366

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ON THE EXISTENCE OF MONOMERIC VANADIUM HEXACARBONYL

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Last year, we published a paper[1] describing the structure and properties of a vanadium hexacarbonyl $V(CO)_6$. More recently, Pruett and Wyman[2] described a vanadium carbonyl, some properties of which (colour, high volatility, air, light and CS_2 sensitivity) closely agree with those observed by us.

They formulated it as dimeric $V_2(CO)_{12}$, on the basis of molecular weight measurements (unspecified method) and magnetic investigations (NMR and EPR), from which diamagnetism was inferred.

On the contrary, our previous formulation was for monomeric vanadium hexacarbonyl. Indeed, the solid was found by us to be paramagnetic ($Xg=+6, 14$ at 20°c.). Moreover, single crystal *X*-ray data bore close resemblance with those of VI Group metal carbonyls (a=11·97; b=11·28; c=6·47A, N=4, space group Pn2_1a or Pnma, to be compared with a=12·02; b=11·23; c=6·48, N=4, space group Pn2_1a for $Mo(CO)_6$). Space group and cell size considerations definitely rule out any possibility of dimeric structure of $V(CO)_6$ in the solid state. As expected, the intensities of *X*-ray reflexions are practically the same in both $Cr(CO)_6$ and $V(CO)_6$.

Owing to the discrepancies with Pruett and Wyman's data, we have now checked our previous findings. Three samples of $V(CO)_6$, namely a sample stored two months at −5°c. after sublimation, a sample freshly sublimed and a sample freshly crystallised from toluene solution at −70°c., were all found paramagnetic for about one electron and indistinguishable by *X*-rays. Their *X*-ray powder spectra are very similar to those of $Cr(CO)_6$ (see Table).

Table

Comparison between the X-ray powder spectra of $V(CO)_6$ *and* $Cr(CO)_6$

$Cr(CO)_6$		$V(CO)_6$	
Interplanar distance (A)	*Intensity*	*Interplanar distance* (A)	*Intensity*
5·57	m	5·68	m
5·21	w	5·29	w
4·98	m	5·07	m
3·93	w	4·01	w
3·40	v w	3·48	v w
3·15	m w	3·23	m w
2·94	w	3·00	w
2·80	m s	2·86	m s
2·47	m	2·53	m
2·15	w	2·20	w

It is noteworthy that in a set of cryoscopic measurements in hydrocarbons, large association of $V(CO)_6$ was observed by us, but this behaviour is by no means characteristic for this carbonyl, as the $Cr(CO)_6$ known to be monomeric[3] and $Mo(CO)_6$ are found to be even more anomalous according to the poor solvent properties of hydrocarbons for these carbonyls.

The following molecular weight at the indicated weight percentage concentration were recorded in cyclohexane: $V(CO)_6$=458 (0·5%[2]) $Cr(CO)_6$=608 (0·15%), 628 (0·3%); $Mo(CO)_6$=611 (0·28%) to be compared with diphenyl=152 (0·21%); $V(CO)_6$ in benzene=524 (1%). Thus no sure statement on the molecular structure of $V(CO)_6$ in hydrocarbon solutions can be made on the basis of cryoscopic data.

Concluding, the $V(CO)_6$ prepared by us has an unpaired electron and is monomeric in the solid state, as confirmed by *X*-ray data and the high volatility.

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Comment by Dr. R. L. Pruett

The data presented by Natta *et al.* concerning magnetic investigations are of a more exact nature and, combined with the *X*-ray findings, point toward the monomeric $V(CO)_6$ in the solid state. Most of our work was conducted in hydrocarbon solutions. The NMR spectrum of $[V(CO)_6]_n$ in benzene-cyclohexane solution contains sharp lines. This is interpreted to show diamagnetism.[1] The molecular weight in cyclohexane indicates a dimeric state, and this method has been used successfully for determination of the molecular weight of dimanganese decacarbonyl.[2] As a comparison material, we also determined the molecular weight of t.-butylbenzene chromium tricarbonyl at the same concentration in cyclohexane (Found: 286. Calc. 270). It is interesting to note that the molecular weight (458) in cyclohexane found by Natta *et al.* is a near duplicate of ours (459) although the concentrations were quite different (0·5% and 1% respectively).

The high volatility of the crystalline material may be taken only as a suggestion of structure since it does not compare favourably with either $Cr(CO)_6$ or $Mn_2(CO)_{10}$.

The infrared spectrum of $[V(CO)_6]_n$ in cyclohexane shows a single absorption, as yet unresolved, at 1980 cm.$^{-1}$. This may be compared with dicobalt octacarbonyl in n-hexane[3] in which the non-bridging carbonyls absorb at 2073, 2043 and 2025 cm.$^{-1}$ and with dimanganese decarbonyl in cyclohexane, which absorbs[2] at 2020, 2010, and 1996 cm.$^{-1}$. The gas phase spectrum of the $[V(CO)_6]_n$ would certainly be of interest.

In view of the additional data now available, the change of colour from dark blue in the solid state to yellow-orange in inert solvents may be of greater significance. A change from monomeric state in crystalline form to dimeric state in solution is not improbable.

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