}$ and $K_D = 0.139\ \mathrm{sec^{-1}}$.

Figure 7. Effect of perchloric acid concentration on the rate of oxidation by chromium(VI) (O) and chromium(V) (●) in 97% acetic acid containing 0.0247 M cyclobutanol.

using these constants are shown as the upper curve in Figure 6. An excellent fit to the experimental points was obtained. The corresponding curve for the chromium(V) oxidation is drawn to give a good fit to the experimental points and was not independently calculated.

The above rate constants may be compared with those for isopropyl alcohol: $k_M = 0.294\ \mathrm{sec^{-1}}$ and $k_D = 0.174\ \mathrm{sec^{-1}}$. Since the values of k_M depend on just the initial shapes of the preoxidation equilibrium and oxidation rate curves, they are subject to a large and not easily measured uncertainty. Thus, the difference in the two values of k_M may not be significant. On the other hand, the values of k_D are well determined. The value for cyclobutanol is only slightly smaller than that for isopropyl alcohol despite the increase in strain on going from cyclobutanol to cyclobutanone. It is clear that the major factor which leads to the higher overall rate of oxidation of cyclobutanol as compared to isopropyl alcohol is the difference in the equilibrium constants for ester formation.

It is difficult to compare the values for oxidation by chromium(V) because it is not possible to separate the rate constant into an equilibrium constant and a rate constant for the decomposition of the presumed chromium(V) ester. The observed rate constants are greater with cyclobutanol than with isopropyl alcohol.[2] It is probable that this is due to a higher formation constant for ester formation with the former.

Rate of Formation of Cyclobutanone. It is known that both cyclobutanone and γ-hydroxybutyraldehyde are formed in the oxidation of cyclobutanol.[4] Using the kinetic parameters summarized above, it is possible to predict the concentration of cyclobutanone as a function of time based on several possible schemes. A frequently considered, but now less probable scheme, involves only chromium(VI) and chromium(V) (Scheme I). Since chromium(IV) has been shown to effect
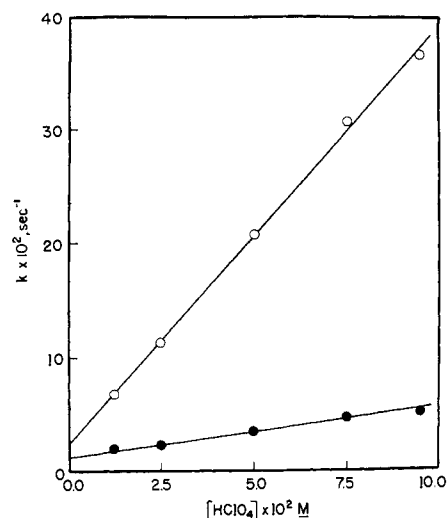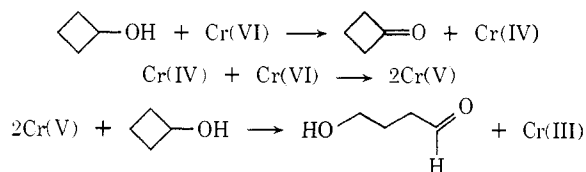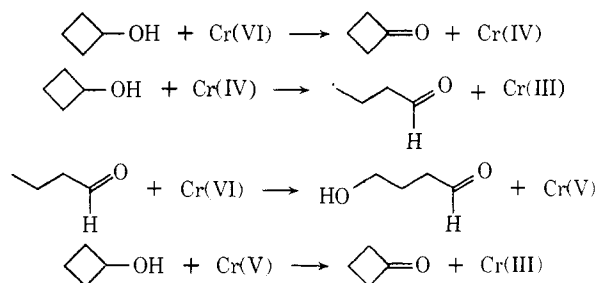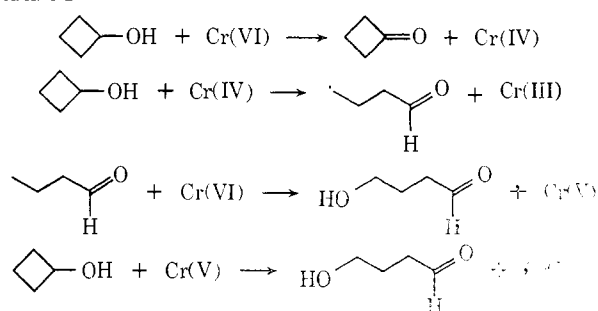
Scheme I

cleavage of cyclobutanol,[4] two other schemes may be considered which differ only in whether chromium(V) gives cyclobutanone or γ-hydroxybutyraldehyde (Schemes II and III, respectively).

Scheme II

Scheme III

Schemes I and III predict 33% cyclobutanone and 67% cleavage whereas Scheme II predicts 67% cyclobutanone and 33% cleavage. Thus, a determination of the amount of cyclobutanone formed after the reaction has been completed will serve to differentiate between Scheme II and the other reaction paths. A study of the rate of formation of cyclobutanone and a comparison with the calculated concentration will give further evidence for a reaction scheme. Such a comparison also will show whether or not the kinetic parameters obtained from the spectrometric studies are correct.

The results of this investigation are shown in Table IV, and a comparison with the calculated curves is pre-

Table IV. Rate of Formation of Cyclobutanone in the Chromic Acid Oxidation of Cyclobutanol in 97% Acetic Acid, 15.0° [a]

Time, sec	[Cr-(VI)], mM	Peak area ratio[b]	[Cyclo-butanone], mM	% cyclo-butanone
1.53	4.66	0.400 ± 0.002	0.906 ± 0.004	13.0 ± 0.1
2.07	4.66	0.594 ± 0.017	1.338 ± 0.038	19.1 ± 0.6
3.59	4.66	0.800 ± 0.015	1.803 ± 0.034	25.8 ± 0.5
4.86	4.36	0.871 ± 0.012	1.963 ± 0.027	30.0 ± 0.4
7.18	4.58	1.222 ± 0.030	2.763 ± 0.068	40.2 ± 1.0
8.67	4.68	1.317 ± 0.001	2.979 ± 0.002	42.4 ± 0.1
10.76	4.34	1.374 ± 0.059	3.117 ± 0.133	47.9 ± 2.0
12.32	4.54	1.469 ± 0.079	3.337 ± 0.178	49.0 ± 1.6
13.20	4.66	1.576 ± 0.005	3.565 ± 0.010	51.1 ± 0.1
15.52	4.38	1.409 ± 0.037	3.206 ± 0.085	48.8 ± 1.3
17.99	4.54	1.598 ± 0.015	3.630 ± 0.035	53.3 ± 0.5
20.16	4.34	1.643 ± 0.008	3.728 ± 0.018	57.3 ± 0.3
21.82	4.54	1.691 ± 0.071	3.824 ± 0.162	56.2 ± 2.3
∞	5.07	2.263 ± 0.046[c]	5.098 ± 0.105	67.0 ± 1.1

[a] [ROH] = 0.0580 M, [H⁺] = 0.0125 M, μ = 0.184 M (NaClO₄). [b] Ratio of areas for cyclobutanone and internal standard. The values are the averages for three gc injections. [c] Average of three runs.

sented in Figure 8. An excellent fit is obtained with Scheme II showing that cyclobutanone is the exclusive product of the oxidation by chromium(V) under the reaction conditions. Roček has studied the oxidation of cyclobutanol by chromium(V) generated by a different reaction and has reached the same conclusion.[7]

The several studies of oxidation by chromium(V) indicate that it behaves in a fashion analogous to chromium(VI). The oxidation of alcohols[2,7] and of aldehydes[8] in aqueous acetic acid by either species leads to a two-electron oxidation and no cleavage. In acetic anhydride, both species again react with aldehydes by the same process—but here a one-electron oxidation is observed.[9] The principal difference between aqueous acetic acid and acetic anhydride is that ester formation with the hydrate of the aldehyde is not possible in the latter medium. This has led us to propose that oxidations of aldehydes by chromium(VI) and -(V) may both involve initially a one-electron transfer.[8] When an ester is the intermediate, the second electron may be transferred intramolecularly leading to an apparent two-electron oxidation. The same may be the case in the oxidation of alcohols. The purpose of the ester intermediate may be to bring the oxidant and substrate into close proximity and thereby facilitate two successive one-electron transfers.[2]

Experimental Section

Materials. Cyclobutanol was prepared by the acid-catalyzed isomerization of cyclopropylmethanol.[10] It was purified by gas

(7) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **96**, 534 (1974).
(8) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **96**, 1889 (1974).
(9) K. B. Wiberg and P. Lepse, *J. Amer. Chem. Soc.*, **86**, 2612 (1964).
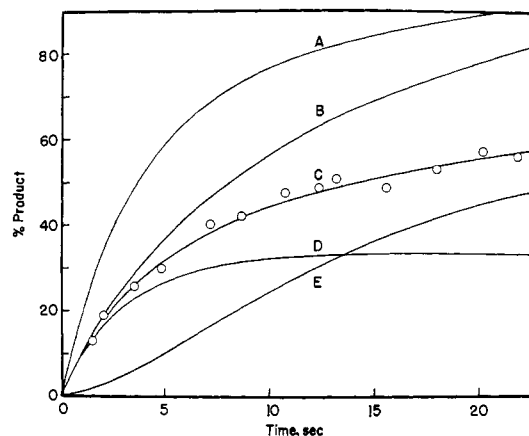
Figure 8. Rate of formation of products in the chromic acid oxidation of cyclobutanol in 97% acetic acid. Curve A gives the calculated total products for Schemes II and III, and curve B gives the corresponding values for Scheme I. Curve C gives the calculated amount of cyclobutanone expected for Scheme II whereas curve D gives the amount of cyclobutanone which would have been produced if Schemes I or III were operative. Curve E gives the amount of product derived from Cr(V) for Scheme I. The circles indicate the experimental data for the formation of cyclobutanone.

chromatography using a 0.75 in. × 7 ft 20% Carbowax 400 column. Cyclobutanone was prepared by the reaction of ketene with diazomethane.[11] Purification was effected by gas chromatography.

The acetic acid solutions were prepared as described previously and contained 97% acetic acid by weight.[2] Chromium(II) perchlorate solutions were prepared by the reduction of chromium(III) perchlorate with amalgamated zinc under nitrogen. The chromium(II) concentration was determined by reaction with excess iron(III) followed by titration of the iron(II) produced with standard potassium dichromate solution using *N*-phenylanthranilic acid as the indicator.

Analytical reagent grade chromium trioxide was dried and stored over phosphorus pentoxide. All other materials were analytical reagent grade.

Kinetics. The reactions were studied using a stopped-flow system as described previously.[2] Data for 5–6 wavelengths (100 points/run with two different time intervals, three runs/wavelength) were analyzed simultaneously by the method of least squares in order to obtain the rate constants, and the absorptivities. In fitting the preoxidation equilibrium data, it was not possible to use the molar absorptivity previously used for diisopropyl chromate (2900). The data required a larger value (3450) in order to fit both the kinetic and equilibrium data.

Stoichiometry Experiments. The concentration of cyclobutanone as a function of reaction time was determined by rapidly mixing chromic acid and cyclobutanol solutions, and then rapidly adding a chromium(II) solution at a given time.[2] The concentration of cyclobutanone in each solution was determined by gas chromatography using a ¹/₈ in. × 7 ft 20% Carbowax 400 column and a flame ionization detector. Diethyl ketone was used as an internal standard. When the reaction was allowed to proceed to completion, the yield of cyclobutanone was 67%. It was not possible to analyze for the cleavage product by gas chromatography as it was not stable under the conditions used.

When the stoichiometry was determined in water using 5 × 10⁻³ M chromium(VI), 0.116 M cyclobutanol, and 0.164 M perchloric acid, the yield of cyclobutanone at complete reaction was 62 ± 1%.

(10) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).
(11) I. V. Machinskaya, G. P. Smirnova, and V. A. Barkhash, *J. Gen. Chem. USSR*, **31**, 2363 (1961).