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Oxidation of Azide and Azidopentaamminechromium(III) by Peroxymonosulfate in Aqueous Solution[1a]

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The oxidation of azide by peroxymonosulfate has been studied in acid, neutral, and basic solutions, and the oxidation of $Cr(NH_3)_5N_3^{2+}$ by peroxymonosulfate has been studied in acid. The reaction with azide obeys the rate law $k_1[N_3^-][HSO_5^-]$ in acid and neutral solution and the rate law $k_2[N_3^-][SO_5^{2-}]$ in base. The reaction with $Cr(NH_3)_5N_3^{2+}$ obeys the rate law $k_3[Cr(NH_3)_5N_3^{2+}][HSO_5^-]$. At 25 °C, $k_1 = 0.66$ L/(mol s), $k_2 = 0.0076$ L/(mol s), and $k_3 = 0.013$ L/(mol s). Oxygen-18 tracer experiments show that the reactions proceed by transfer of a terminal peroxide oxygen of the peroxymonosulfate to the reductant.

Introduction

The reactivity of reducing anions in aqueous solution may be expected to vary depending on whether they are present as free ions, are protonated, or are coordinated to substitution-inert metal cations. One such reducing anion is the azide ion, N_3^-. Nitrous acid reacts at comparable rates with HN_3 and with coordinated azido complexes to produce N_2 and N_2O as the sole oxidation products.[2] Most other oxidants, however, show less easily predictable behavior. Thus, while the 1-equiv oxidants Ce(IV), Co(III), and Mn(III) produce a stoichiometric amount of N_2 from HN_3, their reactions with azido complexes are quite complicated.[3] Most multiequivalent oxidants, if they react at all with hydrazoic acid, yield a variety of higher oxidation states of nitrogen in addition to N_2 and N_2O.[4] Under certain conditions BrO_3^- produces a stoichiometric amount of N_2 and N_2O from HN_3, but it is completely unreactive toward azido complexes.[5]

We have found the peroxymonosulfate ion, HSO_5^-, to be an interesting reagent in this context. It reacts rather cleanly with $Cr(NH_3)_5N_3^{2+}$ to produce $Cr(NH_3)_5NO^{2+}$ and N_2 and with HN_3 and N_3^- to produce N_2O and N_2 in a 1:2 ratio. Both systems are amenable to kinetic investigation. We have also determined the source of the oxygen in the nitrosyl complex and the nitrous oxide products by means of oxygen-18 tracer experiments.

Experimental Section

Reagents. $[Cr(NH_3)_5N_3](NO_3)_2$ was prepared as previously described.[6] Sodium azide was recrystallized twice as described by Browne,[7] and solutions were standardized by the cerate procedure.[3a] Potassium peroxymonosulfate was obtained from E. I. du Pont Company as "Oxone", a mixture of composition $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Solutions of this salt were assayed iodometrically. Solutions containing HSO_5^- with the terminal peroxide oxygen enriched in oxygen-18 were prepared by the reaction of HO*F with HSO_4^-.[8] Solutions containing HSO_5^- with all oxygens *except* the terminal peroxide oxygen enriched in ^{18}O were prepared by the reaction of normal HOF with bisulfate that had been enriched in ^{18}O.[8] The enriched bisulfate was made by oxidation of SO_2 with bromine in enriched water.[8] Other reagents were commercial products of analytical reagent grade. Distilled water was redistilled before use first from alkaline permanganate and then from acidic dichromate.

Stoichiometry Studies. The stoichiometry of the reaction between HSO_5^- and $Cr(NH_3)_5N_3^{2+}$ was determined during most of the individual kinetic experiments. After approximately 70% reaction, three aliquots were taken. One was assayed for HSO_5^- by iodometric titration. A second was treated with excess sodium nitrite, which quantitatively converts $Cr(NH_3)_5N_3^{2+}$ to $Cr(NH_3)_5H_2O^{3+}$. The $Cr(NH_3)_5NO^{2+}$ was then isolated from this aliquot by ion-exchange separation at 2 °C and assayed by a total chromium determination.[9] The third aliquot was separated by ion exchange at 2 °C; the chromium content of the 2+ fraction in this aliquot gave the sum of $Cr(NH_3)_5N_3^{2+}$ and $Cr(NH_3)_5NO^{2+}$. Traces of aquo- and sulfatochromium(III) ammine species were observed during this separation. Blank experiments indicated that approximately a 3% loss of $Cr(NH_3)_5N_3^{2+}$ occurs via hydrolysis during the reaction. Separate experiments showed that the "$Cr(NH_3)_5NO^{2+}$" fraction was typically contaminated with about 15% of $Cr(NH_3)_4(H_2O)NO^{2+}$. This latter species was separated by elution with a solution 0.2 M in NaCl and 0.01 M in NaOH. Both $Cr(NH_3)_5NO^{2+}$ and $Cr(NH_3)_4(H_2O)NO^{2+}$ were characterized by visible absorption spectra.[10]

The stoichiometry of the slow reaction between HSO_5^- and azide in acid was determined after approximately 90% reaction by sealing a suitable reaction mixture containing excess HN_3 in a glass ampule and allowing the reaction to proceed at 50 °C. Blank experiments showed that the HSO_5^- and HN_3 separately suffered <2% decomposition in acid solution during the time required (ca. 24 h). The reaction was quenched by cooling the mixture to 0 °C, and the ampule was opened. One aliquot was assayed iodometrically for HSO_5^-. Another was analyzed for HN_3 by injection into a solution of Ce(IV) in 1 M H_2SO_4; the consumption of Ce(IV) was promptly determined spectrophotometrically. This procedure is quite satisfactory provided that the HSO_5^- concentration is low; otherwise a continuous slow consumption of Ce(IV) is observed after the very rapid HN_3 reaction. A mixture of HSO_5^- and Ce(IV) cannot be accurately titrated iodometrically, since very erratic and low titers are obtained. We have no explanation for this observation.

The more rapid reactions between peroxymonosulfate and azide in neutral and basic solutions were allowed to proceed to completion, and the remaining N_3^- was assayed by the cerate procedure. Both reactants were found to be stable individually in the reaction media for the time periods required.

To determine gaseous reaction products, we used a vessel shaped like an inverted Y. An azide solution was placed in one arm of the Y and a peroxymonosulfate solution was placed in the other. After evacuation and outgassing of the system, the two solutions were mixed. When reaction was complete, the gaseous products were removed with a Toepler pump and were separated into one fraction that was volatile at liquid nitrogen temperature and another that was volatile at dry ice temperature. The amount of gas in each of the fractions was determined by gas volumetry, and each fraction was also subjected to mass spectrometric analysis.

Kinetic Studies. The reactions of peroxymonosulfate with $Cr(NH_3)_5N_3^{2+}$ and with azide in neutral and basic solutions were carried out in thermostated vessels. Aliquots were periodically removed and assayed for peroxymonosulfate. For studies of the reaction between HSO_5^- and azide in acid, a special reaction vessel was used to minimize evaporation of hydrazoic acid. In this case, all the reagents except the NaN_3 were allowed to reach temperature equilibrium in a thermostated 100-mL glass syringe fitted with a capillary tip. The reaction was initiated by addition of the NaN_3. Initially there was no gas space in the syringe. Aliquots were injected periodically into a small flask cooled to 0 °C, and samples were removed for assay. During the course of the reaction, a gas space built up due to the production of N_2 and N_2O. Evaporation of the very soluble HN_3 into this small gas volume was slight.

The kinetic data were analyzed by a least-squares adjustment to the functional form: $\ln([\text{peroxymonosulfate}]/[\text{azide}]) = kt + I$.

Tracer Studies. The source of the 2–8 times enriched oxygen-18 was either solvent water, terminally labeled $O_3SOO^*H^-$, or nonterminally labeled $O_3^*SO^*OH^-$.[8] The N_2O product was isolated by

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Table I. Reaction of Peroxymonosulfate with Hydrazoic Acid and Azide Ion

T, °C	$[HSO_5^-]_0$, M	$[HN_3]_0$, M	$[H^+]$, M	I, M[a]	10^4k, $M^{-1}\ s^{-1}$	$10^4k\,[H^+]$, $M^{-2}\ s^{-1}$
50.0	0.0329	0.0517	0.186	0.27	7.29	1.36
50.0	0.0620	0.0517	0.186	0.30	10.0	1.86
50.0	0.0100	0.102	0.135	0.26	8.46	1.14
50.0	0.0100	0.102	0.143[b]	0.29	11.0	1.57
50.0	0.0101	0.102	0.0401	0.20	27.1	1.09
50.0	0.0102	0.102	0.398	0.55	3.24	1.29
50.0	0.0102	0.102	0.398[c]	0.55	3.31	1.32
50.0	0.0103	0.102	0.198	0.55	6.79	1.34
50.0	0.0100	0.102	0.0982	0.55	15.5	1.52
50.0	0.0106	0.0285	0.0985	0.55	18.2	1.79
50.0	0.0102	0.102	0.0482	0.55	30.5	1.47
						av 1.43 ± 0.19
40.0	0.0101	0.102	0.0482	0.55	14.0	0.682
30.0	0.0101	0.102	0.0482	0.55	6.46	0.316

T, °C	$10^3[HSO_5^-]_0$, M	$10^3[N_3^-]_0$, M	~pH[d]	I, M[a]	k, $M^{-1}\ s^{-1}$
25.0	1.01	2.02	7.0	0.55	0.657
15.0	1.01	2.02	7.0	0.55	0.310
5.0	1.01	2.02	7.0	0.55	0.147

T, °C	$[SO_5^-]_0$, M	$[N_3^-]_0$, M	$[OH^-]$, M	I, M[a]	10^3k, $M^{-1}\ s^{-1}$
25.0	0.0100	0.0291	0.10	0.55	7.79
25.0	0.0100	0.0291	0.50	0.55	7.47
15.0	0.0100	0.0291	0.10	0.55	3.73
5.0	0.0100	0.0291	0.10	0.55	1.38

[a] Ionic strength adjusted with $NaClO_4$. [b] 0.20 M H_2SO_4; no added $HClO_4$. [c] 0.052 M added HSO_4^-. [d] $H_2PO_4^-$–HPO_4^{2-} buffer.

the vacuum-line techniques already described for the determination of reaction stoichiometry. $Cr(NH_3)_5NO^{2+}$ was separated and precipitated, and its oxygen converted to CO_2 by the methods described elsewhere.[8] The N_2O and CO_2 isotopic analyses were carried out with a Consolidated 21-620 and a Nuclide RMS-6 mass spectrometer, respectively. The techniques used for isotopic analysis of the oxygen in water, sulfate, and peroxymonosulfate have been detailed elsewhere.[8]

Results

Reaction Stoichiometries. The stoichiometry ratios (where f = formed and c = consumed) ($[Cr(NH_3)_5NO^{2+}]_f + [Cr(NH_3)_4(H_2O)NO^{2+}]_f)/[Cr(NH_3)_5N_3^{2+}]_c = 0.93 \pm 0.08$ and $[HSO_5^-]_c/[Cr(NH_3)_5N_3^{2+}]_c = 1.09 \pm 0.05$ were determined for the reaction between $Cr(NH_3)_5N_3^{2+}$ and HSO_5^- at approximately 70% completion. As already noted, the $Cr(NH_3)_4(H_2O)NO^{2+}$ constituted about 15% of the product. This species probably arises largely from aquation of $Cr(NH_3)_5NO^{2+}$. Our results indicate that the major path in this system is the reaction

$$Cr(NH_3)_5N_3^{2+} + HSO_5^- \rightarrow Cr(NH_3)_5NO^{2+} + HSO_4^- + N_2$$

For the reaction of peroxymonosulfate with azide, the ratio of azide consumed to peroxymonosulfate consumed was found to be 1.15, 1.05, and 0.89 at pH 1.3, 7.0, and 13.0, respectively. The product ratio $[N_2O]/[N_2]$ was found to be 0.48, 0.52, and 0.41 at pH 1.3, 6.6, and 13.8, respectively. In neutral and alkaline solution the reaction was allowed to go to completion, and the ratio of N_2 produced to peroxymonosulfate consumed was found to be 0.98 and 0.80, respectively, at pH 6.6 and 13.8. It was not practical to obtain gas analyses after completion of the reaction in acid solution under the conditions of our kinetic studies because of the low rate. An attempt to obtain such information under drastic conditions ($[HN_3]_0 = 0.5$ M; $[HSO_5^-]_0 = 0.1$ M; pH ~1) led to the unexpected results $[N_2]_f/[HSO_5^-]_c = 1.72$ and $[N_2O]/[N_2] = 0.20$! Nevertheless, under the conditions that prevail in our kinetic studies, it appears that the *principal* overall reactions are

$$2HN_3 + 2HSO_5^- \rightarrow 2N_2 + N_2O + 2HSO_4^- + H_2O$$

$$2N_3^- + 2HSO_5^- \rightarrow 2N_2 + N_2O + 2SO_4^{2-} + H_2O$$

$$H_2O + 2N_3^- + 2SO_5^{2-} \rightarrow 2N_2 + N_2O + 2SO_4^{2-} + 2OH^-$$

in acid, neutral, and basic solutions, respectively.

Table II. Reaction of Peroxymonosulfate with Azidopentaamminechromium(III)[a]

T, °C	$[H^+]_0$, M	10^2k, $M^{-1}\ s^{-1}$	T, °C	$[H^+]_0$, M	10^2k, $M^{-1}\ s^{-1}$
25.0	0.20	1.35	14.5	0.20	0.820
25.0	0.050	1.19	35.0	0.20	2.41
25.0	0.0025[b]	1.42	45.0	0.20	3.75

[a] $[HSO_5^-]_0 = 0.010$ M; $[Cr(NH_3)_5N_3^{2+}]_0 = (4.8\text{-}6.7) \times 10^{-3}$ M; $I = 0.20$ M. [b] H_3PO_4–$H_2PO_4^-$ buffer.

Table III. Activation Parameters for Peroxymonosulfate Reactions

reaction	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(mol deg)
$HSO_5^- + HN_3$; 0.0482 M $[H^+]$	14.5 ± 0.3	−31 ± 1[a]
$HSO_5^- + N_3^-$; pH ~7.0	11.8 ± 0.3	−20 ± 1
$SO_5^{2-} + N_3^-$; 0.10 M $[OH^-]$	14.0 ± 1.1	−21 ± 4
$HSO_5^- + Cr(NH_3)_5N_3^{2+}$; 0.20 M $[H^+]$	8.60 ± 0.33	−38 ± 1

[a] Computed by using $k[H^+]$.

Kinetic Results. The empirical rate laws for all of these reactions were found to be first order in each of the reactants. Satisfactory fits to the bimolecular rate equation were obtained up to 60–80% of complete reaction. Values of the bimolecular rate parameters are presented in Tables I and II.

No significant dependence of the rate on hydrogen ion concentration was observed except for the reaction between azide and peroxymonosulfate in acid solution. In this medium, the predominant species present are HN_3 and HSO_5^-, and the reaction shows a rather clear inverse first-order dependence on hydrogen ion concentration, as is shown by the last column of Table I. The results in Table I also show the rate of the HSO_5^-–HN_3 reaction to be substantially unaffected by added sulfate or bisulfate.

The activation parameters determined from the temperature dependences of the reactions are summarized in Table III.

Tracer Results. The reactions of peroxymonosulfate with azidopentaamminechromium(III) at pH ~1 and with azide at pHs of ca. 1, 6.6, and 13.8 were carried out in water that was eightfold enriched in ^{18}O. The oxygen of the Cr-

Table IV. Summary of Activation Parameters for Reactions of Peroxymonosulfate Ion (HSO_5^-)

substrate	I, M	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol deg)	ref
N_3^-	0.55	11.8	−20	this work
$(NH_3)_5$-CrN_3^{2+}	0.20	8.6	−38	this work
ClO_2^-	0.80	15.5	−15	14a
Cl^-	0.50	14.0	−24	14b
NO_2^-	1.5	12.6	−20	14c
Br^-	0.20	10.0	−25	14b
I^-	0.20	7.3	−19	14d

$(NH_3)_5NO^{2+}$ and N_2O produced was not detectably enriched, indicating that less than 2% of this oxygen came from solvent. A reaction was also carried out at pH ~1 between azide and $O_3{}^*SO{}^*OH^-$, in which all oxygens in the peroxymonosulfate *except* the terminal peroxide oxygen were sevenfold enriched in ^{18}O. Again no enrichment was found in the oxygen of the N_2O product, indicating that at least 98% of this oxygen came from the terminal peroxide oxygen of the peroxymonosulfate. An additional experiment was carried out at pH ~1 in which $Cr(NH_3)_5N_3^{2+}$ was permitted to react with $O_3SOO{}^*H$ in which the terminal oxygen contained 0.479 atom % ^{18}O. The oxygen of the $Cr(NH_3)_5NO^{2+}$ product was found to contain 0.416 atom % ^{18}O. Taking normal oxygen to be 0.204 atom % ^{18}O, this indicates that 77% of the oxygen in the nitrosyl product came from the terminal peroxide oxygen of the peroxymonosulfate.

Discussion

In the reaction of peroxymonosulfate with azide, the N_3^- ion appears to be the reactive species even in acidic solution, where HN_3 is the predominant form. Extrapolation of $k[H^+]$ from Table I to 25 °C and division by the bimolecular rate constant in neutral solution lead to a value of 3.1×10^{-5} M for the ionization constant of HN_3. The NBS value is 2.40×10^{-5} M;[11] the difference is almost certainly due to effects of the medium. The changes observed in the activation parameters in going from acid to neutral solution compare well with the NBS values for the heat and entropy of ionization of HN_3: $\Delta H = 3.6$ kcal/mol and $\Delta S = -9.1$ cal/(mol deg).[11]

Our tracer results indicate that these reactions proceed via transfer of oxygen from the oxidant to the reductant. In the oxidation of free azide, the transferred oxygen comes entirely from the terminal peroxide oxygen of the peroxymonosulfate. In the oxidation of $Cr(NH_3)_5N_3^{2+}$, the results obtained with $O_3SOO{}^*H^-$ could be interpreted to indicate that the nitrosyl product contains some oxygen that was originally bonded to sulfur. It seems more likely, however, that in this case also, only terminal peroxide oxygen is transferred and that the slightly low enrichment of the $Cr(NH_3)_5NO^{2+}$ results from partial exchange of the nitrosyl in the course of the isolation of the product. A similarly low apparent extent of transfer to $Cr(NH_3)_5N_3^{2+}$ is observed when $HO{}^*F$ is the oxidant.[8] In any event, it would appear that transfer of a terminal peroxide oxygen is the predominant mode of reaction in all cases. In the case of $Cr(NH_3)_5N_3^{2+}$, the oxygen transfer leads directly to the formation of bound nitrosyl after loss of N_2. In the case of free azide, the first step is most likely the formation of nitroxyl, HNO or NOH, which can dimerize to form first hyponitrous acid, $H_2N_2O_2$, and then N_2O.[12,13] Our results indicate that nitroxyl does not exchange oxygen with solvent prior to or during the dimerization process. The low N_2O/N_2 ratio obtained in alkaline solution may reflect some formation of the relatively stable trans hyponitrite.[12,13]

It is perhaps worth emphasizing that azide reactions can be very complex. Although the reaction paths that we are considering appear to predominate under the experimental conditions that we have chosen, our stoichiometry results suggest that under other conditions it may be necessary to consider quite different reactions.

The activation parameters for the oxidation of a number of anions by peroxymonosulfate have been determined previously and are summarized in Table IV.[14] These reactions have been interpreted in terms of nucleophilic attack on the peroxide oxygen. In the present work we have obtained direct evidence for such a mechanism.

The azide species that we have studied show increasing reactivity in the order $HN_3 <<< Cr(NH_3)_5N_3^{2+} < N_3^-$, while HSO_5^- is a more reative oxidant than SO_5^{2-}. The enhanced reactivity of HSO_5^- is consistent both with an electrostatic effect and with a weakening of the peroxide bond by the proton. The reactivities of the various azide species, however, are more difficult to rationalize. The reactivity of N_3^- probably reflects its high basicity, which makes it readily able to accept an oxygen atom. However, the extreme unreactivity of HN_3 is surprising.

The situation becomes even less clear if we compare peroxymonosulfate with other oxidants. Both nitrous acid and bromate react readily with HN_3 and very slowly, if at all, with N_3^-. Nitrous acid also reacts rapidly with coordinated azide, to which bromate is quite inert. The relative reactivities of these oxidants toward HN_3 and N_3^- can be accounted for if we consider that NO_2^- and BrO_3^-, but not HSO_5^-, are likely to be labilized by protonation. This effect presumably overrides the basicity of N_3^- and makes nitrite and bromate unreactive toward it. A similar argument has been used to explain the difference between hydrogen ion catalyzed oxidations by bromate and pH-independent or base-catalyzed oxidations by perbromate.[15] The inertness of bromate toward coordinated azide, however, seems mystifying, and we must admit that our knowledge of the comparative redox behavior of these species remains quite incomplete.

Hitherto only hypofluorous acid has been found to oxidize coordinated azide to nitrosyl.[8,16] Peroxymonosulfate is a more convenient reagent, and its reaction with azido complexes may have applications in synthesis. It may be that only nitrosyl complexes of the NO^- class[17] can be formed in this way, although this supposition has yet to be tested.

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Registry No. HSO_5^-, 12188-01-1; N_3^-, 14343-69-2; $Cr(NH_3)_5N_3^{2+}$, 22317-10-8.

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Electrochemical and Chemical Oxidation of π-Bonded [Bis(diphenylarsino)methane]chromium and -molybdenum Dicarbonyl Complexes

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Electrochemical oxidation of the complexes $M(CO)_2DAM$ [M = Cr, Mo; DAM = bis(diphenylarsino)methane] in dichloromethane, acetone, and acetonitrile shows some unusual reaction pathways. At mercury electrodes the reversible steps

$$2M(CO)_2DAM + 2Hg \rightleftharpoons 2[HgM(CO)_2DAM]^+ + 2e^-$$

$$2[HgM(CO)_2DAM]^+ \overset{K}{\rightleftharpoons} [Hg(M(CO)_2DAM)_2]^{2+} + Hg$$

are seen in all solvents. Controlled potential electrolyses at a potential corresponding to the limiting current of the reversible polarographic wave generate the mercury cations. Under voltammetric conditions at a platinum electrode $Cr(CO)_2DAM$ undergoes the reversible one-electron oxidation

$$Cr(CO)_2DAM \rightleftharpoons [Cr(CO)_2DAM]^+ + e^-$$

in acetone and dichloromethane under all conditions and in acetonitrile at low temperature. A further irreversible process

$$[Cr(CO)_2DAM]^+ \xrightarrow{-e^-} [Cr(CO)_2DAM]^{2+} \rightarrow \text{products}$$

is also observed. Controlled potential electrolysis at a potential corresponding to the voltammetric one-electron oxidation at 20 °C indicates a two-electron oxidation. However, in acetone or dichloromethane at −78 °C, an n value of 1.0 is obtained at platinum and the cation $[Cr(CO)_2DAM]^+$ is stable on the synthetic time scale at low temperatures. When the temperature is raised, the cation disproportionates to $Cr(CO)_2DAM$ and non-carbonyl-containing species. In contrast to $Cr(CO)_2DAM$, $Mo(CO)_2DAM$ undergoes irreversible oxidation at platinum under all conditions and only non-carbonyl-containing products are obtained from controlled potential electrolysis. Chemical reactions with Hg(II), Ag(I), and iodine are consistent with electrochemical data. In acetonitrile, oxidation with $NOPF_6$ gives the cations $[M(CO)_2(NO)DAM(CH_3CN)_2]^+$ and these can be isolated as hexafluorophosphate salts. For M = Mo, $[Mo(CO)_2NO(CH_3CN)_3]^+$ is also formed. The chemical reactions and electrochemical data can be used to provide a systematic account of reaction pathways for oxidation of the $M(CO)_2DAM$ complexes.

Introduction

Electrochemical and chemical investigations have shown that complexes of the type *cis*-$M(CO)_2(L\text{-}L)_2$ (M = Cr, Mo, W; L-L = DPM (bis(diphenylphosphino)methane), DPE (1,2-bis(diphenylphosphino)ethane)) undergo oxidation to form the paramagnetic cations *trans*-$[M(CO)_2(L\text{-}L)_2]^+$.[1-7] However, under some conditions, seven-coordinate oxidation state II complexes can be obtained.[3,8]

Recently,[9] a mixture of *trans*-$[Cr(CO)_2(DMPE)_2]^+$ and *trans*-$[CrH(CO)_2(DMPE)_2]^+$ has been reported to form from the oxidation of *cis*-$Cr(CO)_2(DMPE)_2$ [DMPE = 1,2-bis(dimethylphosphino)ethane] with $NOPF_6$ in methanol, whereas in acetonitrile, the sole product was *cis*-$[Cr(CH_3CN)(CO)_2(DMPE)_2]^{2+}$, a seven-coordinate dipositive cation, indicating that the solvent played an important role in determining the oxidation product in this type of dicarbonyl complex. This kind of behavior appears to be characteristic of group 6 dicarbonyl complexes.

An alternative kind of dicarbonyl complex is possible when a phenyl or arene group π bonds to the metal, and oxidation studies on this kind of complexes have also provided some interesting data.[10-12] For example, Connelly and Johnson[12] have examined the oxidation of $(\pi\text{-}C_6Me_{6-n}H_n)Cr(CO)_2$(alkyne) [$n$ = 0, 1; alkyne = $PhC{\equiv}CPh$, $MeOC_6H_4C{\equiv}CC_6H_4OMe$] with $NOPF_6$, $AgPF_6$, and I_2. In methanol/toluene and dichloromethane, the cationic species $[(\pi\text{-}C_6Me_{6-n}H_n)Cr(CO)_2(\text{alkyne})]^+$ was isolated. However, for alkyne = $MeOC_6H_4C{\equiv}CC_6H_4MeO$ (n = 0, 1), oxidation with $NOPF_6$ gave unstable monocations and the end product was $[(\pi\text{-}C_6Me_{6-n}H_n)Cr(CO)_2NO]^+$.

Furthermore, oxidation of $[(\pi\text{-}C_6Me_6)Cr(CO)_2L]$ (L = phosphine or phosphite)[13] with $NOPF_6$ in methanol/toluene gave a mixture of $[(\pi\text{-}C_6Me_6)Cr(CO)_2NO]^+$ and $[(\pi\text{-}C_6Me_6)Cr(CO)(NO)L]^+$. A reaction scheme was established to explain the data obtained under various conditions.

Work on the oxidation of these various dicarbonyl complexes has provided a wide range of interesting reaction pathways. However, oxidation of the complexes $M(CO)_2DAM$ (M = Cr, Mo; DAM = bis(diphenylarsino)methane),[14] which have an unusual structure[15] (see Figure 1) in the sense that both L and

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