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# Organochromium(III) Complexes Derived from Nitriles

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Reactions of chromium(II) perchlorate with acidified solutions of hydrogen peroxide in water containing modest concentrations of an organic nitrile (RCN) give rise to the cationic organochromium complexes $CrCH_2CN^{2+}$ (RCN = acetonitrile), $CrCH_2CH_2CN^{2+}$ (propionitrile), and $CrCH_2CH(CH_3)CN^{2+}$ (isobutyronitrile). These cyanoalkyl complexes are quite resistant to decomposition in aqueous perchloric acid and can be separated by ion-exchange chromatography. Their composition was established by identification of the organic bromide formed by reaction with aqueous bromine. The complexes react with $Hg^{2+}$ first to form the corresponding $HgR^+$ and then (if excess organochromium is present) $HgR_2$. Kinetic studies for the first stage of this reaction were carried out. The data are consistent with a bimolecular electrophilic substitution process ($S_E2$ mechanism).

## Introduction

A "modified Fenton's reagent", consisting of $Cr^{2+}$ and $H_2O_2$ in aqueous perchloric acid, can be used to generate organochromium cations derived from appropriate organic cosolvents. Thus $CrCH_2OH^{2+}$, $CrCH(CH_3)OH^{2+}$, or $CrC(CH_3)_2OH^{2+}$ is formed when methanol, ethanol, or 2-propanol, respectively, is added prior to reaction.[2-4] It is of interest to examine whether the same method might be extended to other organic substrates, and we thus chose to examine certain alkylnitriles: first to explore the generality of the preparative method, second to learn which organochromium complex(es) might form from a molecule such as propionitrile which has carbon atoms $\alpha$ and $\beta$ to the CN group to which chromium might form a $\sigma$ bond after hydrogen atom abstraction, and third to study the chemistry and reactivity of the organochromium complexes so prepared.

The carbon-centered radicals are produced by a reaction of the hydroxyl radical which is formed in the initial step of the reaction between chromium(II) ions and hydrogen peroxide (eq 1).

$$Cr^{2+} + H_2O_2 \xrightarrow{k_1} CrOH^{2+} + HO\cdot \qquad k_1 = (2.8 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}\,{}^4 \tag{1}$$

When the substrate is acetonitrile, only a single carbon-centered radical is possible. An alternative addition reaction analogous to that found[5] for hydrogen cyanide, $HCN + HO\cdot \rightarrow HC(OH){=}N\cdot$, may occur. The competing reactions are

$$\begin{aligned} CH_3CN + HO\cdot &\rightarrow H_2O + \cdot CH_2CN \\ &\rightarrow CH_3C(OH){=}N\cdot \end{aligned} \tag{2}$$

Indeed, the yield of $CrCH_2CN^{2+}$ is modest, suggesting competitive reaction pathways. On the other hand, with substrates such as propionitrile and isobutyronitrile, two carbon-centered products may arise from hydrogen abstraction.[6] Discounting any addition processes, the competing reactions are

$$\begin{aligned} CH_3CH_2CN + HO\cdot &\xrightarrow{a} H_2O + CH_3\dot{C}HCN \\ &\xrightarrow{b} H_2O + \cdot CH_2CH_2CN \end{aligned} \tag{3}$$

$$\begin{aligned} (CH_3)_2CHCN + HO\cdot &\xrightarrow{a} H_2O + (CH_3)_2\dot{C}CN \\ &\xrightarrow{b} H_2O + \cdot CH_2CH(CH_3)CN \end{aligned} \tag{4}$$

Table I. UV-Visible Spectra of Organochromium(III) Ions Derived from Organic Nitriles

| RCN precursor | complex formed | $\lambda_{max}$/nm ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) |
|---|---|---|
| acetonitrile | $CrCH_2CN^{2+}$ | 528 (30), 406 (80), 260 (3200) |
| propionitrile | $CrCH_2CH_2CN^{2+}$ | 524 (16), 396 (230), 264 (3530) |
| isobutyronitrile | $CrCH_2CH(CH_3)CN^{2+}$ | 530 (14), 398 (238), 265 (3280) |

Only a single organochromium product was isolated from each reaction under the conditions employed. The organochromium complexes formed were $CrCH_2CN^{2+}$, $CrCH_2CH_2CN^{2+}$, and $CrCH_2CH(CH_3)CN^{2+}$. The absence of organochromium cations derived from the $\alpha$-cyanoalkyl radicals produced in reactions 3a and 4a probably arises from their ready decomposition via homolysis as commented upon in the Interpretation and Discussion.

## Results

**Organochromium Cations.** Each reaction was carried out under $Cr^{2+}$-scrubbed nitrogen and occurred as expected, producing a solution having the characteristic UV-visible absorption spectrum of an organochromium complex (Table I). These complexes, whether retained in the reaction solution or isolated as a given species with use of ion-exchange chromatography, proved rather kinetically stable toward protonolysis. In this respect they resembled more such haloalkyl complexes[7] as $CrCH_2Cl^{2+}$, rather than alkyl or hydroxyalkyl complexes[4] which are subject to a more facile protonolysis reaction (eq 5).

$$CrR^{2+} + H_3O^+ \rightarrow Cr^{3+}(aq) + H_2O \tag{5}$$

It was necessary to learn whether a given reaction formed a single organochromium complex or a mixture. Each complex eluted as a single band, but the chromatographic separation, while quite effective in the separation of Cr(III) complexes of different charge and constitution, could not necessarily be relied on to separate two similar organometallic complexes. Therefore we sought to characterize the complex(es) formed on the basis of their reactions. The complexes react with aqueous bromine, as do the simple alkyls,[8] to yield the corresponding cyanoalkyl bromide (eq 6). The organic products

$$(H_2O)_5CrR^{2+} + Br_2 \xrightarrow{H_2O} Cr(H_2O)_6^{3+} + RBr + Br^- \tag{6}$$

from the reaction with the (approximately) equivalent quantity of bromine were extracted into methylene chloride and iden-

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tified by $^1$H NMR as $BrCH_2CH_2CN$ (from $CrCH_2CH_2CN^{2+}$, derived from propionitrile) and $BrCH_2CH(CH_3)CN$ (from $CrCH_2CH(CH_3)CN^{2+}$, derived from isobutyronitrile). The spectra matched published spectra precisely[9] and were particularly clean with not a hint of the products $CH_3CH(Br)CN$ or $(CH_3)_2C(Br)CN$. This establishes that a single organochromium complex, as indicated, had been isolated from the reaction.

**Reaction of (Cyanoalkyl)chromium Ions.** The three complexes examined do not react with such oxidants as $Cu^{2+}$, $Fe^{3+}$, or $Co(NH_3)_5F^{2+}$. Thus neither a direct reaction, as found for the $\alpha$-hydroxyalkyls[3] with $Cu^{2+}$ and $Fe^{3+}$, nor an indirect oxidation via homolysis to $Cr^{2+}$ and cyanoalkyl radical, as found for $\alpha$-hydroxyalkyls and $CrCH_2C_6H_5^{2+}$,[10] occurs. On the other hand solutions of the complexes (except $CrCH_2CN^{2+}$) need to be handled in an inert atmosphere, presumably because there is a direct reaction with $O_2$ as in the case of the isopropylchromium cation $CrCH(CH_3)_2^{2+}$.[11] We did not explore the oxygen reaction further than that, however, and cannot comment on any similarities or differences in mechanism. Surely $O_2$ does not react solely by homolysis; however, for all of the other listed trapping agents for homolysis fragments would then also have reacted.

The reaction with aqueous bromine, referred to in the preceding section, is apparently an electrophilic process as shown by eq 6. Mercury(II) perchlorate reacts readily with the cyanoalkyl complexes, with a variable proportion of the sequential reactions of eq 7 and 8 occurring when $Hg^{2+}$ and

$$CrR^{2+} + Hg^{2+} \rightarrow Cr^{3+} + HgR^{+} \qquad (7)$$

$$CrR^{2+} + HgR^{+} \rightarrow Cr^{3+} + HgR_2 \qquad (8)$$

$CrR^{2+}$ (R = $CH_2CN$, $CH_2CH_2CH_2CN$, or $CH_2CH(CH_3)CN$) are mixed in comparable concentration. The UV spectra showed no $Hg_2^{2+}$ was formed in the reaction because its intense absorption ($\epsilon_{236} = 2.8 \times 10^4$ $M^{-1}$ $cm^{-1}$) was absent. Attempts were made to isolate the $HgR^+$ formed in eq 7 as the $Cl^-$ salt, to confirm the stoichiometry and products shown. Addition of $Cl^-$ and evaporation produced impure mercurous chloride, or RHgCl contaminated with $Hg_2Cl_2$; since $Hg_2^{2+}$ was not formed in the original reaction we can only speculate that it arose from decomposition of RHgCl during workup and isolation.

**Kinetics of Reactions with $Hg^{2+}$.** Although the rates of reaction in eq 7 and 8 can be made competitive at low concentrations of $Hg^{2+}$, a large excess of this ion is sufficient to ensure only eq 7 occurs since $k_8 \ll k_7$. Each reaction, when studied in the presence of a large excess of $Hg^{2+}$, followed a precise first-order kinetic equation, with the absorption spectrum of the organochromium complex completely gone at the end of reaction. This further supports our earlier conclusion that but a single $CrR^{2+}$ is present in solution in that a mixture would have followed a complicated kinetic relationship.

The concentration of $Hg^{2+}$ was varied in each reaction but always maintained in large excess over that of $CrR^{2+}$, the latter typically present initially at (3–7) × $10^{-5}$ M. The pseudo-first-order rate constants are directly proportional to $[Hg^{2+}]$, as depicted in Figure 1. The kinetic data for eq 7 are thus described by the rate law

$$-d[CrR^{2+}]/dt = k_{Hg}[CrR^{2+}][Hg^{2+}] \qquad (9)$$

Values of $k_{Hg}$ ($M^{-1}$ $s^{-1}$) at 25.0 ± 0.1 °C are 9.8 ± 0.3 for $CrCH_2CN^{2+}$, 81.0 ± 3.0 for $CrCH_2CH_2CN^{2+}$, 25.4 ± 0.1 for $CrCH_2CH(CH_3)CN^{2+}$.

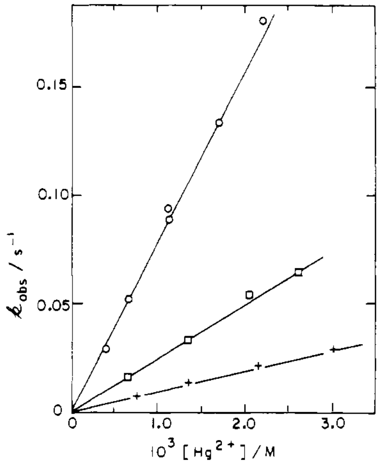

**Figure 1.** Plots illustrating the linear dependence of the pseudo-first-order rate constants for reactions of (cyanoalkyl)chromium(III) complexes with the concentration of mercury(II) ion according to eq 9. The data depicted are for reactions of $CrCH_2CN^{2+}$ (+), $CrCH_2CH(CH_3)CN^{2+}$ (□), and $CrCH_2CH_2CN^{2+}$ (○) at 25.0 ± 0.1 °C and ionic strength 1.0 M in aqueous perchloric acid.

In the studies of $CrCH_2CH_2CN^{2+}$, the rate constant was constant over the range 0.25–1.0 M $H^+$, with ionic strength maintained at 1.0 M by addition of lithium perchlorate. The value of $k_{Hg}$ proved to be independent of $[H^+]$ over this range. In addition, the rate constant for the same complex was evaluated at four temperatures in the range 12.4–30.2 °C. The data were accurately correlated by the activated complex theory equation, the activation parameters being $\Delta H^{\ddagger} = 28.9 \pm 1.9$ kJ $mol^{-1}$ and $\Delta S^{\ddagger} = -111 \pm 6$ J $mol^{-1}$ $K^{-1}$.

## Interpretation and Discussion

One must ask why only the one complex was produced from either of the two nitriles which produce two carbon-centered radicals upon reaction with hydroxyl radicals (eq 3 and 4) and why it is the products isolated correspond to abstraction of a $\beta$-hydrogen atom. We discount the possibility that the published results[6] showing substantial quantities of both carbon-centered free radicals by ESR spectroscopy are in error. While yields were not given, the spectra suggested an appreciable quantity of each is formed. Moreover, it is not plausible that either of the radicals would fail to combine with $Cr^{2+}$ since the reaction $Cr^{2+} + R\cdot \rightarrow CrR^{2+}$ occurs readily for a wide range of free radicals showing but a modest variation in rate with changes in the nature of R·.[11] Also, if one sought to blame the absence of species such as $CrCH(CH_3)CN^{2+}$ and $CrC(CH_3)_2CN^{2+}$ on some reaction of the $\alpha$-cyanoalkyl radicals prior to Cr–C bond formation or to some special instability of $\alpha$-cyanoalkyl complexes, then the formation of the highly stable complex $CrCH_2CN^{2+}$ derived from acetonitrile would be most anomalous. For reasons cited above it is highly unlikely that a second organochromium complex would have gone undetected. Finally, then, we are led to the conclusion that the two $\alpha$-cyanoalkyl complexes (but not $CrCH_2CN^{2+}$) were formed but lost prior to isolation. It is now known[13] that increasing substitution on the carbon atom bound to chromium greatly increases the rate of bond homolysis reactions evidenced by (among other things) the increases in homolysis rate along the series $CrCH_2OH^{2+}$ (≪7 × $10^{-5}$ $s^{-1}$), $CrCH(CH_3)OH^{2+}$ (7 × $10^{-4}$ $s^{-1}$) and $CrC(CH_3)_2OH^{2+}$ (1.3 × $10^{-1}$ $s^{-1}$). For a complex such as that formed from the 2-cyano-2-propyl radical, we propose that decomposition occurs so readily that the

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formation process is reversed and the material lost prior to isolation (eq 10). This proposal requires no special reactivity

$$CrC(CH_3)_2CN^{2+} \rightarrow Cr^{2+} + \cdot C(CH_3)_2CN \qquad (10)$$

for complexes formed from $\alpha$-cyano radicals and is completely consistent with the long lifetime of the relatively unhindered $CrCH_2CN^{2+}$ and with the chemistry of the closely related $\alpha$-hydroxyalkyl analogues. It may be possible to stabilize $CrC(CH_3)_2CN^{2+}$ against homolysis by addition of excess $Cr^{2+}$, just as $CrC(CH_3)_2OH^{2+}$ can be stabilized, but this was not investigated.

The complexes investigated were not subject to detectable homolysis as evidenced by lack of ready reaction with reagents such as $Cu^{2+}$, $Fe^{3+}$, and $Co(NH_3)_5F^{2+}$ which would scavenge a product from a reaction analogous to eq 10. This lack of reactivity is not surprising for these complexes again because the $\alpha$-carbon atom is relatively unsubstituted. And the unhindered $CrCH_2CN^{2+}$, like $CrCH_2OH^{2+}$, would not tend to undergo ready homolysis.

Reactions of $Hg^{2+}$ with alkylchromium(III) complexes have been studied in some detail[14] and are recognized as electrophilic processes involving direct attack of $Hg^{2+}$ at the $\alpha$-carbon. The present data are in keeping with this picture in several respects: (1) an electronegative substituent on the carbon atom bound to chromium (as in $CrCH_2X^{2+}$) greatly lowers the rate of reaction; compare, for example, $CrCH_2CH_3^{2+}$ ($k_{Hg} = 1.40 \times 10^5$ $M^{-1}$ $s^{-1}$)[14] to $CrCH_2Cl^{2+}$ ($5.90 \times 10^{-1}$ $M^{-1}$ $s^{-1}$),[14] $CrCH_2OH^{2+}$ ($2.3 \times 10^2$ $M^{-1}$ $s^{-1}$),[13] and the present $CrCH_2CN^{2+}$ (9.84 $M^{-1}$ $s^{-1}$); (2) substitution $\beta$ to chromium has minimal effect. For example the three complexes studied here all show nearly the same reactivity (within a factor of 9), just as alkylcobaloximes do[15] for the similarly substituted analogues with ethyl, *n*-propyl, and isobutyl groups. Alternatively one can compare the relative reactivities of $CrCH_2CH_3^{2+}$ and $CrCH_2CH_2CH_3^{2+}$ (relative rate, 4.0:1.0) with $CrCH_2CH_2CN^{2+}$ and $CrCH_2CH(CH_3)CN^{2+}$ (3.2:1.0). It should be noted, in view of the well-recognized sensitivity of rates of such reactions to $\alpha$ substituents and their insensitivity to $\beta$ substituents, that the kinetic data provide confirming evidence of the structure assigned to the complexes; complexes derived from the products of eq 3a and 4a would be expected to react very much slower.

## Experimental Section

The chemicals were purchased as reagent-grade materials or prepared as described previously.[4,8,12] The reactions to prepare the new cyanoalkyls were conducted by dripping a deaerated solution of hydrogen peroxide in dilute perchlorate acid into a well-stirred aqueous solution of $Cr(ClO_4)_2$ containing some 3–8% by volume of the desired nitrile until $H_2O_2$ was in ca. 10% excess. The complexes were absorbed onto a column of Dowex 50W-X8 which was then rinsed free of nitrile and excess peroxide with use of 0.02 M perchloric acid, followed by elution of the dipositive organochromium cation with 0.7–0.8 M acid, leaving $Cr(H_2O)_6^{3+}$ on the resin column. The complexes were isolated and stored under nitrogen because they decomposed notably faster when exposed to air. The absorption spectra are given in Table I. The molar absorptivities were based on spectrophotometric analysis of the complexes as chromate ions after heating in alkaline peroxide. Yields of the (cyanoalkyl)chromium(III) ions were not determined, but especially low conversion to $CrCH_2CN^{2+}$ was noted. The $\beta$-cyanoalkyl complexes were also formed in considerably less than the theoretical quantity, consistent with the suggested homolytic decomposition of any $\alpha$-cyanoalkyl complex formed.

Bromination reactions were conducted by slowly adding aqueous bromine in slightly less than the required amount and then extracting products into methylene chloride. Procedures for the kinetic experiments were described previously.[14]

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**Registry No.** $(H_2O)_5CrCH_2CN^{2+}$, 76068-68-3; $(H_2O)_5CrCH_2CH_2CN^{2+}$, 76068-69-4; $(H_2O)_5CrCH_2CH(CH_3)CN^{2+}$, 76068-70-7; $CH_3CN$, 75-05-8; $CH_3CH_2CN$, 107-12-0; $(CH_3)_2CHCN$, 78-82-0; $Hg^{2+}$, 7439-97-6.

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# Kinetics and Mechanism of Iodination of Para-Substituted Benzylbis(dimethylglyoximato)(pyridine)cobalt(III). High Reactivity of the Base-Off Form

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A kinetic study of the iodination of $p$-$XC_6H_4CH_2Co(DH)_2(py)$ (X = methoxy, methyl, H, chloro, nitro; DH = monoanion of dimethylglyoxime; py = pyridine) revealed the rate-determining dissociation of pyridine and subsequent rapid reaction of the base-free form with iodine. The high reactivity of the base-free form is discussed in relation to inner-sphere electron transfer. The rates of dissociation of pyridine showed a Hammett-like linear free-energy relationship with a $\rho^+$ of −1.48.

The mechanism of cleavage of the carbon–cobalt bond is a subject of considerable interest because of the importance in vitamin $B_{12}$ chemistry, and evidence as to the formation and participation of radical species in the cleavage of the carbon–cobalt bond has accumulated in both chemical and biological fields. Reversible generation of organic free radicals and $B_{12r}$ was detected during the coenzyme $B_{12}$-dependent reactions with dioldehydrase[3] and ethanolamine ammonialyase,[4] an alkyl–cobalt bond dissociates on photolysis into an organic free radical and cobalt(II),[5] and free-radical substi-

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