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Chain Mechanism for the Autoxidation of the Isopropylchromium(III) Cation

Sir:

Primary organochromium cations in the series $(H_2O)_5CrR^{2+}$ are stable toward molecular oxygen in aqueous solution; exceptions are the benzylchromium(III) ion (which reacts indirectly by unimolecular homolysis[1]) and isopropylchromium(III) ion (and other secondary and tertiary alkyls) whose unusual reaction with O_2 is the subject of this report.

Solutions of $(H_2O)_5CrCH(CH_3)_2^{2+}$ were prepared and purified as before.[2] Kinetic studies of its reaction with oxygen were carried out using both spectrophotometric techniques and an oxygen sensing electrode. In the former case, a gentle stream of a known O_2–N_2 mixture was bubbled continuously through the spectrophotometric cell, but out of the optical path, to ensure a constant concentration of dissolved oxygen.[3]

Attempts were made to fit the data by a number of kinetic equations, but only a rate law with a 3/2-power dependence on $[CrCH(CH_3)_2^{2+}]$ gave an acceptable fit within a given run and a constant value of k_{exp} over the concentration ranges examined. A convincing illustration of the 3/2 order comes from a log-log plot of the instantaneous reaction rate vs. $[CrR^{2+}]_{\mathrm{av}}$. A plot incorporating data from a number of runs is shown in Figure 1. The data were properly analyzed by plots constructed according to the integrated 3/2-order rate law

$$-d[CrCH(CH_3)_2^{2+}]/dt = k_{\mathrm{exp}}[CrCH(CH_3)_2^{2+}]^{3/2}$$

The kinetic data and reaction conditions are summarized in Table I, and the average value of k_{exp} is 0.60 ± 0.10 $dm^{3/2}\ mol^{-1/2}\ s^{-1}$. The reaction rate is independent of both $[H^+]$ and $[O_2]$ over the ranges studied.

The organic products[4] consist of acetone primarily (~60% at 0.002 M H^+ to 70 ± 5% at 0.1 M H^+) and smaller amounts of 2-propanol (~30% at 0.002 M H^+ to ~20% at 0.10 M H^+); 2-propyl hydroperoxide was not detected. Although Cr(III) (a mixture of mainly $Cr(H_2O)_6^{3+}$ and smaller amounts of dimeric species) is the primary chromium product, small but reproducible yields of $HCrO_4^-$ were found (26% at 0.01 M H^+, 13% at 0.1 M H^+, 9% at 0.9 M H^+).

The following chain mechanism is consistent with the data presented:[5,6]

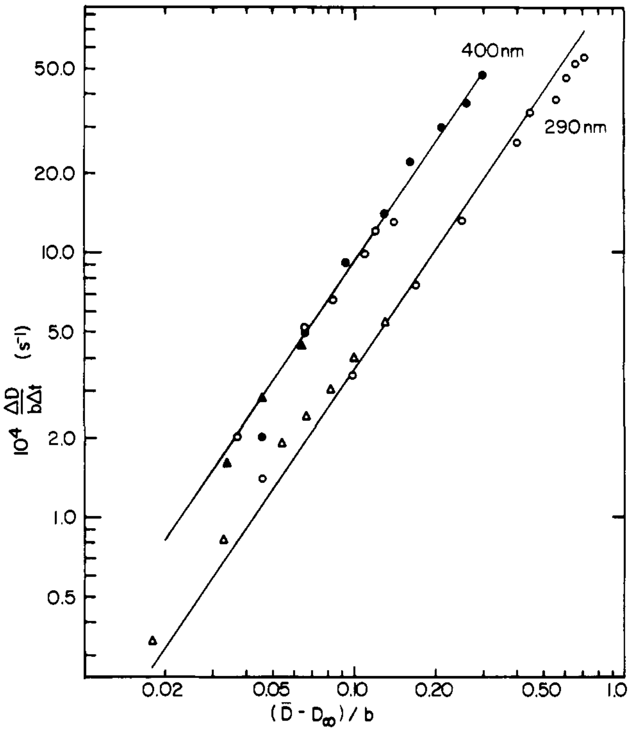

Figure 1. Determination of the 3/2 reaction order from the slopes of plots of log (instantaneous reaction rate) vs. log (mean concentration of isopropylpentaaquochromium(III) ion). Both rates and concentrations are expressed in absorbance units per 1-cm optical path, *D/b*. The plots represent data from four runs at two wavelengths with $10^3[i\text{-}C_3H_7Cr^{2+}]_0$ = 1.0 (●); 0.50 (○); 0.20 (▲); 0.10 (△). The solid lines are drawn to have slopes of exactly 3/2.

Initiation

$$CrCH(CH_3)_2^{2+} \xrightarrow{1} Cr^{2+} + \cdot CH(CH_3)_2 \qquad (1)$$

Propagation

$$O_2 + \cdot CH(CH_3)_2 \xrightarrow{2} \cdot OOCH(CH_3)_2 \qquad (2)$$

$$CrCH(CH_3)_2^{2+} + \cdot OOCH(CH_3)_2 \xrightarrow{3} CrOOCH(CH_3)_2^{2+} + \cdot CH(CH_3)_2 \qquad (3)$$

Termination

$$2\cdot OOCH(CH_3)_2 \xrightarrow{4} (CH_3)_2C{=}O + (CH_3)_2CHOH + O_2 \qquad (4)$$

With the steady-state approximation for the chain-carrying intermediates and the assumption of a long chain length, the derived rate equation shows the proper form and identifies the experimental rate constant as the composite $k_{\mathrm{exp}} = k_3(k_1/2k_4)^{1/2}$.

The mechanism shows the isopropylperoxochromium(III) cation as the immediate product of eq 3. This species is analogous to the well-characterized isopropylperoxocobaloxime, which has been prepared by the reaction of molecular oxygen with isopropylcobaloxime.[7] Since the $CrOOCH(CH_3)_2^{2+}$

Table I. Kinetic Data for the Reaction of O_2 and $(H_2O)_5CrCH(CH_3)_2^{2+}$ in Aqueous Perchloric Acid[a]

	initial concn ranges, M			
	$[H^+]$	$10^3[O_2]$[a]	$10^3[CrCH(CH_3)_2^{2+}]$	k, $dm^{3/2}\ mol^{-1/2}\ s^{-1}$ (runs)
spectrophotometry[b]	0.01–0.10	0.19–1.1	0.1–1.0	0.60 ± 0.10 (26)
O_2 electrode[c]	0.01	0.27	0.09–0.12	0.62 ± 0.11 (2)

[a] Using air, pure oxygen, and a calibrated 52:48 mixture of O_2–N_2. [b] μ = 1.00 M ($HClO_4$, $LiClO_4$); T = 25.0 ± 0.5 °C. [c] $\mu = [H^+]$; T = 22 ± 1 °C.

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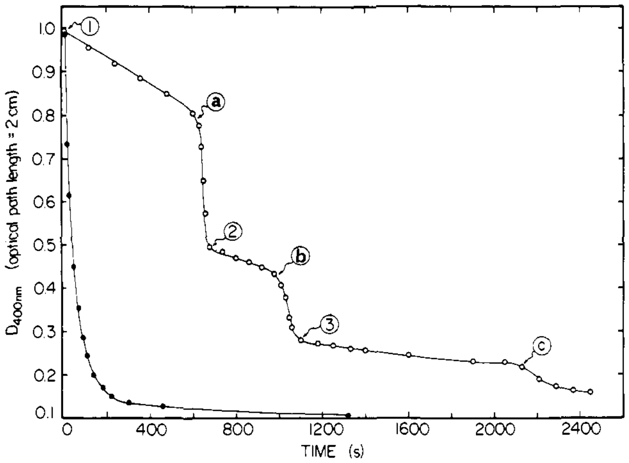

Figure 2. Illustrating the effects of incremental additions of iron(II) ion on the rate of reaction of $CrCH(CH_3)_2^{2+}$ with O_2. The runs shown (○) had $[CrR^{2+}]_0 = 0.95 \times 10^{-3}$ M and $[O_2]_0 = 1.1 \times 10^{-3}$ M (held constant by continuous bubbling). At the three points designated by arrows 1-3, Fe^{2+} was injected; the concentrations (M × 10^3) of Fe^{2+} and $CrCH(CH_3)_2^{2+}$ at these points are, respectively, (1) 0.58, 0.95; (2) 0.28, 0.51; (3) 0.27, 0.29. Points marked a, b, and c are presumably the times at which the inhibiting Fe^{2+} has been consumed, permitting resumption of the rapid chain reaction. For comparison, the continuously decreasing trace (●) shows the steady reaction at approximately the same initial concentration, 1.0×10^{-3} M CrR^{2+}, without added iron(II).

cation has not been identified among the products, it is postulated to react rapidly with H_3O^+ to produce the ultimate products. Considering what is known about the acid decomposition of the cobalt analogue in both nonaqueous[8a] and aqueous[8b] solutions, formation of acetone is readily accounted for by the reaction

$$(H_2O)_5CrOOCH(CH_3)_2^{2+} + H^+ \rightarrow Cr(H_2O)_6^{3+} + (CH_3)_2C{=}O \quad (5)$$

We postulate that the peroxochromium complex, unlike its cobaloxime analogue, is susceptible to internal oxidation-reduction. Such processes are invoked to account for the minor products, $HCrO_4^-$ and 2-propanol, and constitute reasonable chemistry for this species considering other Cr(III)-peroxide reactions.[9] The unavailability of this species for direct study and observation greatly limits further conclusions concerning its reactivity.

Using an estimate for k_1 ($<10^{-6}$ s^{-1}, based on our observation that homolytic scission[1] fails to occur in preference to acidolysis[10] in the presence of other mild oxidants) and the value[11] $2k_4 = 3 \times 10^6$ dm^3 mol^{-1} s^{-1}, the estimated value of k_3 is $\sim 10^6$ dm^3 mol^{-1} s^{-1}, consistent with this reaction being sufficiently rapid to act as a propagating step. The expression for the chain length from this mechanism is

$$\frac{k_3(k_1/2k_4)^{1/2}[CrCH(CH_3)_2^{2+}]^{3/2}}{k_1[CrCH(CH_3)_2^{2+}]}$$

which corresponds to a chain length of 19 000 at $[CrR^{2+}] = 10^{-3}$ M.

Addition of Fe^{2+} prior to or during the reaction produces a dramatic lowering of rate, which we attribute to its chain-breaking reaction with the propagating isopropylperoxy radical:[12]

$$Fe^{2+} + \cdot OOCH(CH_3)_2 \overset{H^+}{=} Fe^{3+} + (CH_3)_2C{=}O + H_2O \quad (6)$$

Provided that iron(II) is added at a concentration less than that of the organochromium cation, the rapid chain reaction will then resume after a substantial subsequent period during which Fe^{2+} is oxidized. Injection of small quantities of Fe^{2+} throughout the reaction gives rise to repeated interruption and reinitiation of the main reaction as shown in Figure 2. During the interrupted segments, the remaining rate is some three-four times faster than the nonradical spontaneous acidolysis, $CrCH(CH_3)_2^{2+} + H_3O^+ = Cr^{3+}_{aq} + C_3H_8$, suggesting that reaction 6 competes favorably but not exclusively with the chain-propagation step. Owing to these factors, the rate during the inhibition period does not provide an independent measure of k_1.[5,13]

The chain mechanism in reactions 1-4 bears a strong resemblance to that claimed in other systems,[14-16] particularly the autoxidation of organoboranes.[17] The results reported here appear to be the first indication of such processes in organochromium chemistry,[18] however, and may be of broader relevance in considerations of the homogeneous activation of molecular oxygen.[19]

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A Novel Phase Transfer Catalyst Capable of Facilitating Acid-Catalyzed and/or Electrophilic Reactions

Sir:

Since the beginning of the 1970s, phase transfer catalysis (PTC)[1,2] has rapidly developed as a synthetic technique. Indeed, the development of and the interest in PTC is as widespread in industrial circles as in the academia. The general