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DISPROPORTIONATION REACTIONS OF THE ACETONITRILE DERIVATIVES OF GROUP VI HEXACARBONYLS

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Summary

The disproportionation reactions of [$M(CO)_{6-n}(CH_3CN)_n$] (M = Cr, Mo, W; n = 1—3) proceed in solution according to the sequence $M(CO)_3(CH_3CN)_3 \rightarrow M(CO)_4(CH_3CN)_2 \rightarrow M(CO)_5(CH_3CN) \rightarrow M(CO)_6$. Rapid changes are observed in Nujol and acetone at ambient temperature, but in acetonitrile comparable changes require higher temperatures. Additional carbon monoxide groups are provided by the complete decomposition of part of the sample of the complex but free carbon monoxide is not detected in solution. The observed disproportionation reactions enable the use of $M(CO)_3(CH_3CN)_3$ complexes for the synthesis of $M(CO)_4$ derivatives to be rationalised. The nature of an intermediate absorbing at 1996 cm^{-1} in the IR spectrum is discussed.

Introduction

Substitution reactions of Group VI metal hexacarbonyls have been widely studied [1], and those involving acetonitrile investigated in depth [2, 3]. Ultraviolet irradiation affords a clean and efficient method of effecting substitution, and monitoring of the reactions by IR spectroscopy has revealed a series of stepwise substitution reactions, for example eqn. 1 [2, 3].

$$W(CO)_6 \xrightarrow[h\nu]{CH_3CN} W(CO)_5(CH_3CN) \xrightarrow[h\nu]{CH_3CN} W(CO)_4(CH_3CN)_2 \xrightarrow[h\nu]{CH_3CN} W(CO)_3(CH_3CN)_3 \quad (1)$$

It was noted that as the irradiation continued the concentrations of the tetra- and tri-carbonyl species increased, but that if the resultant mixture was allowed to stand after irradiation, $W(CO)_6$ was reformed in appreciable amounts [2]. Whether this latter process involved "free" carbon monoxide, generated in the substitution reactions (1) and dissolved in solution or decomposition of part

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of the sample to a lower carbonyl-containing compound is not known. The presence of equilibria involving the liberated carbon monoxide and the four complexes was inferred, and supported by the conditions under which the complexes are most efficiently prepared.

We embarked on a study of the decomposition reactions of $[M(CO)_{6-n}(CH_3CN)_n]$ (M = Cr, Mo, W; n = 1—3) in an attempt to detect any intermediates formed, and to establish the sequence of reactions followed. The initial use of substitution products rather than the hexacarbonyls was preferred since the possibility that any additional carbonyl groups originated from free carbon monoxide [remaining in solution after the substitution reactions of $M(CO)_6$] is eliminated. The only source then becomes the carbonyl complexes themselves.

The relative lability of acetonitrile complexes compared with similar complexes having aromatic amine and phosphine ligands renders them useful catalysts [4] and starting materials for other substituted carbonyl complexes [5, 6]. Indeed $[M(CO)_3(CH_3CN)_3]$ (M = Cr, Mo, W) have been used as sources of $M(CO)_3$ [5] and even $M(CO)_4$ moieties [6]. The generation of metal carbonyl units different from those originally introduced into solution may arise by either of two processes illustrated in eqns. 2 and 3. The carbonylation reaction

$$M(CO)_3(CH_3CN)_3 + CO \rightleftharpoons M(CO)_4(CH_3CN)_2 + CH_3CN \quad (2)$$

$$2M(CO)_5(CH_3CN) \rightarrow M(CO)_6 + M(CO)_4(CH_3CN)_2 \quad (3a)$$

$$5M(CO)_4(CH_3CN)_2 \rightarrow 4M(CO)_5(CH_3CN) + 6CH_3CN + M \text{ (in some form)} \quad (3b)$$

(2) becomes possible only if carbon monoxide is generated by decomposition of part of the sample. Attempts were made using a high pressure IR cell to detect "free" carbon monoxide generated and new carbonyl complexes such as $[M(CO)_2(CH_3CN)_4]$ and $[M(CO)(CH_3CN)_5]$ which may be stabilised sufficiently in the closed system to be detected. Such acetonitrile complexes are not known and the accepted reason for substitution reactions of the hexacarbonyls terminating at $M(CO)_3(CH_3CN)_3$ complexes relates to the relative σ- and π-bonding capacities of carbonyl and acetonitrile ligands [1]. However disproportionation reactions may involve the transient formation of mono- and di-carbonyl complexes, and if so the high pressure equipment makes their detection possible.

Experimental

$M(CO)_5(CH_3CN)$ [1, 7, 8], $M(CO)_4(CH_3CN)_2$ [1, 7], and $M(CO)_3(CH_3CN)_3$ [9] (M = Cr, Mo, W) were synthesised by standard methods. Spectroscopic grade acetonitrile and acetone were used without further purification, but were degassed and stored under nitrogen before use. All manipulations were performed in a dry nitrogen atmosphere or against counterflows of nitrogen gas in an effort to eliminate aerial oxidation.

For the spectral study a specially constructed high pressure IR cell [10] was used in association with a Perkin—Elmer 257 spectrophotometer.

In a typical experiment ca. 50—70 mg of the complex under study was dissolved in a ca. 25 ml of solvent, and the solution syringed into the high pressure cell against a counter current of nitrogen. After sealing the cell, spectra were recorded in the 2200—1550 cm^{-1} region, against solvent in an identical reference cell. For example in experiment 5 summarised in Table 1, the initial spectrum of

$W(CO)_3(CH_3CN)_3$ at 20° and 27 atm. pressure of nitrogen consisted of two strong absorptions at 1910 and 1790 cm^{-1}. On warming to 50° new absorptions appeared at 2018 and 1842 cm^{-1} but did not achieve more than weak to medium intensity after 1 h. Further heating up to 150° slowly over a further 2½ h caused an increase in the intensity of the latter two absorptions and the appearance of a new strong band at 1895 cm^{-1}. This absorption appeared initially as a shoulder on the 1910 cm^{-1} peak, then became of equal intensity before becoming the main component. At 150° a shoulder was discernible at ca. 1930 cm^{-1}, and on further heating to 220° over ¾ h this absorption became more intense at the expense of the absorptions at 2018 m, 1895 vs and 1842 s cm^{-1}. The absorptions at 1910(sh) and 1790 cm^{-1} became less intense before disappearing on the temperature reaching 220°. On standing at this temperature for a further 16 h the asymmetrical absorption at 1934 cm^{-1} dominated the spectrum, but shoulders at 2018, 1895 and 1842 cm^{-1} were still detectable although with very little intensity. A slight inflection at ca. 1970 cm^{-1} had also appeared. On cooling to room temperature after a total reaction time of ca. 20 h no further changes in the spectrum occurred.

By reference to the reported spectra of $W(CO)_{6-n}(CH_3CN)_n$ complexes we have assigned absorptions at 1910 s and 1790 s cm^{-1} to $W(CO)_3(CH_3CN)_3$ [11, 12], absorptions at 2018 m, 1896 vs and 1842 s to $W(CO)_4(CH_3CN)_2$ [11, 12], the absorption at 1934 vs cm^{-1} to $W(CO)_5(CH_3CN)$ [11, 12] and the inflection at 1970 cm^{-1} to $W(CO)_6$ [11]. Absorptions additional to that in the 1930 cm^{-1} region have been assigned to $W(CO)_5(CH_3CN)$ [11, 12] but in this study a weak absorption at 2068 cm^{-1} persisted through the experiment and obscured any other absorption in this region of the specturm, and the asymmetrical absorption at 1934 cm^{-1} appears to embrace the two absorptions reported at 1948 and 1931 cm^{-1} for a n-hexane solution [11, 12].

Solid non-carbonyl decomposition material was present in the cell at the end of all the experiments, but was not studied further.

Results and discussion

The spectral changes occurring for $M(CO)_{6-n}(CH_3CN)_n$ complexes in acetonitrile, acetone and Nujol solutions were followed, details of the changes which occurred being summarised in Table 1. The complexes were identified by use of published IR spectra [11, 12] and spectra of authentic samples.

Rapid changes in the IR spectra of solutions of complexes resulted when Nujol and acetone were the solvents, the final product being the metal hexacarbonyl. More controlled changes could be affected using acetonitrile as the solvent and was generally preferred although the final products in this case were invariably $M(CO)_5(CH_3CN)$ complexes.

The results collected in Table 1 indicate that complexes of the type $M(CO)_{6-n}(CH_3CN)_n$ may be present in solution together with complexes having a lower degree of carbonyl substitution. The proportion of each complex depends on the age of the solution, the solvent used and on the temperature. Consequently, reactions of $M(CO)_3(CH_3CN)_3$ complexes, for example, may lead to tri-, tetra- or penta-carbonyl complexes [and $M(CO)_6$] depending on the reaction conditions and general stability of the resultant complexes to undergo similar changes. Indeed, although this study has been directed towards acetonitrile

TABLE 1

DETAILS OF CHANGES OCCURRING FOR $[\mathrm{M(CO)_{6-\mathit{n}}(CH_3CN)_{\mathit{n}}}]$ (M = Cr, Mo, W; n = 1–3) COMPLEXES IN SOLUTION UNDER HIGH PRESSURES OF NITROGEN WITH INCREASING TEMPERATURE AND/OR AGE OF THE SOLUTION

Experiment	Solvent	Initial pressure N_2	Experimental results
1	CH_3CN	55 atm.	$\mathrm{Cr(CO)_3L_3} \xrightarrow[3\ \mathrm{h}]{20-150^\circ} \begin{array}{l}\mathrm{Cr(CO)_4L_2}\\ \mathrm{+Cr(CO)_5L}\\ \mathrm{+Cr(CO)_6(t)}\end{array} \xrightarrow[1\ \mathrm{h}]{150^\circ} \begin{array}{l}\mathrm{Cr(CO)_5L}\ ^a\\ \mathrm{+Cr(CO)_6(t)}\end{array} \xrightarrow{>150^\circ} \text{decomposition}$
2	CH_3CN	55 atm.	$\mathrm{Cr(CO)_4L_2} \xrightarrow{25-125^\circ} \mathrm{Cr(CO)_5L}\ ^a \xrightarrow{>150^\circ} \text{decomposition}$
3	CH_3CN	40 atm.	$\mathrm{Mo(CO)_3L_3} \xrightarrow[18\ \mathrm{h}]{20-150^\circ} \begin{array}{l}\mathrm{Mo(CO)_4L_2}\\ \mathrm{+Mo(CO)_5L(mi)}\end{array} \xrightarrow{170^\circ} \begin{array}{l}\mathrm{Mo(CO)_5L}\\ \mathrm{+Mo(CO)_4L_2(mi)}\end{array}$
4	CH_3CN	40 atm.	$\mathrm{Mo(CO)_4L_2} \xrightarrow[1\ \mathrm{h}]{25-100^\circ} \begin{array}{l}\mathrm{Mo(CO)_5L} \xrightarrow{100-150^\circ} \mathrm{Mo(CO)_6}\\ \mathrm{Mo(CO)_5L}\ ^a \xleftarrow{160^\circ} \mathrm{Mo(CO)_6}\end{array}$
5	CH_3CN	27 atm.	$\mathrm{W(CO)_3L_3} \xrightarrow[3\frac{1}{2}\ \mathrm{h}]{20-150^\circ} \begin{array}{l}\mathrm{W(CO)_3L_3}\\ \mathrm{+W(CO)_4L_2}\end{array} \xrightarrow[\frac{3}{4}\ \mathrm{h}]{150-280^\circ} \begin{array}{l}\mathrm{W(CO)_4L_2}\\ \mathrm{+W(CO)_5L(t)}\end{array} \xrightarrow[16\mathrm{h}]{220^\circ} \begin{array}{l}\mathrm{W(CO)_5L}\\ \mathrm{+W(CO)_4L_2(t)}\end{array} \xrightarrow{20^\circ} \begin{array}{l}\mathrm{W(CO)_5L}\\ \mathrm{+W(CO)_4L_2(t)}\end{array}$
6	CH_3CN	27 atm.	$\mathrm{W(CO)_4L_2} \xrightarrow[\frac{1}{4}\ \mathrm{h}]{130^\circ} \begin{array}{l}\mathrm{W(CO)_4L_2(ma)}\\ \mathrm{+W(CO)_5L}\\ \mathrm{+W(CO)_6}\end{array} \xrightarrow[\frac{1}{2}\ \mathrm{h}]{150^\circ} \begin{array}{l}\mathrm{W(CO)_4L_2(ma)}\\ \mathrm{+W(CO)_5L(mi)}\\ \mathrm{+W(CO)_6(ma)}\end{array} \xrightarrow[\frac{1}{2}\ \mathrm{h}]{150^\circ} \begin{array}{l}\mathrm{W(CO)_5L(ma)}\ ^b\\ \mathrm{+W(CO)_4L_2(mi)}\end{array}$
7	CH_3COCH_3	130 atm.	$\mathrm{W(CO)_4L_2} \xrightarrow[\frac{3}{4}\ \mathrm{h}]{20^\circ} \mathrm{W(CO)_5L} \xrightarrow[1900\ \mathrm{psi}]{50-130^\circ} \mathrm{W(CO)_6}$
8	Nujol	68 atm.	$\mathrm{W(CO)_4L_2} \xrightarrow[1\frac{1}{2}\ \mathrm{h}]{20^\circ} \mathrm{W(CO)_5L} \xrightarrow{100^\circ} \mathrm{W(CO)_6}$
9	Nujol	1 atm.	$\mathrm{W(CO)_5L} \xrightarrow[\frac{1}{2}\ \mathrm{h}]{40^\circ} \mathrm{W(CO)_6}$

[a] Prolonged standing of the reaction mixture at the maximum temperature used in the synthesis produced decomposition. [b] The reaction mixture remains unchanged on cooling to 20°; ma = major product; mi = minor product; t = trace of product.

complexes because of their synthetic and catalytic importance [4—6], the changes observed may be common to many other similar derivatives. For example, *cis*-$Mo(CO)_4(PPh_3)_2$ can be precipitated from a solution originating from $Mo(CO)_3(PPh_3)_3$ [13], and $Cr(CO)_4$(pyridine)$_2$ decomposes to $Cr(CO)_5$(pyridine), pyridine and a chromium containing, non-carbonyl compound [14]. By contrast not all complexes undergo these changes, *fac*-$Mo(CO)_3(PhCONH_2)_3$ for example remaining unchanged in solution over long periods even at high temperatures [15].

In the spectra changes observed for each complex studied no evidence was apparent for the formation of complexes such as $[M(CO)(CH_3CN)_5]$ and $[M(CO)_2(CH_3CN)_4]$ with fewer carbonyl groups than the initial complex introduced. Nor did the intensity of carbonyl absorptions of highly substituted complexes, i.e. $M(CO)_3(CH_3CN)_3$, increase at the expense of lesser substituted complexes i.e. $M(CO)_4(CH_3CN)_2$. Indeed all changes detected followed the sequence shown in eqn. 4, and a mechanism involving disproportionation reactions of the

$$M(CO)_3(CH_3CN)_3 \rightarrow M(CO)_4(CH_3CN)_2 \rightarrow M(CO)_5(CH_3CN) \rightarrow M(CO)_6 \qquad (4)$$

type 3a involving the above four complexes cannot be predominant. Such a mechanism has been suggested for M = W [2].

Mechanisms 1 and 3b are dependent on the availability of carbon monoxide, which can originate only from decomposition of part of the sample either to a non-carbonyl or to a lower carbonyl containing complex. Mono- and di-carbonyl complexes were not detected in the studies and if involved in the process their rate of decomposition must exceed their rate of formation. In other words, the eventual product of the decarbonylation process is a non-carbonyl material. Evidence for such a material being formed was obtained on opening the reaction vessel at the end of each study. The transfer of carbon monoxide may be a direct process between complexes or it may involve liberation of the free ligand. Attempts to detect "free" carbon monoxide were unsuccessful, but it may be concluded that if the latter process does operate then the amount of "free" ligand remains small, and below the detection limit of the equipment used. Since the conversion of the higher substituted complexes to lower substituted complexes appeared to be achieved in high yield, allowance being made for an appropriate proportion of the initial complex to decompose to furnish carbon monoxide, then the uptake of carbon monoxide is efficient at ambient temperatures.

Although the tri-substitution products may be synthesised from the hexacarbonyls by prolonged reflux in acetonitrile [3], when in a closed system the reactions appear to be limited to the formation of $M(CO)_5(CH_3CN)$ complexes. This is illustrated by the transient formation of $W(CO)_6$ from $W(CO)_3(CH_3CN)_3$, and its subsequent reaction with acetonitrile to form $W(CO)_5(CH_3CN)$, and by the reaction of $Mo(CO)_6$ with acetonitrile at 160° to form $Mo(CO)_5(CH_3CN)$, which is known to be unstable under normal conditions [9]. Further substitution involving the elimination of carbon monoxide may be prevented by the build-up of carbon monoxide in the closed system.

An interesting feature associated with the spectral changes of $W(CO)_4(CH_3CN)_2$ was the appearance of a strong absorption at 1996 cm^{-1} which could not be assigned to any of the $W(CO)_{6-n}(CH_3CN)_n$ complexes previously reported. The new complex appeared to be formed at the expense of $W(CO)_4(CH_3CN)_2$ and on the disappearnace of the new complex the amount of $W(CO)_5(CH_3CN)$ was increased. Two interpretations appear feasible, the formation of *trans*-$W(CO)_4(CH_3CN)_2$ or the formation of a dinitrogen complex (which appears less likely). If the 1996 cm^{-1} absorption is a $\nu(CO)$ stretching frequency, which seems highly probable, the increase of the frequency compared with that of $W(CO)_6$ is not inconsistent with the replacement of two *trans*-carbonyl groups in $W(CO)_6$ by acetonitrile molecules. Although electronic factors may imply a small resultant lowering in the stretching frequency these are not the sole considerations. The different ligands in *cis*-positions to the four equatorial carbonyl groups in *trans*-$W(CO)_4(CH_3CN)_2$ compared with $W(CO)_6$ will cause changes in the force constants and a mixing of the carbonyl and nitrile vibrations. The small difference in frequencies observed on changing the nature of the complex are well within the range expected for changes in force constants accompanying such changes in structure [16]. Thus the observed spectrum may well be interpreted as arising from *trans*-$W(CO)_4(CH_3CN)_2$.

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