

382. *The Anionic Halogenopentacarbonyls of Chromium, Molybdenum, and Tungsten.*

By E. W. ABEL, I. S. BUTLER, and J. G. REID.

The new complex ions $[\text{M}(\text{CO})_5\text{X}]^-$, where $\text{M} = \text{Cr}, \text{Mo},$ and W , and $\text{X} = \text{Cl},$ and Br , have been prepared as the tetra-alkylammonium salts. The carbonyl stretching modes in the infrared spectra of all nine of the known halogenocarbonyl anions of the Group VI metals have been recorded.

To date, the halogenopentacarbonyl complexes of the Group VI metals have been restricted to the anionic iodo-compounds $[\text{M}(\text{CO})_5\text{I}]^-$ ($\text{M} = \text{Cr}, \text{Mo},$ or W)^{1,2} and the neutral paramagnetic complex $\text{Cr}(\text{CO})_5\text{I}$.³ We now report the halogenopentacarbonyl metal anions $[\text{M}(\text{CO})_5\text{X}]^-$, where $\text{M} = \text{Cr}, \text{Mo},$ or W and $\text{X} = \text{Cl}$ or Br .

Interaction of the tetra-alkylammonium halides and the metal hexacarbonyls in diethylene glycol dimethyl ether at 120° produced a virtually quantitative yield of each complex ion as the tetra-alkylammonium salt: $\text{R}_4\text{N}^+\text{X}^- + \text{M}(\text{CO})_6 \longrightarrow \text{R}_4\text{N}^+[\text{M}(\text{CO})_5\text{X}]^- + \text{CO}$. Efforts to prepare the fluoropentacarbonyl metal anions in a similar manner have not been successful. A reaction, with evolution of carbon monoxide, does take place between the tetra-alkylammonium fluoride and the metal hexacarbonyls, but no product containing a fluorocarbonyl metal anion could be isolated. This failure is in line with previous observations,^{4,5} and it appears that, even if formed, the fluorocarbonyl derivatives are too unstable to be isolated; only one successful preparation of a metal carbonyl fluoride has been recorded.⁶

¹ Fischer and Öfele, *Z. Naturforsch.*, 1959, **14b**, 763; *Chem. Ber.*, 1960, **93**, 1156.

² Abel, Bennett, and Wilkinson, *Chem. and Ind.*, 1960, 442.

³ Behrens and Zizlsperger, *Z. Naturforsch.*, 1961, **16b**, 349.

⁴ Abel, Hargreaves, and Wilkinson, *J.*, 1958, 3149.

⁵ Hargreaves and Peacock, *J.*, 1958, 2170.

⁶ Sharp, *Proc. Chem. Soc.*, 1960, 317.

Potassium iodide is known² to react with molybdenum hexacarbonyl to produce the salt $[\text{K digly}_3][\text{Mo}(\text{CO})_5\text{I}]$. We now find that all the alkali-metal halides react with the Group VI metal hexacarbonyls. Efforts to obtain crystalline salts caused decomposition, but the infrared spectra of the solutions indicated the presence of the $[\text{M}(\text{CO})_5\text{X}]^-$ ions. In the reactions between the alkali-metal iodides and molybdenum hexacarbonyl, solid compounds of the type $[\text{M digly}_n][\text{Mo}(\text{CO})_5\text{I}]$ ($\text{M} = \text{Li, Na, K, Rb, or Cs}$) were isolated, but the degree of etheration varied, depending on the method of working up. Only in the case of the potassium salt, where $n = 3$, was a definite stoichiometric etherate isolable.²

All the tetra-alkylammonium salts of the halogenopentacarbonyl metal ions form diamagnetic yellow crystals, stable in the dark in an inert atmosphere, but slowly decomposing in air or bright light. They are soluble in water, alcohols, acetone, chloroform, and polyethers, and are insoluble in diethyl ether, light petroleum, and benzene.

It was found impossible to obtain consistently accurate infrared spectra of these ions in solution, owing to slow decomposition and concomitant appearance of spurious absorption peaks. For this reason we believe that some of the previous spectra² for the anionic pentacarbonyl iodides in solution probably report peaks which are due to decomposition products. All the values reported in Table I were obtained from potassium bromide discs, in which no decomposition took place, and no evidence of halogen exchange was noted. Each compound gave the expected three well-defined bands, and only in the case of the iodides was a slight splitting observed in the intense (*E*) band. Solution spectra of the iodides obtained rapidly in the region 1880–1940 cm^{-1} showed the doublets to be non-existent in solution, and thus probably the result of solid-state splitting, due to the size of the co-ordinated iodide ion.

The spectra are similar to those of the isoelectronic and isostructural halogenopentacarbonyls of manganese and rhenium. The major difference is the considerable shift of all absorptions to lower frequencies by 80–150 cm^{-1} . These lowered frequencies in the anionic species are to be expected, as a consequence of the increased metal-carbon back-bonding encouraged by the negative charge on the metal.

The detailed assignment of the absorbance maxima in Table I follows those for the corresponding neutral $\text{M}(\text{CO})_5\text{X}$ species by Orgel.⁷

TABLE I.

Infrared spectra in the CO stretching region of the ions $[\text{M}(\text{CO})_5\text{X}]^-$.

	<i>A</i> ^{1b}	<i>E</i>	<i>A</i> ^{1a}		<i>A</i> ^{1b}	<i>E</i>	<i>A</i> ^{1a}
$\text{Cr}(\text{CO})_5\text{Cl}$...	2056w	1912s	1875m	$\text{W}(\text{CO})_5\text{Cl}$...	2061w	1904s	1869m
$\text{Cr}(\text{CO})_5\text{Br}$...	2058w	1906s	1875m	$\text{W}(\text{CO})_5\text{Br}$...	2064w	1904s	1868m
$\text{Cr}(\text{CO})_5\text{I}$...	2055w	1930sh; 1914s	1853m	$\text{W}(\text{CO})_5\text{I}$...	2058w	1926sh; 1911s	1840m
		1917 (in CHCl_3)				1915 (in CHCl_3)	
$\text{Mo}(\text{CO})_5\text{Cl}$...	2064w	1913s	1871m				
$\text{Mo}(\text{CO})_5\text{Br}$...	2064w	1914s	1875m				
$\text{Mo}(\text{CO})_5\text{I}$...	2061w	1947sh; 1925s	1860m				
		1928 (in CHCl_3)					

EXPERIMENTAL

Infrared spectra were recorded for potassium bromide discs on a Unicam S.P. 100 spectrophotometer with sodium chloride optics. Tetraethylammonium chloride tetrahydrate was dehydrated at 120°/0.1 mm., and all other tetra-alkylammonium halides were dried over phosphorus pentoxide.

Interaction of Tetra-alkylammonium Halides with the Hexacarbonyls of Chromium, Molybdenum, and Tungsten.—The halide (~0.5 g.) was heated with an excess (~1 g.) of the hexacarbonyl in diethylene glycol dimethyl ether (20 c.c.) at 120° until the steady evolution of carbon monoxide ceased. The mixture was filtered hot under an atmosphere of nitrogen. Adding light

⁷ Orgel, *Inorg. Chem.*, 1962, 1, 25.

petroleum (b. p. 40–60°) (50 c.c.) to the cooled filtrate gave yellow crystals of the *tetra-alkyl-ammonium halogenopentacarbonylmetallate* (see Table 2). After removal of the excess solvent by decantation, the crystals were rapidly washed with light petroleum (2 × 20 c.c.), and the excess of solvent was removed at reduced pressure (20°/0.1 mm.). The absence of excess of hexacarbonyl in the final sample was ensured by vacuum-treatment at 60°/0.001 mm. for 1 hr.

TABLE 2.

$R_4N^+[M(CO)_5X]^-$			Found (%)				Required (%)			
R	M	X	C	H	M	Hal	C	H	M	Hal
Et	Cr	Cl	43.3	5.7			43.6	5.6		
Et	Mo	Cl	38.6	5.9			38.9	5.0		
Et	W	Cl	32.4	4.3	37.7	7.1	31.9	4.1	37.6	7.3
Et	Cr	Br	39.1	5.4	12.9		38.8	5.0	12.4	
Et	Mo	Br	34.7	5.5			35.3	4.6		
Et	W	Br	28.0	4.0	33.8		29.2	3.7	34.5	
Et	Cr	I	35.2	5.5			34.8	4.5		
Bu	Mo	I	41.7	5.8		21.6	41.7	6.0		21.0
Bu	W	I	34.7	5.5	26.4	17.7	36.4	5.2	26.6	18.3

Interaction of the Alkali-metal Iodides with Molybdenum Hexacarbonyl.—As in the above preparations, the halide was heated with an excess of carbonyl in diethylene glycol dimethyl ether. The yellow crystalline products were all etherated but the extent of etheration could be varied by vacuum- and heat-treatment, rendering analyses meaningless. All the salts, however, had three distinct metal-carbonyl C–O stretching modes in the region 2067–1860 cm.^{-1}

The authors thank the Department of Scientific and Industrial Research for a maintenance grant (I. S. B.), and the Ethyl Corporation for a gift of metal carbonyls.

DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
THE UNIVERSITY, BRISTOL, 8.

[Received, August 1st, 1962].