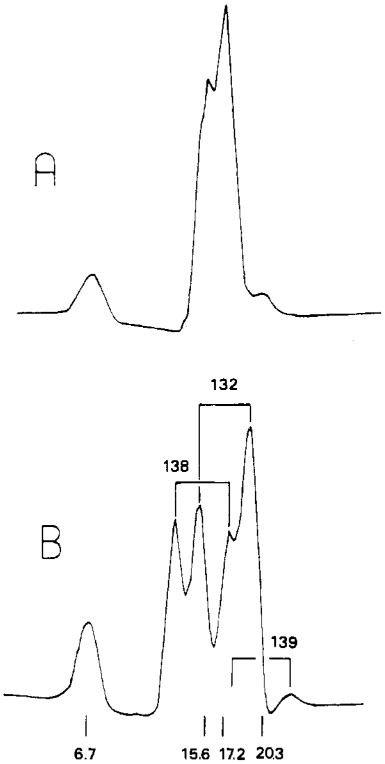

Figure 2. The ^{11}B NMR of $Na_4B_{12}H_{11}SSB_{12}H_{11}$: (A) hydrogen decoupled; (B) coupled. Chemical shifts in ppm relative to $Et_2O{\cdot}BF_3$ are given below the peaks. Coupling constants in Hz are shown above.

erages out the hyperfine splitting by the thiol proton.

If the free radical is of the thiyl or thiol type, homolytic fissioning of the disulfide must be discounted since such a mechanism would give rise to a first-order rate dependence on the disulfide concentration and a zeroth order dependence on the oxygen concentration. However, our kinetic runs showed that the reaction rate is strongly dependent on the oxygen concentration. They also indicated a rate dependence on both the hydrogen ion and disulfide concentrations.

Another means by which a free radical could be formed under our experimental conditions involves a one-electron autoxidation mechanism. A multielectron oxidation mechanism seems unlikely as the first oxidized derivative of the disulfide, $B_{12}H_{11}SOSB_{12}H_{11}^{4-}$, does not readily produce free radicals in acidic media, and this species is surprisingly reluctant to undergo further oxidation.[23]

The surprisingly long lifetime of these anionic radicals may be explained by postulating that their electrostatic repulsion in solvents other than water inhibits their recombination.

Finally, preliminary biological testing of the disulfide in tumor-bearing rats has been carried out and will be reported elsewhere.[24] Whether the derived radical is produced in vivo has not been resolved.

Acknowledgment. This work was supported in part by ERDA Contract No. E(11-1)-3334 and in part by a Fellowship, No. CA-43443, awarded by the National Cancer Institute DHEW to E.I.T. We are most grateful to C. S. Liu and R. C. Lord for obtaining the Raman spectra and express our gratitude to W. Hull for obtaining the ^{11}B NMR spectra and to C. Young for obtaining the ESR spectra.

Registry No. $Cs_4B_{12}H_{11}SSB_{12}H_{11}$, 62962-07-6; $Cs_2B_{12}H_{11}SH$, 12448-23-6; $Na_4B_{12}H_{11}SSB_{12}H_{11}$, 62962-06-5.

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(20) The nature of our experimental conditions did not allow the absorbance to be measured for $t < t_{0.05}$. A plot of log ([S]/[S]$_0$) vs. time was linear for $t < t_{0.66}$ but did not pass through the origin as expected. A better fit can be obtained if we assume that there is an initial leap of absorbance to $0.05A_{max}$ followed by a first-order reaction. Strictly for the purpose of reporting our data we will assume this model. Now the disulfide concentration can be expressed as $[S] = [S]_0(1 - (A - 0.05A_{max})/0.95A_{max})$. A least-mean-squares fit of ln [S] vs. t for the integrated expression at several temperatures gave good correlations ($r^2 = 0.99$) with the following first-order rate constants: 8.2×10^{-4}, 265.7 K; 1.8×10^{-3}, 276.2 K; 7.1×10^{-3}, 298.2 K.
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Kinetics and Mechanism of the Nitrogen(IV) Oxidation of Molybdenum(V)

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Received November 19, 1976 AIC60826J

As a continuation of our earlier studies[1,2] concerning the oxidation of $MoOCl_3(OPPh_3)_2$ by nitrate and nitrite ions, we here report the oxidation of this complex by nitrogen(IV) oxide. This study is also of interest since no information concerning the kinetics and mechanism of nitrogen(IV) oxidations of transition metal centers appears to have been reported.

Experimental Section

All manipulations were performed under an atmosphere of purified nitrogen. Dichloromethane (normal commercial grade) was purified by distillation from CaH_2 and equilibrium mixtures of NO_2/N_2O_4 in this solvent were prepared by the appropriate dilution of liquid N_2O_4 (BDH Chemicals, s.g. 1.49, 99.5%). $MoOCl_3(OPPh_3)_2$ was prepared as described previously[3] and Ph_3PO (BDH Chemicals), was used without further purification. Infrared and UV/vis spectra were recorded, respectively, on Perkin-Elmer 257 and Unicam SP800 spectrophotometers.

CH_2Cl_2 solutions of the reactants were prepared immediately prior to the study and transferred using syringe techniques to the storage

Table I. Kinetics Data[a] for the Oxidation of $MoOCl_3(OPPh_3)_2$ by Nitrogen(IV) Oxides at 25 °C

10^4[Mo(V)], M	10^3[N(IV)]$_{total}$, M	10^3[Ph_3PO], M	k_{obsd}, s^{-1}
3.26	1.20		0.061
3.26	2.30		0.119
3.26	3.20		0.189
3.26	4.00		0.237
3.26	5.00		0.288
3.26	10.0		0.76, 0.76[b]
3.26	15.0		1.36, 1.38[c]
3.26	20.0		2.26
3.26	23.0		3.21
3.26	27.5		4.00
1.00	10.0		1.24
2.00	10.0		1.05
5.00	10.0		0.595
5.00	10.0	0.50	0.485
5.00	10.0	1.50	0.269
5.00	10.0	5.00	0.066

[a] Data obtained at 310 nm unless indicated otherwise. [b] 350 nm. [c] 290 nm.

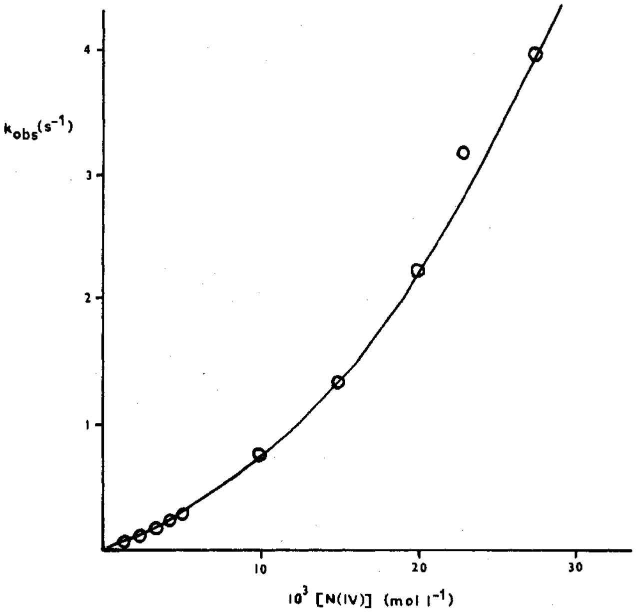

Figure 1. Variation of k_{obsd} with total [N(IV)] for the oxidation of $MoOCl_3(OPPh_3)_2$ by NO_2/N_2O_4. Experimental data are shown by circles; the continuous function was calculated according to the mechanism (1)–(3) (see text), assuming $k_2 = 50\ M^{-1}\ s^{-1}$ and $k_3K_1 = 3.3 \times 10^3\ M^{-2}\ s^{-1}$.

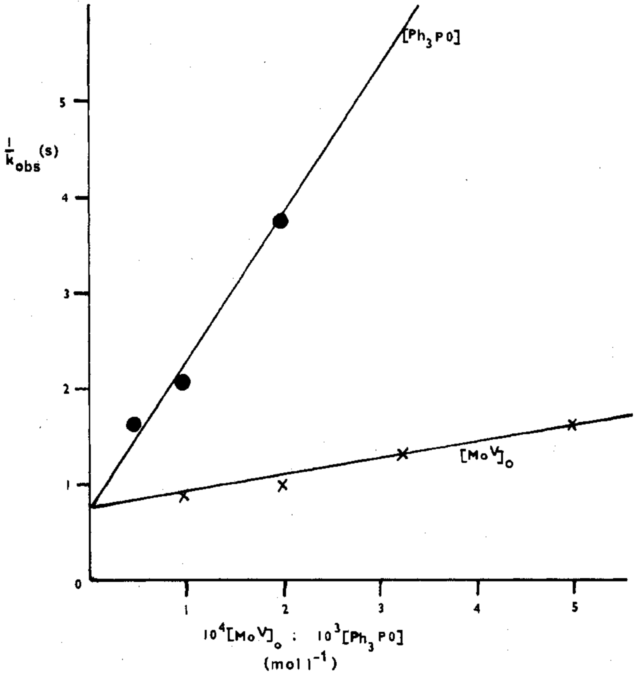

Figure 2. Variation of k_{obsd} with $MoOCl_3(OPPh_3)_2$ (×) and added Ph_3PO (●).

chambers of an Aminco-Morrow stopped-flow apparatus coupled to a Beckman DU spectrophotometer. A nitrogen atmosphere was maintained above the solutions which were thermostated for ca. 15 min at 25 ± 0.1 °C. Reactions were followed by monitoring transmittance changes with time, these data being stored using a DASAR facility. The reactions carried out under stopped-flow conditions were monitored principally at 310 nm, although experiments monitored at other wavelengths confirmed that a single-step rate process was occurring. Particular care was taken in checking experiments over short reaction times since oxidation of $MoOCl_3(OPPh_3)_2$ by both nitrate[1] and nitrite[2] occurs within 100 ms. Rate constants were evaluated from plots of log $(D_t - D_\infty)$ vs. time (D_t = absorbance at time t and D_∞ = absorbance after ca. 10 half-lives) which were generally linear for at least 4 half-lives. Pseudo-first-order conditions were employed throughout this study with [N(IV)] in excess, and the variation of the observed rate constants with [N(IV)], [Mo(V)], and [Ph_3PO] investigated.

Results

The data obtained are listed in Table I and the variation of the observed rate constant, k_{obsd}, with total [N(IV)] is illustrated in Figure 1. In this figure the continuous function has been calculated assuming the mechanism (1)–(3). The

$$2NO_2 \underset{\text{rapid}}{\overset{K_1}{\rightleftharpoons}} N_2O_4 \tag{1}$$

$$NO_2 + Mo(V) \xrightarrow{k_2} Mo(VI) + NO^+ \tag{2}$$

$$N_2O_4 + Mo(V) \xrightarrow{k_3} Mo(VI) + NO^+ + NO_2 \tag{3}$$

resultant rate expression is given by (4), where, for 3.26×10^{-4}

$$-d[Mo(V)]/dt = k_2[NO_2][Mo(V)] + k_3K_1[NO_2]^2[Mo(V)] \tag{4}$$

M [$MoOCl_3(OPPh_3)_2$], $k_2 = 50 \pm 8\ M^{-1}\ s^{-1}$ and $k_3K_1 = 3.3\ (\pm 0.5) \times 10^3\ M^{-2}\ s^{-1}$.

A slight inverse dependence of k_{obsd} upon [$MoOCl_3(OPPh_3)_2$] was obtained and, since a similar but more marked inverse dependence was observed upon the addition of Ph_3PO (Figure 2), the preequilibrium (5) is suggested.

$$MoOCl_3(OPPh_3)_2 \xrightarrow{K_5} MoOCl_3(OPPh_3) + Ph_3PO \tag{5}$$

The identification of the reaction products was effected in several ways. Analyses of the molybdenum-containing product were consistent with its formulation as $MoO_2Cl_2(OPPh_3)_2$. Anal. Calcd for $C_{36}H_{30}Cl_2MoO_4P_2$: C, 57.2; H, 4.0; Cl, 9.4. Found: C, 56.8; H, 4.0; Cl, 9.4. The infrared and UV/vis spectra were identical with those recorded for samples of $MoO_2Cl_2(OPPh_3)_2$ prepared[4] in an alternative manner. Spectrophotometric studies of the reaction for a 1:1 ratio of Mo(V) and N(IV) indicated a complete conversion to Mo(VI) according to the stoichiometry of (6). Under these conditions,

$$Mo(V) + N(IV) \rightarrow Mo(VI) + N(III) \tag{6}$$

the only nitrogen(III)-containing species identified was NOCl by the comparison of its infrared and UV/vis spectra in CH_2Cl_2 solution with those recorded for authentic (BDH) samples of this compound. These spectral data were obtained for the solutions immediately subsequent to reaction and for the volatiles distilled from this solution at room temperature under a reduced pressure.

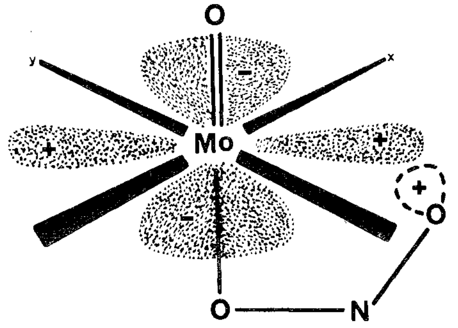

Figure 3. Suggested geometric arrangement for the redox reaction between $MoOCl_3(OPPh_3)$ and NO_2, allowing for overlap of the d_{xy} orbital of the former with the a_1' (N–O σ^*, O–O σ) orbital of the latter.

NOCl was also obtained by reacting NO_2^- with $MoOCl_4$.

Discussion

The oxidation of Mo(V) by N(IV) in CH_2Cl_2 solution has been shown to occur in one observable step, the kinetic data for which are consistent with concomitant pathways involving terms in $[NO_2]$ and $[NO_2]^2$. Although the term in $[NO_2]$ is interpreted simply as a reaction between Mo(V) and NO_2, it is not essential to consider the term in $[NO_2]^2$ as involving N_2O_4. One alternative here is the disproportionation (7),

$$2NO_2 \rightarrow NO^+ + NO_3^- \qquad (7)$$

followed by the reaction of NO_3^- with $MoOCl_3(OPPh_3)_2$ in an analogous manner to that described previously.[1]

The dependence of k_{obsd} upon the initial $MoOCl_3(OPPh_3)_2$ and added Ph_3PO concentrations suggests that the dissociation (5) of Ph_3PO from the parent molybdenum complex is essential for reaction. Plots of $1/k_{obsd}$ vs. $[Ph_3PO]$ and $[MoOCl_3(OPPh_3)_2]$ (Figure 2) are linear and, since the expression

$$k_{obsd} = \frac{(k_2[NO_2] + K_1k_3[NO_2]^2)K_5}{K_5 + [Ph_3PO]} \qquad (8)$$

adequately describes the data, it appears that only the five-coordinate $MoOCl_3(OPPh_3)$ species is reactive. Solving (8) for K_5 gives a value of 5.1×10^{-4} M, which is far higher than previous estimates[5] for this dissociation of $MoOCl_3(OPPh_3)_2$ in CH_2Cl_2 solution. Consequently, a special interaction between nitrogen(IV) oxides and either $MoOCl_3(OPPh_3)$ or Ph_3PO is suggested and, in view of the interactions between donor solvents and nitrogen(IV) oxides characterized earlier,[6] the $Ph_3PO–NO_2/N_2O_4$ interactions seem the more probable.

Because of the interpretive difficulties of the reaction pathway involving $[NO_2]^2$ terms, we can only discuss the process which is first order in $[NO_2]$. It is not possible to present a definite mechanism for this process; however, considerations of the kinetic data obtained and the likely requirements[7,8] for this redox reaction lead to a suggested mechanism. As shown in Figure 3, an NO_2 molecule could achieve a weak coordination to $MoOCl_3(OPPh_3)$ trans to the oxo group which would facilitate electron transfer from the molybdenum $4d_{xy}$ orbital into the a_1' (N–O σ^*, O–O σ) half-filled orbital[9] of the NO_2. "O^{2-}" transfer could then occur to afford the *cis*-dioxomolybdenum(VI) and NO^+ moieties in an manner analogous to that demonstrated here between $MoOCl_4$ and NO_2^-. The observations that the NO_2 oxidation proceeds at a much slower rate than the NO_3^- and NO_2^- oxidations and with S_N2 rather than S_N1 behavior are suggested to arise primarily because of the very poor coordinating ability of NO_2. Thus, for process 5 followed by (9) (where

$$MoOCl_3(OPPh_3) + X \rightarrow MoOCl_3(OPPh_3)X \qquad (9)$$

X = NO_3^-, NO_2^-, Cl^-, Br^-, or NO_2), for NO_3^-, NO_2^-, Cl^-, or Br^- the rate-determining step[1-3] is the dissociation of (5), whereas for NO_2 it is probably the association of (9). This latter process for NO_2 is also considered to be significantly slower than the ligand reorganization about the molybdenum(V) center which leads to the redox process and some further observations are perhaps useful in this respect. Approximation to the highest reasonable symmetry of the reactant centers (Mo^VO, $\sim C_{4v}$; coordinated NO_3^-, NO_2^-, and NO_2, $\sim C_{2v}$, C_s, and C_s, respectively), plus the criterion that there should be significant overlap between the highest filled orbital of the reductant and the lowest orbital or partially filled MO of the oxidant, leads to the formal conditions that NO_3^- and NO_2^- should achieve coordination via one oxygen atom at one of the four sites cis to the oxo group of the Mo^VO center,[1,2] whereas for NO_2, one of the oxygen atoms should simply approach the molybdenum(V) between two of these cis sites (Figure 3).

Conclusion

The oxidation of $MoOCl_3(OPPh_3)_2$ by NO_3^-, NO_2^-, or NO_2 each produces a *cis*-dioxomolybdenum(VI) center and NO_2, NO, or NO^+, respectively, by a one-electron-transfer process which also involves the transfer of one oxygen atom from the oxidant to the reductant. The differences in kinetic behavior observed, for NO_2 on the one hand as compared to NO_3^- and NO_2^- on the other, are considered to arise, primarily, because of the poor ligating characteristics of NO_2.

Acknowledgment. We thank the SRC for financial support including the award of a Postdoctoral Fellowship (M.R.H.).

Registry No. $MoOCl_3(OPPh_3)_2$, 19247-59-7; NO_2, 10102-44-0.

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Electrode Reaction Pathways for the Reduction of Chromium(III)–Ammine Complexes at Mercury Electrodes

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Received January 21, 1977 AIC70051U

In recently reported studies[1] criteria were described for distinguishing between inner- and outer-sphere reaction pathways for the electroreduction of eight pentaaquo complexes of chromium(III). Similar experiments have now been conducted with a large set of ammine complexes of Cr(III) to explore more fully the general applicability of the proposed diagnostic criteria. The results reveal significant differences in the kinetic behavior of the aquo and ammine complexes which make it somewhat less straightforward to infer mechanisms for the latter set of complexes on the basis of the previously proposed criteria.[1] The purposes of this note are to report the most relevant electrode kinetic data obtained for the chromium(III)–ammine complexes, to compare them with corresponding data for the analogous aquo complexes, and to