angular bonded oxygen in Co(acacen)BO$_2$[18] and Co-(salen)BO$_2$.[19] However, any ν_{O_2} absorption may be obscured by strong porphyrin bands in the 900–1500-cm^{-1} region or may be greatly temperature dependent as has been found for Fe($\alpha,\alpha\cdot\alpha,\alpha$-TpivPP)(1-MeIm)-O$_2$.[20] Further studies to resolve this apparent paradox are underway.

Ambient temperature oxygenation of Co(II) porphyrins is not limited to the "picket fence" porphyrins. The five-coordinate complex, Co(TPP)(1-MeIm), 4, in toluene solution does not appreciably oxygenate at 25°, though oxygenation has been detected in toluene glasses at $-195°$.[21] However, treatment of polystyrene-bonded imidazole, 5,[22] with Co(TPP), afforded 6 whose

6
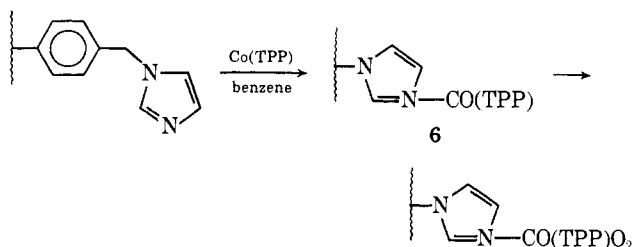
esr spectrum suggests five-coordinate Co(II) ($g = 2.30$). Exposing 6 to dry air or oxygen at 25° gives a new peak at $g = 2.03$ with corresponding decrease in the intensity of the broad peak at $g = 2.30$. As with 2 the degree of oxygenation seems dependent on p_{O_2} but quantitative determination of the extent of oxygenation has not been made.

The greater extent of oxygenation of the "picket fence" cobalt porphyrin, 1, the polymer substituted cobalt porphyrin, 6, and CoHb compared with the structurally similar cobalt porphyrins, Co[(p-OCH$_3$)-TPP]B and Co(PDME)B, at 25° is remarkable. We propose that these equilibrium changes arise from restrictions in the extent of solvation of the unoxygenated and/or oxygenated complexes within the "picket fence" cavity, the solid cross-linked polystyrene, and the globin cavity compared with simple cobalt porphyrins in solution. Whether the effect is enthalpic and/or entropic must await precise measurements of O$_2$ binding constants over a range of temperatures. It is apparent that the oxygen binding site of hemoproteins may experience an environment more like a solid than a solution. This is yet another way in which the protein influences the chemistry of the porphyrin.

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(19) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).
(20) J. P. Collman, R. R. Gagne, H. B. Gray, and J. Hare, *J. Amer. Chem. Soc.*, **96**, 6522 (1974).
(21) H. C. Stynes and J. Ibers, *J. Amer. Chem. Soc.*, **94**, 5125 (1972).
(22) J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 2048 (1973).

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Three-Electron Oxidations. VIII. Direct Evidence for the Synchronous Character of Three-Electron Oxidations[1,2]
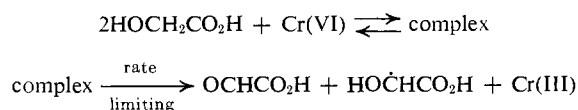
Sir:

We have recently found[3] that a number of chromium(VI) oxidations proceeds through an intermediate formed from one molecule of chromic acid and two molecules of organic substrates. The reaction results in a one-electron oxidation of the second molecule, and we proposed that both of these reactions may proceed simultaneously in a rate-limiting step leading directly from chromium(VI) to chromium(III) without the necessity of forming an unstable chromium(IV) intermediate. We felt that the ability to avoid the formation of the chromium(IV) intermediate is the main reason for the unusual ease with which the oxidative decomposition of these termolecular complexes take place.

However, an alternate mechanism consisting of a rate-limiting two-electron oxidation followed by a rapid one-electron oxidation could not be completely excluded. Such a mechanism would be consistent with our results, provided that the lifetime of the chromium(IV) intermediate was too short to allow any ligand exchange with the solvent or with other substrates to occur. The plausibility of this alternate two-step mechanism has increased as a result of our recent observation that the chromic acid oxidation of alcohols is strongly catalyzed by picolinic acid,[4] and that of iodides by oxalic acid,[5] without any noticeable oxidation of the organic acid.

In all previously investigated cases the one-electron oxidation involved a carbon–carbon bond cleavage in oxalic acid[3a,b,d] or in a tertiary hydroxy acid (2-hydroxy-2-methylbutyric acid).[3c] We now found that the chromic acid oxidation of glycolic acid yields glyoxylic acid, formaldehyde, and carbon dioxide if the oxidation is carried out at relatively low concentrations of glycolic acid; however, only glyoxylic acid is formed at high glycolic acid concentrations. A kinetic study revealed that the reaction proceeds through a transition state containing one molecule of glycolic acid at low concentrations and two molecules of the acid at high concentrations.[6]

At high glycolic acid concentrations the reaction is best described as a three-electron oxidation.

$$2HOCH_2CO_2H + Cr(VI) \rightleftarrows complex$$

$$complex \xrightarrow[\text{limiting}]{\text{rate}} OCHCO_2H + HO\dot{C}HCO_2H + Cr(III)$$

We also found that the chromic acid oxidation of a mixture of isopropyl alcohol and glycolic acid results in a cooxidation reaction leading to acetone and glyoxylic acid. When the reaction is carried out in the presence of acrylonitrile, which acts as a free radical scavenger, only acetone is isolated, indicating that

(1) Part VII: F. Hasan and J. Roček, *J. Org. Chem.*, in press.
(2) This investigation was supported by the National Science Foundation.
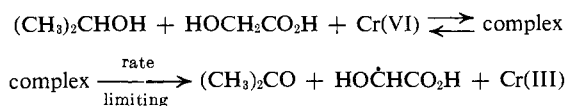(3) (a) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972); (b) *ibid.*, **94**, 9073 (1972); (c) *ibid.*, **95**, 5421 (1973); (d) *ibid.*, **96**, 534 (1974).
(4) J. Roček and T. Y. Peng, to be submitted for publication.
(5) G. Vandegrift and J. Roček, to be submitted for publication.
(6) F. Hasan and J. Roček, to be submitted for publication.

isopropyl alcohol undergoes a two-electron and glycolic acid a one-electron oxidation. In both the three-

$$(CH_3)_2CHOH + HOCH_2CO_2H + Cr(VI) \rightleftharpoons complex$$

$$complex \xrightarrow[\text{limiting}]{\text{rate}} (CH_3)_2CO + HO\dot{C}HCO_2H + Cr(III)$$

electron oxidation of glycolic acid and in the cooxidation reaction, only carbon–hydrogen bonds are broken. This makes it possible to use deuterium substitution to examine whether the two steps occur simultaneously or consecutively. If the rate-limiting step was a one- or two-electron oxidation leading to a discrete intermediate, then an isotope effect of the same magnitude should be observed for the oxidation of glycolic acid at low and high concentrations and only one of the two substrates in the cooxidation should exhibit an isotope effect; a synchronous mechanism should lead to a substantially large isotope effect at high concentrations of glycolic acid, and to a significant isotope effect for both substrates in the oxidation.

Glycolic-d_2 acid was prepared by LiAlD$_2$ reduction from diethyl oxalate, 2-deuterio-2-propanol from acetone.[3a] The kinetic determination of isotope effects was carried out at three concentrations of glycolic acid: at the lowest concentration the reaction proceeded almost entirely (>99.4%) via the 1:1 glycolic acid–chromic acid complex; at high concentrations of glycolic acid the reaction via the 2:1 complex acquires an increasingly important role. The concentrations of isopropyl alcohol and glycolic acid in the cooxidation ensured that 98% of the observed reaction rate was due to the cooxidation reaction.

The results are summarized in Table I. For the

Table I. Chromic Acid Oxidation of Glycolic Acid and Cooxidation of Isopropyl Alcohol and Glycolic Acid at 25°. Perchloric Acid = 0.628 M

Glycolic acid, M	Isopropyl alcohol, M	$10^3 k_H$, sec^{-1}	$10^3 k_D$, sec^{-1}	k_H/k_D
0.0145		0.0826	0.0134	6.15
3.20		4.20	0.334	12.6
6.01		13.3	0.365	36.5
1.56	0.36	33.0	5.50[a]	5.96[a]
			5.70[b]	5.75[b]
			0.96[a,b]	34.4[a,b]

[a] $(CH_3)_2CDOH$. [b] $HOCD_2CO_2H$.

oxidation of glycolic acid alone, the isotope effect found at high substrate concentrations is very large and totally incompatible with any mechanism in which only a single carbon–hydrogen bond is broken in the rate-limiting step. In the cooxidation reaction both compounds, isopropyl alcohol as well as glycolic acid, exhibit an isotope effect of a magnitude typical for primary kinetic deuterium isotope effects. When both substrates are deuterium labeled an isotope effect of $k_H/k_D = 34.4$ is obtained. This value is almost precisely equal to the product of the separate isotope effect obtained for each of the two substrates.

It is interesting to note that the isotope effect for the one-electron oxidation of glycolic acid, both in the cooxidation and in the oxidation of glycolic acid, is of the same magnitude as the effect for the two-electron oxidations. In this respect, the one-electron oxidation

occurring as part of the three-electron oxidation differs remarkably from the much lower isotope effects ($k_H/k_D = 1.7$–2.4) found for one-electron oxidations by chromium(IV),[7] providing additional evidence that the one-electron oxidation taking place within the termolecular complex is quite different from the oxidation by Cr(IV)$_{aq}$.

The results obtained in this study provide conclusive evidence that *the two bond-breaking processes taking place during the three-electron oxidation occur simultaneously. Consequently, the three-electron oxidation itself proceeds in a single step without the formation of an even short-lived chromium(IV) or chromium(V) intermediate.* The rate-limiting steps for the two reactions can be represented as follows.

$$HO\dot{C}HCO_2H + O\dot{C}HCO_2^- + Cr(III)$$

$$HO\dot{C}HCO_2^- + (CH_3)_2CO + Cr(III)$$
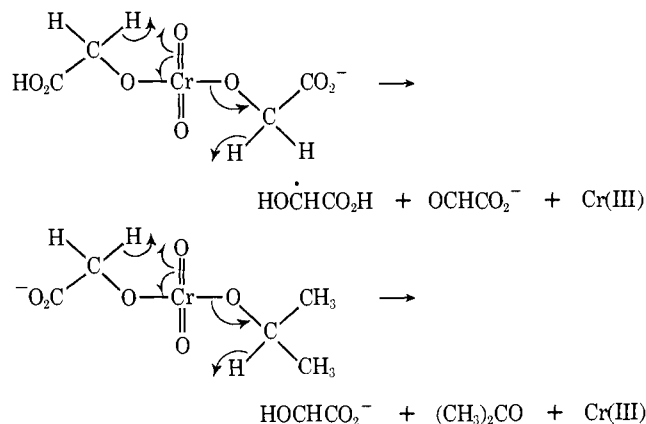
Other transition states involving cyclic complexes between glycolic acid and chromic acid and in which chromium may be octahedral can also be written and should be considered.

(7) J. Roček and C. S. Ng, *J. Amer. Chem. Soc.*, **96**, 1522 (1974).

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Equilibration Studies. Enthalpy Differences between o- and p-Lithioanisoles in Di-n-butyl Ether and Tetramethylethylenediamine

Sir:

Increased understanding of the energies of organometallics will require more thermodynamic information about that class of compounds. However, quantitative thermodynamic data about reactive organometallics has been somewhat difficult to acquire, particularly for the widely used organolithiums and organomagnesiums.[1] We wish to illustrate in this report of the heats

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