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Hexachloroiridate(IV) Oxidation of Hexathiocyanatomolybdate(III). Formation of Molybdenum(IV) and Identification of an Aquation Step Prior to Oxidation to Molybdenum(V)

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Whereas the oxidant $IrCl_6^{2-}$ has been fairly extensively studied,[1] the redox properties of $Mo(NCS)_6^{3-}$ have not previously been investigated.[2] An x-ray crystal structure determination on the adduct, $K_3[Mo(NCS)_6]\cdot CH_3COOH\cdot H_2O$,[3] has provided conclusive evidence for octahedral coordination, as well as for N-bonded thiocyanate. Studies on the rate of NCS^- exchange on $Mo(NCS)_6^{3-}$ have indicated a very inert Mo(III) center.[4]

The potassium and pyridinium salts of the Mo(IV) complex $[Mo(NCS)_6]^{2-}$ have been prepared,[5] and their spectra in nonaqueous media reported.[6] The tendency of Mo(IV) (and other oxidation states of Mo) to utilize higher coordination numbers, e.g., with CN^-, has been noted and the complex $Mo(CN)_8^{4-}$ is now well characterized.[7] Three Mo(V) thiocyanato complexes, $MoO(NCS)_5^{2-}$, $Mo_2O_3(NCS)_8^{4-}$ (μ-oxo), and $Mo_2O_4(NCS)_6^{4-}$ (di-μ-oxo),[8] have been prepared. A feature of these and other Mo(V) complexes is the inclusion of at least one oxo ligand.

This study is concerned with the oxidation of Mo(III) through Mo(IV) to Mo(V) and the restraints imposed by the need to provide an oxo ligand prior to the formation of Mo(V). Although certain aspects of the detailed mechanism remain tentative, detection of a rate controlling first-order process, which involves the Mo(IV) intermediate and which is independent of initial oxidant and reductant concentrations, is regarded as significant.

Experimental Section

Reactants. Hexathiocyanatomolybdate(III) was prepared from $K_3[MoCl_6]$ (Climax Molybdenum Co.) (10 g), which was dissolved in 50 mL of KNCS (7 M) and heated on a steam bath at ca. 60 °C for 2 h. Color changes from red to cherry red to a deep orange were observed. The hot solution was filtered and cooled in ice. Yellow crystals deposited were filtered off and washed with a minimum amount of ice-cooled water. The solid was left to dry overnight over silica gel. Anal. Calcd for $K_3[Mo(NCS)_6]\cdot 4H_2O$: Mo, 15.1; N, 13.3; C, 11.4; S, 30.2; H, 1.26; K, 18.5. Found: Mo, 15.2; N, 13.1; C, 12.4; S, 30.0; H, 1.4; K, 19.0. Details of the spectrum (H_2O), with peaks at 320 nm (ϵ 2.05 × 10^4 M^{-1} cm^{-1}) and 245 nm (ϵ 9.25 × 10^4 M^{-1} cm^{-1}), are in satisfactory agreement with a previously reported spectrum.[2]

Sodium hexachloroiridate(IV), $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson and Matthey) was used without further purification. The peak position at 487 nm (ϵ 4075 M^{-1} cm^{-1}) and a minimum at 460 nm (ϵ 2070 M^{-1} cm^{-1}) were in agreement with literature values.[1] Solutions in dilute acid were stable to aquation over a day.

Other Reagents. Commercially available HCl, NaCl, acetonitrile and acetone were of AnalaR grade purity. Reagent grade LiCl was used.

Stability of Reactants. Solutions of $K_3Mo(NCS)_6$ in H_2O were found to be relatively stable in air at 25 °C, i.e., <5% change in absorbance over 1 h. The same spectrum and stability were observed in both 0.1 M HCl and H_2O. All solutions were stored in ice and used within 3 h of preparation. Spectra in acetonitrile and acetone were the same. Such solutions were stable at 25 °C. Solutions of $IrCl_6^{2-}$ in acetonitrile and acetone were stable for >1 h. The twin peaks ca. 430 nm in aqueous media appear as a single peak in these solvents. The absorption coefficient at 487 nm was 3% greater in nonaqueous media.

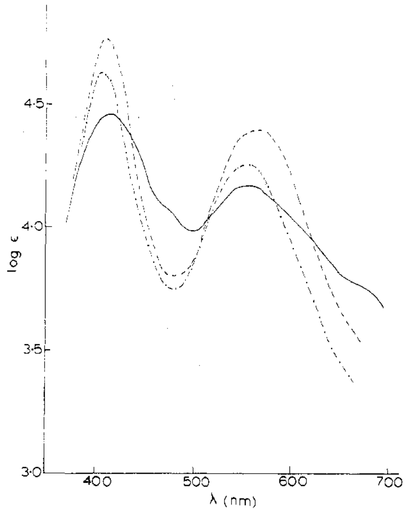

Figure 1. Spectra of the 1:1 product obtained in the $IrCl_6^{2-}$ oxidation of $Mo(NCS)_6^{3-}$ in acetonitrile (–·–) acetone (– –) and 0.10 M aqueous HCl (—). The latter is an intermediate spectrum which was obtained using a stopped-flow spectrophotometer.

Stoichiometries. The stoichiometry for the $IrCl_6^{2-}$ oxidation of $Mo(NCS)_6^{3-}$ in 0.1 M aqueous HCl was determined by adding $IrCl_6^{2-}$ to $Mo(NCS)_6^{3-}$ (in excess) and monitoring absorbance changes at 350 nm for $Mo(NCS)_6^{3-}$. A stoichiometry of 2Ir:1Mo was indicated. By addition of $Mo(NSC)_6^{3-}$ to $IrCl_6^{2-}$ (in excess) and monitoring changes at the $IrCl_6^{2-}$ peak at 487 nm a different stoichiometry of 3Ir:1Mo was obtained. On the stopped-flow time scale a 1:1 stoichiometry was determined by Job's method[9] for the formation of a purple-brown intermediate (λ 540 nm). A 1:1 stoichiometry was obtained for the reaction in acetone and in acetonitrile, in which solution the purple species is the final product. All stoichiometries were to within 10% of quoted values.

Kinetic Studies. A Durrum-Gibson stopped-flow spectrophotometer was used for studies in aqueous solution. The concentration of HCl was varied and the ionic strength adjusted to 1.0 M with NaCl or LiCl. Conventional spectrophotometric studies were made using Unicam SP500 (manual) and SP8000 (recording) instruments. First-order rate constants k_{obsd} were obtained from the slopes (×2.303) of plots of absorbance change $\log (A_t - A_\infty)$ against time. Such plots were linear to at least 3 half-lives.

Results

Spectra of the product obtained in the 1:1 reaction of $Mo(NCS)_6^{3-}$ (ca. 8 × 10^{-5} M) with $IrCl_6^{2-}$ (ca. 1 × 10^{-5} M) in acetonitrile (λ_{max} 560 nm, ϵ 1.8 × 10^4 M^{-1} cm^{-1}; λ_{max} 408 nm, ϵ 4.3 × 10^4 M^{-1} cm^{-1}) and in acetone (λ_{max} 565 nm, ϵ 2.5 × 10^4 M^{-1} cm^{-1}; λ_{max} 410 nm, ϵ 5.8 × 10^4 M^{-1} cm^{-1}) are as shown in Figure 1. The reaction is believed to be as in (1),

$$\mathrm{Mo(III)} + \mathrm{Ir(IV)} \rightarrow \mathrm{Mo(IV)} + \mathrm{Ir(III)} \qquad (1)$$

where the purple color is attributed to the Mo(IV) species. Absorption contributions by Ir(III) in the UV–visible range are relatively small and could be neglected.[1] The rate of decay of the purple color was slow even with 50% H_2O present ($t_{1/2}$ ~ 2 h at 25 °C).

The reaction of $Mo(NCS)_6^{3-}$ with $IrCl_6^{2-}$ in aqueous solutions [HCl] = 0.10 M (I = 0.10 M) gave an intermediate coloration, the decay of which could be monitored by stopped flow. Under these conditions with reactant concentrations $[Mo(NCS)_6^{3-}]$ = (1–5) × 10^{-4} M and $[IrCl_6^{2-}]$ = (0.5–2.5) × 10^{-5} M a first-order process with rate constant k_{obsd} = 6.29 ± 0.12 s^{-1} at 25 °C was obtained. The spectrum of the species undergoing decay is independent of reactant concentrations and $[H^+]$ (extended range 0.05–1.00 M). Comparisons with the nonaqueous spectra, Figure 1, suggest that the Mo(IV) oxidation state is dominant. The effect of $[H^+]$ on k_{obsd} was investigated with I = 1.00 M (NaCl), Table I. Replacement of NaCl by LiCl had no effect on k_{obsd}, Figure 2. Using a

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Table I. Dependence of First-Order Rate Constants, k_{obsd}, for Decay of Intermediate in Oxidation of $Mo(NCS)_6^{3-}$ by $IrCl_6^{2-}$ at 25 °C, λ 550 nm, I = 1.00 M (NaCl) Except as Stated

10^5[Mo(III)], M	10^5[Ir(IV)], M	[H^+], M	k_{obsd}, s^{-1}	k_{calcd},[a] s^{-1}
50.0	2.50	0.050	11.0	10.8
50.0	5.00	0.050	11.1[b]	10.8
10.0	2.50	0.065	10.3	9.8
9.6	0.59	0.10	7.7	8.4
50.0	5.00	0.10	8.2[b]	8.4
20.0	2.50	0.15	6.8 (2)	7.0
50.0	5.00	0.20	6.5[b]	6.4
20.0	2.50	0.25	5.8	5.8
20.0	2.50	0.40	5.0	4.8
10.0	2.50	0.50	5.3	4.6
50.0	5.00	0.50	5.0[b]	4.6
10.0	2.50	0.60	4.9	4.2
10.0	2.50	0.80	4.1	4.0
9.6	0.43	1.00	3.3[c]	3.8

[a] Equivalent to k_{obsd} in eq 2. [b] I = 1.00 M (LiCl). [c] Wavelength varied: k_{obsd} = 3.65 (λ 400 nm), 3.90 (λ 600 nm), and 3.60 s^{-1} (700 nm).

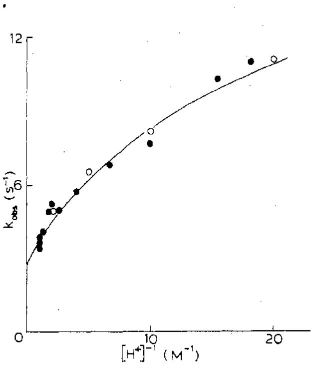

Figure 2. The [H^+] dependence of rate constants k_{obsd} for decay of the intermediate in the $IrCl_6^{2-}$ oxidation of $Mo(NCS)_6^{2-}$ (in excess) in aqueous solution. Ionic strengths were adjusted to 1.00 M with NaCl(●) and LiCl(○).

nonlinear least-squares program[10] the dependence of k_{obsd} on [H^+] (all data in Table I) gave a good fit to (2), which can

$$k_{obsd} = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \tag{2}$$

be derived for a reaction sequence of the kind (3)–(5), where

$$MoOH_2 \overset{K_a}{\rightleftharpoons} MoOH + H^+ \tag{3}$$

$$MoOH_2 \xrightarrow{k_1} \tag{4}$$

$$MoOH \xrightarrow{k_2} \tag{5}$$

(4) and (5) are assigned to thiocyanate aquation steps. Prior formation of an H_2O adduct is required to permit these reactions to occur, see Discussion. Values obtained, K_a = 0.06 ± 0.03 M, k_1 = 2.96 ± 0.3 s^{-1}, and k_2 = 17.4 ± 3.8 s^{-1} at 25 °C, I = 1.00 M, give k_{calcd} in Table I. These rate constants are divisible by two if the Mo(IV) disproportionation mechanism suggested below applies. The rate constants indicate a relatively mild conjugate–base rate enhancement.[11]

Discussion

The stoichiometry for the $IrCl_6^{2-}$ oxidation of $Mo(NCS)_6^{3-}$ is 1:1 in both acetonitrile and acetone. Spectra, Figure 1, are to be compared with that reported by Mitchell and Williams[6] for the Mo(IV) complex $(PyH)_2[Mo(NCS)_6]$ in acetone (λ_{max} 565, ε 2.56 × 10^4 M^{-1} cm^{-1}; λ_{max} 410 nm, ε 6.2 × 10^4 M^{-1} cm^{-1}), where in addition a shoulder (λ 420 nm, ε 5.3 × 10^4 M^{-1} cm^{-1}) was reported. There seems little doubt that in both acetonitrile and acetone the purple Mo(IV) complex, $Mo(NCS)_6^{2-}$, is formed. A 1:1 reaction of $Mo(NCS)_6^{3-}$ and $IrCl_6^{2-}$ is also observed in aqueous solution, but in this case the Mo(IV) species has only a transitory existence. The spectrum obtained by monitoring the initial absorbance generated at different stopped-flow wavelength settings is very similar to the spectra in the nonaqueous solvents, a notable difference being the shoulders ca. 480 and 680 nm. The only measurable stopped-flow process is the first-order decay of the Mo(IV) absorbance. Subsequent changes are rapid.

Since varying amounts of the $Mo(NCS)_6^{3-}$ and $IrCl_6^{2-}$ reactants do not affect the rate of the Mo(IV) decay, a substitution process at the Mo(IV) is suggested. The [H^+] dependence (2) would seem to implicate a coordinated H_2O since we have no evidence for protonation of coordinated thiocyanate. The initially formed Mo(IV) will presumably be octahedral $Mo(NCS)_6^{2-}$ as in nonaqueous solvents. We suggest that in aqueous solution this species can rapidly increase its coordination numbers (6), where n is either 1 or 2,

$$Mo(NCS)_6^{2-} + nH_2O \rightleftharpoons Mo(NCS)_6(H_2O)_n^{2-} \tag{6}$$

and that new species so formed are responsible for the additional absorbance ca. 480 and 680 nm, Figure 1. Aquation of one NCS^- then occurs as in (3)–(5), where this is the process which is monitored on the stopped-flow time scale. At this stage all the oxidant has been consumed.

To account for the 1Mo:2Ir stoichiometry, which is observed in aqueous solutions when the $Mo(NCS)_6^{3-}$ reactant is in excess, a rapid Mo(IV) disproportionation step is proposed. This involves nonidentical Mo(IV) reactants, one of which has a coordination sphere appropriate for oxidation to Mo(V) and the other for reduction back to Mo(III). It is known that in all but a very few cases Mo(V) complexes have one terminal oxygen atom per molybdenum.[12] Therefore the aquation processes (4) and (5), by reducing the number of thiocyanates from 5 to 6, prepare the way for oxidation to an oxo–Mo(V) species. The Mo(IV) disproportionation process involving hexathiocyanato and pentathiocyanato species can then occur. An equivalent of $Mo(NCS)_6^{3-}$ (reactant in excess) is regenerated. Thus from an experiment with $Mo(NCS)_6^{3-}$ in only slight excess it is observed that all the Mo(III) remaining has the spectrum of $Mo(NCS)_6^{3-}$. The overall reaction in aqueous solution can therefore be summarized by (7), where the only

$$Mo(III) + 2Ir(IV) \rightarrow Mo(V) + 2Ir(III) \tag{7}$$

measurable rate process is that involving aquation of the hexathiocyanatomolybdenum(IV) species. Reactions which are believed to be relatively rapid and non-rate-determining are (a) the initial Ir(IV) oxidation of Mo(III), (b) the equilibration process involving addition of H_2O and increase in coordination number prior to the rate-controlling aquation process, and (c) the disproportionation of the Mo(IV) species.

When the $IrCl_6^{2-}$ reactant is in excess a stoichiometry of 1Mo:3Ir is observed consistent with the overall reaction

$$Mo(III) + 3Ir(IV) \rightarrow Mo(VI) + 3Ir(III) \tag{8}$$

Some kinetic studies carried out under these conditions indicated a less than first-order dependence of k_{obsd} on [$IrCl_6^{2-}$]. The further implications of this dependence are not at present understood.

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Registry No. $IrCl_6^{2-}$, 16918-91-5; $Mo(NCS)_6^{3-}$, 35215-16-8.

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Hydrogen Isotope Effects in Titanium Alloy Hydrides

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There are usually quite large differences in stability among the protides, deuterides, and tritides of a given metal or alloy. Such isotope effects have been made the subject of a rather voluminous literature. A list of references up to 1970 is given in an earlier publication from this laboratory.[1] Since that time, a number of other researches in this field have been reported.[2-10] The bulk of the work has dealt with binary hydrides. A few alloys have also been studied, but they form a rather miscellaneous group, from which no generalizations can be derived. It was, therefore, thought worthwhile to examine, in this respect, a series of alloys formed between a single hydride-forming metal and a number of other metals most of which did not themselves form stable hydrides. Titanium was chosen as the constant constituent, since it forms intermetallic compounds or solid solutions with almost every transition element, and many of these alloys were already known to form hydrides. Of particular interest was the periodic trend of the hydrogen isotope effect as a function of the transition metal alloyed with titanium. In order to determine isotope effects on a large number of metal–hydrogen systems in a relatively short time, the method of tritium exchange was chosen. Those systems which have been shown by this test to be of special interest are being subjected to a more exhaustive study, in which *P–C–T* data are being obtained for deuterium as well as protium. The results so far may be considered as of a preliminary nature, but they appear to have enough interest in themselves to warrant publication at this time.

Experimental Section

Small quantities of tritium were introduced into a gaseous hydrogen phase in equilibrium with a quantity of a given metal hydride. A fairly rapid exchange usually occurred, the progress of which was followed by measuring the radioactivity of successive small samples of the gas phase. When no further change took place, equilibrium was assumed to have been reached. From a knowledge of the initial and final amounts of gas phase tritium and the tritium concentration in the gas recovered from the thermally decomposed hydride, the equilibrium constant for isotopic distribution could be derived.

The apparatus used consisted, in essence, of a closed loop of stainless steel tubing through which hydrogen was circulated by a pump. The sample of solid hydride was supported on a frit in one of the vertical members. Typical quantities were as follows: weight of alloy, 10 g; volume of loop, 29 mL; hydrogen pressure, 15.3 atm; amount of tritium introduced, 26 μCi. Temperatures ranged from −20 to +40 °C; for their control, most of the loop was immersed in a circulating bath of water or refrigerated methanol or, for 0 °C, a static ice bath. Pumping action for the gas phase was provided by connecting to the loop a side arm leading to a mercury piston. Check valves above and below the junction of the side arm to the loop provided for the desired one-way circulation of gas. The mercury piston was actuated by a fluctuating hydrogen pressure on the far side of the U-tube that contained it. The fluctuations derived from the alternate heating and cooling of a reservoir of vanadium dihydride, as described in a previous publication.[11] A schematic diagram of the entire gas-handling apparatus is shown in Figure 1.

Tritium determinations were accomplished by gas-phase β counting. For this purpose, a small quantity of the gas in the loop was drawn off into an evacuated proportional counter tube.[12] To this gas (at 0.0658 atm) was then added a quantity of "P-10" counting gas to bring the total pressure to 0.987 atm and a count was obtained using standard electronic equipment. The count rate was usually of the order of 60 000 cpm.

Alloys were made by arc-melting metal components of at least 99.9% purity, obtained from Ventron-Alpha. The alloy buttons were crushed to 20 mesh before use. The granular material was converted to hydride in situ by treatment with tank hydrogen (VHP grade, 99.999% pure from the Matheson Co.). A pressure of 40.8–54.4 atm was applied until no further uptake occurred. Dehydriding was then induced by pumping, first at room temperature, then heating to 450 °C to drive off the last traces. In repeating this cycle several times, an increasingly fast uptake was observed. When no further increase in initial rate occurred, the sample was considered activated. At some point previous to the final hydriding and exchange experiments, the composition of the hydride in equilibrium with high-pressure gas was determined by causing the gas released on dehydriding to expand into calibrated volumes and measuring the pressure. The formulas of the maximum hydride, and of the hydride in equilibrium with the operating pressure of the exchange experiments, were obtained in this manner. They are included in Table I.

The source of tritium was a 1-Ci capsule of T_2 from New England Nuclear which was diluted with about 4×10^6 parts of high-purity normal hydrogen; the final pressure of the mixture was ~60 atm. At the start of a run, the lower half of the loop (that containing the hydride sample) was valved off, a quantity of the dilute tritium was added to the upper half, and more hydrogen was added until the pressure equaled that in the lower half. Tritium was allowed to distribute itself uniformly throughout the upper half, the mixing process being assisted by pressure fluctuations induced by the mercury piston. When analysis of samples showed no further change in tritium activity at the sampling point, its concentration was presumed uniform and the loop valves were opened at "$t = 0$." Samples were taken thereafter every 30 or 60 min at the start and less frequently toward the end until no further change occurred. In many cases the exchange reaction

$$MH_x + HT \rightleftarrows MH_{x-1}T + H_2$$

proved fast compared with the attainment of uniformity in the composition of the circulating gas, and quantitative kinetic data could not be obtained. In other cases reaction took several hours and its progress could be followed.

At the completion of an experiment a tritium material balance was made. The amount of tritium associated with the solid was determined by decomposing the hydride, measuring the volume of gas given off and analyzing it for tritium. In practice this often involved multiple operations, since part of the hydrogen was more tenaciously held than the rest. As will be seen from Table I, good material balances were usually obtained. Even where a deficit of 10% was found, it is not believed that the α values are seriously in error on this account.

Results and Discussion

From the experimental observations there was obtained for each material one or more values of α, the tritium distribution coefficient. It is defined as

$$\alpha = (T/H)_{\text{solid}}/(T/H)_{\text{gas}}$$

It was experimentally determined by dividing the counts per minute of the gas obtained from the solid phase by the counts per minute of the gas phase in equilibrium with the solid phase. It should be independent of concentration in the very dilute region used in our experiments. It can generally be expected

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