sulfite. It is unfortunate that the spectral data, with but few exceptions, were not of sufficient quality to permit even tentative assignments; in general, the bands were broad and diffuse. In support of the oxysulfite formulation, however, it may be noted that bands at 460 and 505 cm^{-1} were observed and that these bands have been assigned by earlier workers[15] to $\nu(\mathrm{U{=}O})$.

With regard to the UO_2 formed by the decomposition of both of the sulfites described above, all initial products contained low levels of sodium. It has been shown earlier[13,16] that this impurity can be eliminated by ignition for longer times at higher temperatures.

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Registry No. $U(SO_3)_2{\cdot}4H_2O$, 61931-01-9; $UO(SO_3){\cdot}4H_2O$, 61966-62-9; $UO(SO_3){\cdot}2H_2O$, 61966-63-0; $UO_2(NO_3)_2$, 10102-06-4; $Na_2S_2O_4$, 7775-14-6.

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Correspondence

On the Reduction of Nitrate by Diammonium Oxopentachloromolybdate(V) in Dimethylformamide

AIC60766H

Sir:

In a recent paper, we reported the results of a kinetic study of the reduction of nitrate by $(NH_4)_2MoOCl_5$ in DMF.[1] More recently, our mechanistic interpretation of these results has been questioned and an alternative mechanism, making use of our kinetic data, proposed by Garner et al.[2] We find it necessary, therefore, to point out the mechanism of Garner et al. is, in fact, not in agreement with our results.

In our original work, we proposed the Cl^- trans to the oxo group of $MoOCl_5^{2-}$ dissociates essentially completely in DMF, giving $MoOCl_4^-$:

$$MoOCl_5^{2-} \rightleftharpoons MoOCl_4^- + Cl^- \qquad (1)$$

In our mechanism, nitrate then displaces a second Cl^-, producing an intermediate $MoOCl_3(NO_3)^-$ complex, which subsequently undergoes electron transfer to give products:

$$MoOCl_4^- + NO_3^- \rightleftharpoons MoOCl_3(NO_3)^- + Cl^- \qquad (2)$$

$$MoOCl_3(NO_3)^- \rightarrow MoO_2Cl_2 + NO_2 + Cl^- \qquad (3)$$

Using ESR, Garner et al. have provided good evidence that the initial reaction 1 produces a six-coordinate species, with a molecule of DMF displacing a Cl^-, again the displacement being essentially complete under the conditions used in our work:[2]

$$MoOCl_5^{2-} + DMF \rightleftharpoons MoOCl_4(DMF)^- + Cl^- \qquad (4)$$

In view of the donor ability of DMF,[3] this is not surprising; it is also easily accommodated in our mechanism, by replacement of the coordinated DMF by NO_3^- in a reaction analogous to (2):

$$MoOCl_4(DMF)^- + NO_3^- \rightleftharpoons MoOCl_3(NO_3)^- + Cl^- + DMF \qquad (5)$$

This in no way affects our kinetic arguments, although, as pointed out by Garner et al.,[2] it may account for the relative slowness of the reaction.

Garner et al., however, have proposed another mechanism to explain our results:

$$MoOCl_4(DMF)^- \rightleftharpoons MoOCl_4^- + DMF \qquad (6)$$

$$MoOCl_4^- + NO_3^- \rightleftharpoons MoOCl_4(NO_3)^{2-} \qquad (7)$$

$$MoOCl_4(NO_3)^{2-} \rightarrow MoO_2Cl_4^{2-} + NO_2 \quad \text{(fast)} \qquad (8)$$

$$MoOCl_4^- + Cl^- \rightleftharpoons MoOCl_5^{2-} \qquad (9)$$

By application of the steady state condition to $MoOCl_4^-$, they obtained the rate expression (P = products):

$$\mathrm{dP}/\mathrm{d}t = \frac{k_6k_7[MoOCl_4(DMF)^-][NO_3^-]}{k_6[DMF] + k_7[NO_3^-] + k_9[Cl^-]} \qquad (10)$$

Unfortunately, these authors state the integrated form of this expression is consistent with our data, when in fact, it is not. Clearly, in their mechanism, since the only source of Cl^- is the initial displacement of a coordinated Cl^- of $MoOCl_5^{2-}$ by DMF (reaction 4), which is very rapid and essentially complete,[2] Cl^- concentration must be constant during the reaction, even when no additional Cl^- has been added. In the presence of excess NO_3^-, this leads to a simple first-order rate expression, which must hold at all Cl^- concentrations:

$$\mathrm{dP}/\mathrm{d}t = k_{\mathrm{obsd}}\,[MoOCl_4(DMF)^-]$$
$$k_{\mathrm{obsd}} = \frac{k_6k_7[NO_3^-]}{k_6[DMF] + k_7[NO_3^-] + k_9[Cl^-]} \qquad (11)$$

As is clearly stated in our paper, however, first-order plots are linear only to ~50% reaction in the absence of added Cl^-, deviating after that in a negative direction.[1] This was shown by us to be due to inhibition by Cl^- released during the reaction. By using a rate expression of the form

$$-\mathrm{d}[Mo(V)]/\mathrm{d}t = k_{\mathrm{obsd}}\,[Mo(V)]/[Cl^-]$$
$$= k_{\mathrm{obsd}}\,[Mo(V)]/(3[Mo(V)]_0 - 2[Mo(V)]) \qquad (12)$$

$$Mo(V) = MoOCl_4^- \text{ or } MoOCl_4(DMF)^-$$

$$[Mo(V)]_0 = [MoOCl_5^{2-}]_0$$

in which Cl^- is a variable, an integrated rate expression was obtained by us which gives linear plots to >90% reaction and consistent rate constants:

$$2[Mo(V)] - 3[Mo(V)]_0 \ln[Mo(V)] = k_{\mathrm{obsd}}\,t + I \qquad (13)$$

Only when excess Cl^- was added did we obtain linear first-order plots, as expected from (12). The mechanism of Garner et al. therefore does not account for the observed Cl^- inhibition in the absence of added Cl^-.

If one assumes the product of reaction 8, $MoO_2Cl_4^{2-}$, dissociates rapidly into MoO_2Cl_2 and $2Cl^-$, then Cl^- must be treated as a variable. Integration of (11) with this assumption gives:

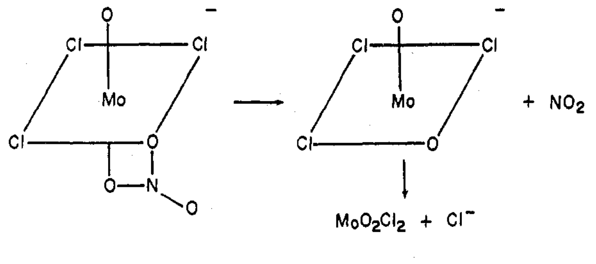
$$2[\mathrm{MoOCl_4(DMF)^-}] - (k_{-6}[\mathrm{DMF}]/k_9 + k_7[\mathrm{NO_3^-}]/k_9 + 3[\mathrm{MoOCl_4(DMF)^-}]_0) \ln [\mathrm{MoOCl_4(DMF)^-}] = k_6k_7[\mathrm{NO_3^-}]t/k_9 + I \tag{14}$$

This expression, while similar in form to our expression 13, is untestable since k_{-6}, k_7, and k_9 are not known nor can they be obtained from a plot of (11) in the presence of excess Cl^-. Furthermore, a comparison of (14) with our expression (13) indicates it would not be consistent with the data unless $3\cdot[\mathrm{MoOCl_4(DMF)^-}]_0 >> k_{-6}[\mathrm{DMF}]/k_9 + k_7[\mathrm{NO^{3-}}]/k_9$ (a further assumption), in which case it would be identical with (13), with $k_{obsd} = k_6k_7[\mathrm{NO_3^-}]/k_9$.

As evidence for their mechanism, Garner, et al. cite a plot of k_{obsd} vs. excess $[\mathrm{NO_3^-}]$ in the absence of added Cl^- (Figure 1 of ref 2) which is linear, and from which they conclude $k_6 \gg k_{obsd}$. It is not possible to come to this conclusion from their integrated rate expression 14, regardless of the assumptions. On the other hand, this conclusion cannot be arrived at on the basis of (11), since this is only applicable in the presence of excess Cl^-. The linear dependence of k_{obsd} on $[\mathrm{NO_3^-}]$ follows directly from (13), of course, since $k_{obsd} = k'[\mathrm{NO_3^-}]$.

Garner et al. also state a plot of $[\mathrm{NO_3^-}]/k_{obsd}$ vs. excess $[\mathrm{Cl^-}]$ supports eq 11. While such a plot is reasonably linear, it has a negative intercept (−52.8 ± 10.7); since the intercept equals $[\mathrm{NO_3^-}]/k_6 + k_{-6}[\mathrm{DMF}]/k_6k_7$ and must be positive, the plot in fact argues against the validity of their mechanism.

Finally, the mechanism of Garner et al. requires a fast isomerization of the $\mathrm{MoOCl_4(NO_3)^{2-}}$ complex formed in reaction 7 in order that an oxygen will be in the required cis position to the Mo(V) oxo group for electron transfer[4] (the NO_3^- must of necessity enter the vacant trans position of $MoOCl_4^{-1}$). In our mechanism, a reasonable possibility exists for the NO_3^- being bidentate in the complex $\mathrm{MoOCl_3(NO_3)^-}$, which gives the cis geometry; this possibility is strongly supported by the observed Cl^- inhibition, a fact of considerable importance in interpreting the mechanism:



Registry No. $(NH_4)_2MoOCl_5$, 17927-44-5; NO_3^-, 14797-55-8.

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Problems in the Study of Aluminum(III) Complexation Kinetics

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Sir:

To both analytical and inorganic chemists, the dynamics of aluminum(III) complex formation has been important, useful, and—most often—puzzling. Recent studies on equilibria in aqueous acidic aluminum(III) solutions[1] and on the kinetics and mechanism of aluminum–salicylate complexation in the same medium[2] have convinced us that analytical and inorganic chemists often work—and publish—in ignorance of one another. Consequently, this letter points out several significant features of aqueous aluminum(III) solutions which constrain dynamical studies of these systems.

Speciation in Aqueous Aluminum(III) Solutions. To effect a separation of aluminum from other ions and at the same time to achieve a reliable quantitative determination of aluminum, Kolthoff and Sandell developed the method of precipitation with 8-hydroxyquinoline.[3] However, their procedure yields low and erratic results unless the analysis is carried out with the prescribed acetic acid–acetate buffer. This observation led to investigations on the species present in aqueous aluminum(III) solutions in the pH range 1–7.[4]

Attempts to characterize partially neutralized aluminum chloride solutions by means of the extent or rate of reaction of aquoaluminum(III) with an organic ligand probably begin with the work of Linnell,[5] who measured the amount of aluminum 8-hydroxyquinolinate precipitated from solution as a function of time by a gravimetric procedure. At about the same time, and independently, Okura, Goto, and Yotuyanagi studied the extraction of the aluminum 8-hydroxyquinolinate into chloroform immediately after mixing the reagents.[6] On the basis of this procedure the aluminum in solution was divided into "extractable" and "unextractable" species. This technique was modified by Turner, who subdivided the aluminum present in solutions of this type into three forms on the basis of relative reaction rates.[7] Evidence for the existence of aluminum species differing in their reactivity toward a complexing ligand could be gathered more easily and reliably following Smith's development of a single-phase spectrophotometric method.[4] This procedure uses the derivative 8-hydroxy-7-iodo-5-quinolinesulfonic acid, or "ferron", which forms a water-soluble aluminum complex whose formation may be followed spectrophotometrically.

Addition of ferron to a partially neutralized solution of $AlCl_3$ at pH 5 leads to a typical result shown in Figure 1. From the dynamics of the trace, three types of aluminum can be identified. Reacting quickest is Al^a; then, the reaction of Al^b occurs. These two reactions, usually requiring no more than 1 h for completion, are followed by the very slow reaction of Al^c, which may last for days. Current analytic investigations are concerned with the nature of Al^b and Al^c; Al^a is assumed to be monomeric.[1]

Dynamics of Aluminum(III) Complex Formation. The rate of exchange of water molecules between bulk solvent and a metal ion's inner coordination shell is a fundamental factor governing the rate of complexation. In 0.5 M $HClO_4$ solutions of $AlCl_3$, this rate constant was measured by Fiat and Connick to be 1.3×10^{-1} s^{-1} at 25 °C by using $H_2{}^{17}O$ NMR line broadening.[8] Earlier, Behr and Wendt had applied the pressure-jump method to solutions of aluminum sulfate in the pH range 1–3.[9] Hydrogen ion dependent relaxation times on the order of 10^{-1} s were measured. These results lead to a less definitive mechanism than the high-acid NMR experiments; however, it is now clear that at least one monomeric species other than Al^{3+}—probably $AlOH^{2+}$—is required to fit the data.[2,10,11]

Sources of Difficulty in the Interpretation of Aluminum(III)