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REACTIONS OF TUNGSTEN(VI) AND MOLYBDENUM(V) CHLORIDES, AND TUNGSTEN(VI) AND MOLYBDENUM(VI) OXYCHLORIDES, WITH AZOXYBENZENE

A. GRECO, F. PIRINOLI and G. DALL'ASTA
Centro Ricerche di Milano, Montedison, Via G. Colombo 81, Milan (Italy)
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Summary

Reactions of W^{VI} and Mo^{V} chlorides with azoxybenzene yield ionic species of W^{VI} and Mo^{VI} oxychlorides in which the cation is a protonated azobenzene. The reaction between $MoCl_5$ or $MoOCl_4$ and azoxybenzene gives, after extraction with methylene chloride—ethanol mixture, the complex [*trans*-$MoOCl_4(OC_2H_5)]^-$ $[C_{12}H_{10}N_2H]^+$. In contrast, $WOCl_4$ reacts with azoxybenzene to give a stable non-ionic adduct in which the organic moiety is coordinated through its oxygen atom *trans* to the W=O bond. Several complexes of substituted azoxybenzene having similar structures are described.

Introduction

The metathesis of olefinic hydrocarbons, discovered by Banks and Bailey some years ago [1], has recently attracted much attention. In spite of many suggestions, however, the mechanism of this reaction has not yet been resolved [2].

Following Dall'asta and Calderon's use of some homogeneous catalysts in the metathesis of cyclic and linear olefins, the ability of oxygenated compounds to act as promoters in this reaction has been demonstrated [3,4].

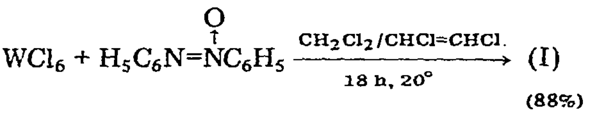
With the aim of clarifying the action of the oxygenated compound on the catalyst, and of obtaining some information on the metal—olefin bond, we have studied the reactions of tungsten(VI) chloride and oxychloride and molybdenum(V) chloride with azoxybenzene (AOB). In this way, we hoped to provide a useful model for the investigation of at least the first reaction stage, which involves the simultaneous complexation of both the oxygenated compound and olefin with the tungsten(VI) halide. Numerous types of promoters have been described, including alcohols, phenols, epoxides, nitro compounds, and peroxides [5], but for the reasons given below we chose to use AOB.

AOB can easily lose its oxygen to give azobenzene (AB), a ligand showing behaviour closely resembling an olefin. AB complexes of transition metals are known [6], and in some of them the complexation was shown to be of the same type that in olefin complexes [7].

Although many complexes of tungsten and molybdenum oxychloride are known [8], there is only one substantiated report of the complexation of transition metals by the azoxy group [9].

Results and discussion

Equimolar amounts of AOB and WCl_6 were found to react in *sym*-dichloroethylene/methylene chloride, under mild conditions to give in high yield a red-orange crystalline product (I) corresponding to the formula $C_{12}H_{11}Cl_5N_2OW$ (eqn. 1).



$$WCl_6 + H_5C_6N{=}\overset{\overset{O}{\uparrow}}{N}C_6H_5 \xrightarrow[18\ h,\ 20^\circ]{CH_2Cl_2/CHCl{=}CHCl} \underset{(88\%)}{(I)} \qquad (1)$$

The product was insoluble in hydrocarbons, slightly soluble in methylene chloride, and could be recrystallized unchanged from warm acetonitrile. Alkaline hydrolysis of (I) gave an impure sample of AB, the main impurity being *para*-chloroazobenzene. Contamination due to organic chlorine was so marked that when methylene chloride was used alone as the solvent, the metal/chlorine ratio was raised from 1/5 to 1/5.5. The chlorination of AB is probably a radical process, occurring during the oxygen attack of AOB on the metal. This side-reaction was reduced by performing the reaction in the presence of a chlorine scavenger (i.e. *sym*-dichloroethylene), but could not be completely eliminated. The IR spectrum of (I) showed a strong sharp band at 983 cm^{-1} attributable to W=O (some 50 cm^{-1} lower than W=O in gaseous $WOCl_4$ [10]), and another at 330 cm^{-1} in the range of metal—chlorine stretching.

The presence of these bands, characteristic of complexes such as $WOCl_4 \cdot L$, $WOCl_4 \cdot L_2$, $WOCl_5^- \cdot L^+$, $WOCl_5^{2-} \cdot 2L^+$ [11], leads to the conclusion that oxygen can be easily abstracted from AOB to afford a more stable species containing a W=O bond. Additional bands at 1586, 770 and 672 cm^{-1} confirm the presence of the AB aromatic system. The ^1H NMR spectrum (CH_3CN) showed two separate multiplets at τ 2.0 and 2.35 ppm, due respectively to aromatic *ortho* and *meta-para* protons, in the expected intensity ratio 4/6, and a third singlet resonance at τ 1.8 ppm corresponding to one proton. The molar conductivity of (I), determined in acetonitrile, was found to be comparable with that of $N(Et)_4Br$, suggesting a monoelectrolyte structure. All these facts left no doubt that (I) was actually an ionic complex of tungsten(VI) oxychloride with protonated AB.

Ionic structures containing protonated azobenzene as the cation have been suggested for a number of compounds: protonated azobenzene occurs in the adduct triphenylphosphine·azobenzene in the presence of perchloric acid [12]; Karasch's complex has been reformulated as a salt of protonated azobenzene [13], and some other salts of protonated azobenzene have been reported recently [14]. The proposed structure takes into account the salt-like character of (I), and explains the resonance at low field in the ^1H NMR spectrum.

When the reaction between WCl_6 and AOB was performed in the presence of an olefin, e.g. cyclooctatetraene, a green product (II) separated. Its analysis corresponds closely to $WOCl_3(ABH)$. Consistently, decomposition in ether gave only AB and no cyclooctatetraene. The IR spectrum of (II) is very similar to that of (I) with the exception of the W=O mode which appears as a strong broad absorption at 855 cm^{-1}; this suggests a polymeric structure with bridged oxygens similar to that found for $WOCl_3$ or $WOBr_3$ [15]. The reduction of W^{VI} to W^{IV} might be due to the presence of the unsaturated hydrocarbon, which acts as a chlorine scavenger. We had found a similar effect in the reduction of tungsten(VI) halides by alkynes in the presence of ethanol [16].

Somewhat different behaviour was observed when $MoCl_5$ was treated with AOB in methylene chloride. The red product which was isolated appeared from its IR spectrum to be impure (despite the results of the elemental analysis which fit well for $MoOCl_4 \cdot ABH$) since two bands of approximately equal intensity were observed in the Mo=O region at 991 and 974 cm^{-1}. However, when the reaction was carried out in benzene and the insoluble red product was extracted with methylene chloride containing a little ethanol (0.2%), the dark solution deposited at —15° black crystals of $[trans\text{-}MoOCl_4(OEt)]^-[ABH]^+$ (III). (III) shows a strong sharp Mo=O band at 986 cm^{-1}, the spectrum otherwise being very similar to those of (I) and (II), apart from additional bands at 1370, 1075, 1023 and 868 cm^{-1}, possibly due to the ethoxy group, and another at 3570 cm^{-1} of uncertain assignment. The last band does not appear in the spectra of (I) and (II). As it was impossible to obtain an NMR spectrum of (III), evidence for the presence of the ethoxy group was obtained from mass spectral data, and, more definitively, from an X-ray structural analysis, which showed oxygen and alkoxy groups in mutually *trans* positions [17]. (III) could also be obtained from the reaction between $MoOCl_4$ and AOB in benzene, followed by extraction of the precipitate with CH_2Cl_2/ethanol (0.2%) in a similar way. The identity of the two products was confirmed by comparison of both IR spectra and single crystal X-ray patterns.

In the last reaction another product slowly separated from the benzene solution. Elemental analysis and IR spectra indicate a dimeric ionic structure with the formula $[Mo_2O_2Cl_4]^-[ABH]^+$ (IV). Three strong bands are observed at 898, 862 and 808 cm^{-1} and these can be attributed to a system of bridged oxygens [18].

The impossibility of obtaining the analogue of (I), corresponding to an Mo^V species, from $MoCl_5$ can be explained in terms of the possible oxidation of Mo^V to Mo^{VI} by the oxygen from AOB, and the tendency of Mo=O species to give polymeric products. In any case, the possibility of attack by the AOB oxygen on molybdenum(V) and tungsten(VI) chlorides to give unstable six- and seven-coordinated species, respectively [19], should be recognised. Such an attack would be followed by fast abstraction of the organic oxygen by the metal, with simultaneous loss of radical chlorine, hydrochloric acid and azobenzene. The AB would be then protonated.

In a further attempt to prepare a complex containing coordinated AOB, we investigated the reaction with $WOCl_4$. A new complex (V), corresponding to the formula $C_{12}H_{10}Cl_4N_2O_2W$, was isolated in high yield (eqn. 2). (V) is a black crystalline solid, and is soluble in benzene, in which it appeared from cryoscopic measurements to be monomeric. It decomposed in dilute alkali to

TABLE 1

PROPERTIES OF $RC_6H_4N{=}N(O)C_6H_4R \cdot WOCl_4$

Compound	R	M.p.	IR data[a] (cm^{-1})	
			W=O	M—Cl
(V)	H	120° (dec.)	983	342
(VI)	2,2'-CH_3	85° (dec.)	986	338
(VII)	4,4'-CH_3	85° (dec.)	992	340
(VIII)	2,2'-Cl	138° (dec.)	980	338
(IX)	4,4'-Cl	185° (dec.)	994	340
(X)	4,4'-OCH_3	172—174° (dec.)	970	335

[a] Determined as Nujol mulls.

give AOB (90%). The IR spectrum revealed a W=O band at 983 cm^{-1} and a sharp W—Cl band at 342 cm^{-1}. This evidence shows that (V) is actually a 1/1 adduct of $WOCl_4$ with AOB, and the equivalence of the four chlorines favours a *trans* structure. Definitive proof was obtained from a single crystal X-ray analysis which revealed that (IV) is a non-ionic complex with AOB coordinated to the tungsten through the oxygen atom in the position *trans* to W=O [17].

By reaction (2) several complexes were synthesised from symmetrically substituted azoxybenzenes (VI) - (X). The complexes (V) - (X) showed significant variations in the position of ν(W=O) in the IR spectra. The main spectroscopic data are listed in Table 1.

$$WOCl_4 + AOB \xrightarrow[20°]{\text{Benzene}} (V)\ (80\%) \qquad (2)$$

Experimental

All operations were carried out under nitrogen with solvents purified by established methods. WCl_6, $WOCl_4$, $MoCl_5$, $MoOCl_4$ and AOB were commercial products (Schuchardt); AOB was recrystallized just before use. *sym*-Disubstituted azoxybenzenes were prepared according to literature methods [20].

IR spectra were recorded on a Perkin—Elmer 221 spectrophotometer in the range 3500 - 650 cm^{-1} and on a Perkin—Elmer 437 spectrophotometer in the range 650 - 250 cm^{-1} using Nujol mulls between NaCl plates and polyethylene sheets respectively. ^1H NMR spectra were recorded on a Jeol 4H 100 radio frequency spectrometer.

Reactions of AOB

(a). With WCl_6. WCl_6 (2.7 g, 6.8 mmoles) in methylene chloride/*sym*-dichloroethylene, 1/1 mixture (50 ml) was stirred with AOB (1.3 g, 6.6 mmoles) in methylene chloride (15 ml) at 0°. The dark solution was then heated to room temperature. After 18 h (I) separated as a crystalline red-orange powder. The product was filtered, washed with methylene chloride/light petroleum and dried in vacuum. A further portion of crystalline product was obtained by cooling the filtrate to — 20° overnight (0.4 g). The total yield was 3.4 g (88%); decomp. > 135° without melting. (Found: C, 25.5; H, 1.8; Cl, 33.0;

N, 4.7; W, 31.9. $C_{12}H_{11}Cl_5N_2OW$ calcd.: C, 25.7; H, 2.0; Cl, 31.7; N, 5.2; W, 32.8%)(I) could be recrystallized from few ml of acetonitrile. ν_{max}: 3170 w, 3070 w, 1586 s, 1535 m, 1450 m, 1415 w, 1390 m, 1332 w, 1310 w, 1243 s, 1177 m, 1162 m, 1023 w, 999 w, 995 w, 983 s, 932 m, 925 m, 884 m, 823 w, 770 s, 672 s, 663 m, 528 m, 518 m 330 s cm^{-1}. ^1H NMR spectrum (CH_3CN) showed peaks at τ 2.0 (m, 4H, aromatic *ortho* protons), 2.35 (m, 6H, aromatic *meta-para* protons), and 1.8 ppm (s, 1H, NH).

(b). With WCl_6 in the presence of cyclooctatetraene. A solution of AOB (0.69 g, 3.5 mmoles) and cyclooctatetraene (1.95 g, 18.3 mmoles) in CH_2Cl_2 (25 ml) at 0° was added dropwise to a stirred suspension of WCl_6 (1.37 g, 3.5 mmoles) in CH_2Cl_2 (25 ml). Stirring was continued at room temperature. After 24 h a green precipitate of (II) separated (1.2 g, 70%). (Found: C, 26.4; H, 2.3; Cl, 21.1; N, 4.0; W, 38.0. $C_{12}H_{11}Cl_3N_2OW$ calcd.: C, 29.4; H, 2.2; Cl, 21.8; N, 5.7; W, 37.6%). ν_{max}(W=O) 855 s(br) cm^{-1}.

(c). With $MoCl_5$ in CH_2Cl_2. $MoCl_5$ (7.5 g, 27.5 mmoles) in CH_2Cl_2 (100 ml) was allowed to react with AOB (5.5 g, 25.5 mmoles) in CH_2Cl_2 (50 ml) at 0° for 2 h. The temperature was maintained at 20° for 40 h. A red crystalline deposit of impure $[MoOCl_4]^-[ABH]^+$ separated (8 g). (Found: C, 33.0; H, 2.5; Cl, 32.5; N, 6.4. $C_{12}H_{11}Cl_4Mo$ ON calcd.: C, 32.9; H, 2.4; Cl, 32.7; N, 6.4%). ν_{max} (Mo=O) 991, 974 s cm^{-1}, comparable intensity.

(d). With $MoCl_5$ in benzene. $MoCl_5$ (2.5 g, 9.2 mmoles) in benzene (35 ml) was allowed to react with AOB (1.6 g, 8.1 mmoles) at room temperature for 1 h. A solid red material was filtered and immediately extracted with ethanol/ CH_2Cl_2 (20 ml, 0.2% of alcohol). The dark solution so obtained was filtered and cooled to —15° to give black crystals of (III) (0.35 g, 8%). (Found: C, 34.4; H, 3.4; Cl, 29.9; Mo, 21.4; N, 6.3. $C_{14}H_{16}Cl_4MoO_2N_2$, calcd.: C, 34.9; H, 3.3; Cl, 29.5; Mo, 19.9; N, 5.8%). ν_{max}: 3570 m, 3180 w, 3120 w, 3050 w, 2985 m, 2940 w, 1590 s, 1542 w, 1457 m, 1403 m, 1370 w, 1343 w, 1245 s, 1174 m, 1162 m, 1072 w, 1023 m, 998 w, 986 s (Mo=O), 927 m, 887 w, 868 w, 770 s, 672 s, 530 m, 515 m, 330 s cm^{-1}.

(e). With $MoOCl_4$. $MoOCl_4$ (2.5 g, 9.8 mmoles) in benzene (40 ml) was allowed to react at room temperature with AOB (2.5 g, 12.6 mmoles) with stirring for 1 h. The filtered red solution was kept at 5°, and red crystals of (IV) separated (0.85 g, 15%). (Found: C, 26.4; H, 2.3; Cl, 26.0; Mo, 34.7; N, 5.1. $C_{12}H_{11}Cl_4Mo_2O_2N_2$, calcd.: C, 26.2; H, 2.0; Cl, 25.8; Mo, 35.0; N, 5.1%.) ν_{max}: 3200 w, 3100 w, 3040 w, 2990 w, 2940 w, 1590 s, 1506 m, 1395 m, 1245 m, 1175 m, 1096 w, 999 w, 976 m, 898 s, 862 s, 808 s, 767 s, 670 m cm^{-1}.

Extraction of the residue with CH_2Cl_2 (2 × 20 ml) containing ethanol (0.2%) gave a brown solution from which (III) separated at — 15° (1.2 g, 26%). (III) was identified by its IR spectrum and X-ray diffraction pattern.

Reactions of $WOCl_4$

(a). With azoxybenzene. $WOCl_4$ (1 g, 2.8 mmoles) was suspended in benzene (40 ml). AOB (0.6 g, 3.3 mmoles) was then added to the stirred suspension. After 90 min light petroleum (30 ml) was added to the filtered dark red solution. On standing at — 5° black crystals of (V) separated (1.4 g, 90%), decomp.>120. Mol. wt. (cryoscopy in benzene) 550 ± 20. (Found: C, 26.6; H,

2.0; Cl, 26.1; N, 5.3; W, 34.0. $C_{12}H_{10}Cl_4N_2O_2W$ calcd.: C, 26.7; H, 1.9; Cl, 26.3; N, 5.1; W, 34.0%; mol. wt. 540). $\nu_{max.}$: 3080 w, 1587 w, 1569 w, 1318 m, 1300 m, 1247 w, 1217 s, 1195 s, 1162 s, 1060 s, 1018 m, 983 s, 963 w, 920 w, 880 s, 825 w, 758 s, 716 w, 672 s, 665 m, 573 w, 518 w, 470 w, 342 s cm^{-1}. ^1H NMR spectrum (C_6D_6) revealed two separated multiplets at τ 2.0 and 3.0 ppm due to aromatic protons of AOB in the expected ratio 4/6.

(b). With 2,2'- and 4,4'-dimethylazoxybenzene, 2,2'- and 4,4'-dichloroazoxybenzene and 4,4'-dimethoxyazoxybenzene. By the procedure used in the preparation of (V) but with the disubstituted symmetric azoxybenzenes in the order mentioned above, (VI),(VII),(VIII), (IX) and (X) were synthesized in yields of > 80%. Elemental and IR data and analyses, as well as some other properties, are shown below.

(VI), red-brown, decomp.>85°. (Found: C, 29.5; H, 2.1; Cl, 24.6; N, 5.0; W, 32.1. $C_{14}H_{14}Cl_4N_2O_2W$ calcd.: C, 29.6; H, 2.5; Cl, 25.0; N, 4.9; W, 32.4%.) ν_{max}: 3080 w, 2990 w, 1602 w, 1587 w, 1480 m, 1462 m, 1430 w, 1380 m, 1302 w, 1235 m, 1216 w, 1205 w, 1194 w, 1165 w, 1130 m, 1067 m, 1045 w, 986 s, 947 w, 914 m, 898 m, 864 w, 771 s, 756 s, 708 s, 679 m, 593 m, 560 w, 535 w, 495 w, 450 m, 338 s cm^{-1}.

(VII), red-brown, decomp.>85°. [Found: C, 29.3; H, 2.6; Cl, 24.4; N, 4.8; W, 32.0. (VI) is the isomer of (V).] ν_{max}: 3080 w, 1955 w, 1605 m, 1568 w, 1505 m, 1467 m, 1380 w, 1320 w, 1300 m, 1230 m, 1208 m, 1170 s, 1125 w, 1113 w, 1067 m, 1036 w, 1016 m, 993 s, 940 w, 913 m, 885 m, 824 s, 756 w, 702 w, 657 w, 518 m, 450 m, 340 s cm^{-1}.

(VIII), red-brown, m.p. 138° (decomp.). Found: C, 23.6; H, 1.5; Cl, 34.4; N, 4.6; W, 29.8. $C_{12}H_8Cl_6N_2O_2W$ calcd.: C, 23.6; H, 1.3; Cl, 35.0; N, 4.8; W, 30.2%.) ν_{max}: 3120 w, 3080 w, 1572 m, 1475 m, 1328 w, 1284 w, 1267 m, 1260 m, 1232 m, 1200 m, 1157 w, 1050 m, 980 s, 957 m, 900 m, 855 m, 762 s, 750 s, 706 w, 520 w, 455 w, 445 w, 338 s cm^{-1}.

(IX), red-brown, decomp.>185°. [Found: C, 23.3; H, 1.8; Cl, 35.2; N, 4.8; W, 30.0. (VIII) is the isomer of (VII).] ν_{max}: 3120 w, 3080 w, 1590 m, 1565 w, 1483 m, 1412 m, 1308 w, 1290 w, 1238 m, 1206 m, 1175 m, 1111 w, 1090 s, 1082 s, 1014 m, 995 s, 958 s, 946 w, 847 m, 832 s, 710 w, 704 w, 515 m, 418 m, 340 s cm^{-1}.

(X), red-violet, m.p. 172 - 174° (decomp.). (Found: C, 27.8; H, 2.4; Cl, 24.0; N, 4.5; W, 30.5. $C_{14}H_{14}Cl_4N_2O_2W$ calcd.: C, 28.0; H, 2.3; Cl, 23.7; N, 4.7; W, 30.7%.) ν_{max}: 3080 w, 1580 s, 1498 m, 1428 m, 1370 m, 1345 w, 1323 m, 1296 w, 1254 s, 1227s, 1181 w, 1150 s, 1120 w, 1037 w, 1002 s, 968 s, 880 w, 838 s, 815 w, 748 w, 560 w, 534 m, 505 w, 335 s cm^{-1}.

Decomposition of (I)

(I) (0.6 g, 1.1 mmoles) was stirred with KOH (2%, 50 ml) in the presence of ethyl ether (50 ml). The organic layer was washed, dried (Na_2SO_4) and evaporated, to leave an orange residue of AB, with some impurity of *para*-chloroazobenzene (0.19 g, 97%). The *para*-chloroazobenzene was isolated by preparative VPC and identified by comparison with an authentic sample.

Decomposition of (V)

Decomposition of (V) was carried out as described for (I). Pure AOB was obtained in 90% yield.

Thermal stability of (V)

(IV) (0.5 g, 9.3 mmoles) dissolved in benzene (20 ml) was heated to 80° for 2 h. A red-brown powder (0.2 g) of indefinite composition separated. (Found: Cl, 21.3; W, 55.15. W/Cl ½). By addition of light petroleum (V) was recovered (0.2 g, 40%) from the filtered dark solution.

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