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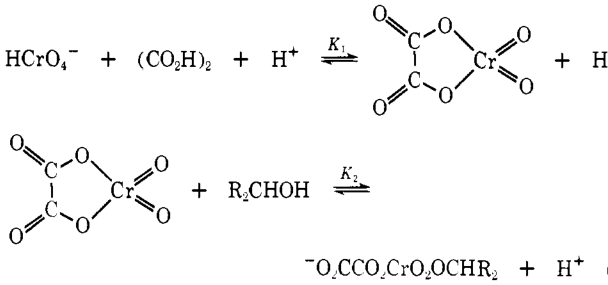
Three-Electron Oxidations. III. The Chromium(V) Oxidation Step[1]

Sir:

In the first paper of this series, we proposed the following mechanism (Scheme I) for the chromic acid cooxidation of oxalic acid and isopropyl alcohol.[2]

Scheme I



(1)

(2)

$$^{-}O_2CCO_2CrO_2OCHR_2 \xrightarrow{k_3} \cdot CO_2^- + CO_2 + R_2CO + Cr(III) \quad (3)$$

$$\cdot CO_2^- + Cr(VI) \xrightarrow{k_4} CO_2 + Cr(V) \quad (4)$$

$$Cr(V) + R_2CHOH \xrightarrow{k_5} Cr(III) + R_2CO + H_2O \quad (5)$$

$$Cr(V) + (CO_2H)_2 \xrightarrow{k_6} Cr(III) + 2CO_2 + H_2O \quad (6)$$

Chromium(V) produced in reaction 4 can react either with isopropyl alcohol (reaction 5) or with oxalic acid (reaction 6).[3] If all chromium(V) formed in reaction 4 reacted with oxalic acid, the total stoichiometry of the reaction would be

$$2Cr(VI) + R_2CHOH + 2(CO_2H)_2 \longrightarrow 2Cr(III) + R_2CO + 4CO_2$$

If, on the other hand, all chromium(V) reacted with isopropyl alcohol, the following stoichiometry would result

$$2Cr(VI) + 2R_2CHOH + (CO_2H)_2 \longrightarrow 2Cr(III) + 2R_2CO + 2CO_2$$

Thus, depending on the concentration of oxalic acid and isopropyl alcohol in the reaction system, the ratio of CO_2:acetone should vary between 4:1 and 1 : 1, provided that the reactivity of chromium(V) toward the two substrates is of comparable magnitude.

Table I and Figure 1 give the dependence of the CO_2:acetone ratio as a function of the isopropyl alcohol:oxalic acid ratio under a variety of conditions.[4] The analyses were carried out under standard conditions at 25°. Acetone was determined gravimetrically as 2,4-dinitrophenylhydrazone from 20-ml samples of the composition given in Table I. Carbon dioxide was determined from a 2-ml sample manometrically in a Warburg apparatus. *The results show that the CO_2:acetone ratio varies within the predicted range and lend significant additional support to the proposed three-electron oxidation process.*

Table I. Effect of Isopropyl Alcohol Concentration on the Ratio of the Products

[*i*-PrOH], *M*	[*i*-PrOH]/[OxH_2][a]	Acetone yield, mmol	CO_2 yield, mmol	CO_2: acetone
(A) [Oxalic Acid] = 0.075 *M*, [Chromium(VI)] = 0.0140 *M*, [Perchloric Acid] = 0.063 *M*				
1.56	40.0	0.280	0.285	1.02
0.78	20.0	0.280	0.290	1.04
0.39	10.0	0.234	0.352	1.50
0.195	5.0	0.218	0.408	1.87
0.098	2.5	0.186	0.468	2.52
0.039	1.0	0.156	0.528	3.38
0.0195	0.5	0.150	0.536	3.58
(B) [Oxalic Acid] = 0.15 *M*, [Chromium(VI)] = 0.0140 *M*, [Perchloric Acid] = 0.125 *M*				
2.34	22.94	0.280	0.290	1.04
1.56	15.29	0.250	0.332	1.33
1.17	11.47	0.250	0.350	1.40
0.78	7.64	0.226	0.384	1.70
0.39	3.82	0.198	0.450	2.27
0.195	1.91	0.176	0.490	2.78
0.098	0.95	0.156	0.536	3.44
0.059	0.57	0.134	0.540	4.03
0.039	0.38	0.140	0.540	3.86
(C) [Oxalic Acid] = 0.15 *M*, [Chromium(VI)] = 0.0157 *M*, [Perchloric Acid] = 0.63 *M*				
3.12	22.84	0.310	0.318	1.02
2.34	17.14	0.295	0.320	1.08
1.56	11.42	0.270	0.390	1.45
1.17	8.57	0.266	0.414	1.56
0.78	5.71	0.250	0.464	1.86
0.39	2.85	0.206	0.534	2.59
0.195	1.42	0.200	0.546	2.73
0.078	0.57	0.176	0.610	3.47
0.039	0.28	0.160	0.644	4.03
0.0195	0.14	0.160	0.640	3.99

[a] [OxH_2] = concentration of undissociated oxalic acid.

In order to estimate the relative reactivity of chromium(V) toward the two substrates, reactions 5 and 6 were rewritten to indicate the mole fraction, *m*, of chromium(V) reacting with the isopropyl alcohol

$$mR_2CHOH + mCr(V) \longrightarrow mR_2CO + mCr(III) \quad (5')$$

$$(1 - m)(CO_2H)_2 + (1 - m)Cr(V) \longrightarrow 2(1 - m)CO_2 + (1 - m)Cr(III) \quad (6')$$

$$m = \frac{k_5[R_2CHOH]}{k_5[R_2CHOH] + k_6[(CO_2H)_2]} \quad (7)$$

The total yield of acetone formed by each two molecules of chromium(VI) reduced is therefore $1 + m$, and

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(1) Part II: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, in press.

(2) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

(3) Actually, at least two different chromium(V) species can be formed, depending on whether the $\cdot CO_2$ radical reacts with free chromic acid or with the chromic acid–oxalic acid complex. As there is sufficient reason to believe that chromium(V) is sufficiently long lived to permit the establishment of a new equilibrium between chromium(V) and the components of the solution, it is not necessary to consider each species separately.

(4) In all substrates ratios given in Table I the cooxidation reaction is by far the most important process taking place. The direct oxidation of isopropyl alcohol accounts for less than 0.5% of the overall reaction, even at the highest alcohol concentration. While the direct oxidation of oxalic acid is more significant, it accounts for a maximum of 16% under the most extreme conditions (lowest alcohol : oxalic acid ratio, last entry in Table I), and is responsible for only 2.7% of the overall reaction containing an equimolar concentration of isopropyl alcohol and of undissociated oxalic acid.

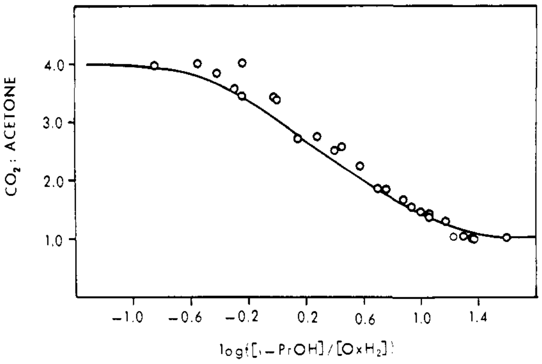

Figure 1. The dependence of the ratio of oxidation products on the substrate ratio in the chromic acid cooxidation of isopropyl alcohol and oxalic acid. The solid line is calculated from eq 9, using the value of $k_5/k_6 = 0.27$.

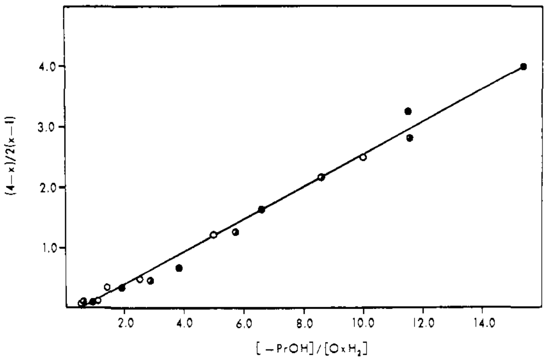

Figure 2. Determination of the relative rates of chromium(V) oxidation of isopropyl alcohol and oxalic acid–perchloric acid: (○), 0.063 *M;* (●), 0.125 *M;* (◑), 0.63 *M.*

the total yield of CO_2 is $2(2 - m)$. The experimental CO_2:acetone ratio, x, is given by eq 8 and 9.

$$\frac{CO_2(\text{yield})}{\text{acetone(yield)}} = x = \frac{2(2 - m)}{1 + m} \qquad (8)$$

$$x = \frac{(k_5/k_6)([R_2CHOH]/[CO_2H]) + 2}{(k_5/k_6)([R_2CHOH]/[CO_2H]) + 0.5} \qquad (9)$$

Equation 10 (from eq 7 and 8) relates the ratio of reaction products to the ratio of the concentrations of the substrates

$$\frac{4 - x}{2(x - 1)} = \frac{k_5}{k_6}\frac{[R_2CHOH]}{[(CO_2H)_2]} \qquad (10)$$

Plotting the data from Table I according to eq 10, one obtains a reasonably good straight line (Figure 2), with a slope $k_5/k_6 = 0.27$. Oxalic acid is thus about 3.7 times more reactive toward chromium(V) than isopropyl alcohol.

This approach is of general utility and will permit the determination of the reactivity of a variety of compounds, relative to oxalic acid, toward chromium(V), provided that they can participate in a cooxidation reaction with oxalic acid similar to isopropyl alcohol.[2]

It is interesting to compare the relative reactivities of the two substrates, oxalic acid and isopropyl alcohol, toward chromium(V) and chromium(VI). Under conditions comparable to these reactions in which chromium(V) reacts 3.7 times faster with oxalic acid than with isopropyl alcohol, chromium(VI) is about 120 times more reactive.[5] The higher reactivity of chromium(VI) toward oxalic acid is most likely due to the availability of the three-electron oxidation mechanism[1] for the latter reaction.

It should be noted that in Figures 1 and 2 all points lie on single lines, regardless of acidity.[6] One can thus conclude that the chromium(V) oxidations of both alcohols and of oxalic acid exhibit the same dependence on acidity. As the chromium(V) oxidation of oxalic acid is independent of acidity,[7] it follows that the chromium(V) oxidation of isopropyl alcohol is also acidity independent within the acidity region covered by the present study. In this respect, the chromium(V) oxidation of isopropyl alcohol differs significantly from the chromium(VI) oxidation, which is well known to be acid catalyzed.[8]

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[5] In 0.097 *M* perchloric acid, the rate of reduction of chromium(VI) by 0.10 *M* isopropyl alcohol is 1.41×10^{-5} sec^{-1} and by 0.097 *M* oxalic acid is 1.70×10^{-3} sec^{-1}.

[6] This is true only provided that undissociated oxalic acid, rather than the total analytical concentration of oxalic acid, is taken into account. This indicates that only undissociated oxalic acid is kinetically active as a reducing agent toward chromium(V). This conclusion parallels our reported findings for chromium(VI).[1]

[7] V. Srinivasan and J. Roček, unpublished results.

[8] F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

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Generation and Reactions of Anions α to the Carbene Carbon Atom of Transition Metal–Carbene Complexes

Sir:

Since stable metal–carbene complexes were first characterized by Fischer[1] in 1964, these complexes have attracted much interest as possible reagents for organic synthesis. To realize this possibility, synthetically useful ways of releasing the carbene ligand from the metal complex and efficient syntheses of a wide variety of metal–carbene complexes must be found. In an attempt to solve the first problem, we recently reported the reaction between metal–carbene complexes and Wittig reagents which gives high yields of vinyl ethers.[2] Here we report the reactions of anions generated α to the carbene carbon atom with electrophilic reagents which allow elaboration upon the structure of simple metal–carbene complexes.

Protons attached to the α-carbon atom in metal–carbene complexes undergo rapid base-catalyzed hydrogen–deuterium exchange with hydroxylic solvents.[3] For instance, the half-life for exchange of the α protons in **1** in acetone–D_2O with no added base is 23 min at 40°.[4] This rapid exchange implies the existence of an intermediate carbanion.

We have now been able to generate solutions of these anions at low temperature in ether solvents. Treatment of a light yellow tetrahydrofuran solution of 50 mg of the cyclic metal–carbene complex **1**[4] at −78°

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[1] E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, 3, 580 (1964); *Chem. Ber.*, **100**, 2445 (1967).

[2] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 94, 6543 (1972).

[3] C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, 7, 390 (1968).

[4] C. P. Casey, *Chem. Commun.*, 1220 (1970).