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The photolysis of the hexacarbonylvanadate(–I) ion

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Thermal cleavage of the metal–carbon bond in the anion $V(CO)_6^-$ is not a facile process. Thus $NaV(CO)_6$ may be refluxed in diglyme in the presence of triphenylphosphine for 24 hours without change[1], and the usual route to substituted V^{-I} carbonyls is via the more labile V^0 species[2]. We wish to report the photochemical cleavage of $V(CO)_6^-$ itself, but to suggest that the preparative use of this reaction may not be easy.

The anion $V(CO)_6^-$ (as sodium diglyme salt), dissolved in 2-methyltetrahydrofuran (MeTHF) and irradiated as a glass at ca. 90 K with filtered light from a medium pressure mercury discharge lamp ($\nu < 30000$ cm^{-1}) gave rise to a species to which we assign the structure $[V(CO)_5MeTHF]^-$ from its IR spectrum [maxima at 1965 cm^{-1} vw (A_1), 1820 cm^{-1} (B_2, correlating with E_g of $V(CO)_6^-$ which we observe at 1894 cm^{-1} in $V(CO)_6^-$ itself under our conditions), 1795 cm^{-1} vs (E), 1758 cm^{-1} ms(A_1)]. We reject the formulation $V(CO)_5^-$ since such a species would be expected[3] to show a smaller shift relative to the (IR and Raman[4]) frequencies of $V(CO)_6^-$ itself. Irradiation with less rigorously filtered light ($\nu < 35000$ cm^{-1}) caused production of other, uncharacterised species.

The photochemical process was rapidly reversed when the glass was allowed to soften and warm towards room temperature, the starting material being regenerated quantitatively inside an hour. Irradiation of $V(CO)_6^-$ in MeTHF at room temperature in a sealed IR cell in the presence of triphenylphosphine, using filtered or unfiltered light, produced no net reaction. Irradiation of $V(CO)_6^-$ in MeTHF in the presence of triphenylphosphine in a photochemical reactor from which CO could escape produced a pale, highly air-sensitive, material, obviously different from $V(CO)_5PPh_3^-$; less than one molecule of gas per $V(CO)_6^-$ was evolved.

We conclude that when retained in solution CO competes successfully with MeTHF and PPh_3 for $V(CO)_5^-$; this is not totally surprising, though the difference between $V(CO)_5^-$ and $Cr(CO)_5$ is very marked. Other, unknown complications arise when the CO is allowed to escape.

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