

ORGANOMETALLIC COMPOUNDS XXIX.* THE FLASH PHOTOLYSIS OF CHROMIUM HEXACARBONYL

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SUMMARY

The flash-photolysis of chromium hexacarbonyl in cyclohexane yields a transient species (A), whose half-life at room temperature is approximately 6 msec. It is converted into a second transient species (B) which recombines with carbon monoxide yielding chromium hexacarbonyl. It is assumed that (A) and (B) are isomeric chromium pentacarbonyls which show quite different reactivities towards various ligands. The behaviour of both intermediates is discussed in terms of orbital symmetry.

INTRODUCTION

The photochemistry and photochromism of $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}$ or W) have been examined by several groups. Low-temperature experiments by Sheline *et al.*¹ and by Rest and Turner² suggest that the primary photoproduct is a square pyramidal metal pentacarbonyl, which rearranges to a trigonal bipyramid when the matrix is allowed to soften to about 160°K. The rate of recombination of an intermediate with carbon monoxide has been studied by McIntyre³. We describe below our investigation of the flash photolysis of chromium hexacarbonyl in cyclohexane at room temperature.

RESULTS AND DISCUSSION

The flash photolysis of a well degassed cyclohexane solution of $\text{Cr}(\text{CO})_6$ (approximately $10^{-4} M$) yields two consecutive transient species**, the first of which (A) shows a clean unimolecular decay, and the second (B) behaves in a more complicated fashion. Since these intermediates show very different properties, we shall discuss them separately.

* For Part XXVIII, see ref. 6.

** Preliminary experiments with $\text{Mo}(\text{CO})_6$ give similar results.

Intermediate (A)

The absorption spectrum of this first transient, recorded by monitoring the decay at various wavelength, shows a broad band with a maximum around 483 nm. Its disappearance follows strictly unimolecular kinetics, with an average rate constant of $1.7 \times 10^2 \text{ sec}^{-1}$; the absorption does not drop to zero, however, because the second species absorbs slightly at this wavelength.

An interesting characteristic of this intermediate is that when the solution is equilibrated with 0.2 atm or even with 1.0 atm of carbon monoxide, the rate constant is practically unaffected. Thus the conversion of the first transient into the second does not involve CO^* , and a reasonable hypothesis is to assume that it is the species observed at low temperature¹, i.e. the square pyramidal isomer of $\text{Cr}(\text{CO})_5$. Support for this was found by the steady irradiation of a glassy methylcyclohexane/isopentane solution of $\text{Cr}(\text{CO})_6$ at 77°K. The red colour which appeared showed a broad maximum around 485 nm. These are the experimental conditions which allowed Sheline *et al.* to record the IR spectrum of the first transient and to assign a C_{4v} square pyramidal structure to it.

Other potential ligands were examined. It appears that H_2 , N_2 and apparently O_2 do not react with this first intermediate.

Interestingly, acetone appears to react very rapidly with species (A). When a solution of $\text{Cr}(\text{CO})_6$ in cyclohexane, equilibrated with 1.0 atm of CO and containing 3×10^{-3} to $8 \times 10^{-3} \text{ M}$ acetone, is flashed, the first transient does not appear on the time scale of our experiments. Instead, a new compound is formed which decays very slowly, and the spectrum of which (λ_{max} approximately 447 nm) is different from that of $\text{Cr}(\text{CO})_5$ (A). This suggests that the reaction between square pyramidal $\text{Cr}(\text{CO})_5$ and acetone is very fast compared with its isomerisation to the trigonal bipyramid².

Intermediate (B)

When the low temperature matrix is allowed to thaw, the absorption spectrum undergoes a steady change, showing first isosbestic points, and turning eventually to a new spectrum with a maximum around 438 nm. These are the conditions used by Sheline *et al.*¹ when they assigned a D_{3h} symmetry to the second transient in the case of $\text{Mo}(\text{CO})_5$. This yellow intermediate has an absorption spectrum which is similar to that observed for transient (B) in the room temperature flash experiments.

In solution, transient (B) decays slowly in well degassed solutions by approximately second order kinetics, but technical difficulties (see Experimental part) prevented our deriving a good rate constant. When the solutions are equilibrated with CO, the disappearance of (B) is accelerated and is clearly pseudo-unimolecular, the rate constants being 2.7 sec^{-1} with 0.2 atm of CO and 10 sec^{-1} with 1.0 atm of CO. This process thus clearly involves the bimolecular recombination of (B) with carbon monoxide, giving the $\text{Cr}(\text{CO})_6$ back, as was shown by the UV spectra recorded after numerous flashes.

That (B) is formed directly from (A) was shown by monitoring its appearance at 440 nm; the absorbance increases unimolecularly with a rate constant of about $1.7 \times 10^2 \text{ sec}^{-1}$.

* The recombination of transient (A) with CO can however be induced by irradiation²

** A direct reaction of acetone with electronically excited $\text{Cr}(\text{CO})_6$ cannot be excluded at present.

The (B) isomer of $\text{Cr}(\text{CO})_5$ reacts not only with CO ; its disappearance is also strongly accelerated when the deoxygenated solution is saturated with N_2 under 1.0 atm. Molecular oxygen interacts with (B), inducing irreversible changes and leading to the formation of a green precipitate. Even H_2 appears to affect the lifetime of the second transient, and yields a new compound; this observation has led to a useful synthetic method⁴.

The complexes formed from either form of $\text{Cr}(\text{CO})_5$ with acetone, N_2 or H_2 slowly return to chromium hexacarbonyl in the presence of excess carbon monoxide.

Theoretical aspects

The $\text{Cr}(\text{CO})_5$ (A) and (B) show markedly different properties towards nucleophiles, and the question arises whether this is due to any special orbital arrangement. If we assume that the entering ligand attacks the square pyramid along the C_4 axis, and the trigonal bipyramid on one of the equatorial edges, a group-theoretical study of these structures and processes requires the second intermediate to be regarded as a species with C_{2v} rather than D_{3h} symmetry.

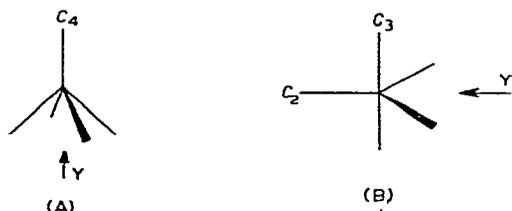


Fig. 1.

There is a second reason for rejecting D_{3h} symmetry for (B). The representation Γ_σ for the σ framework is split into $\Gamma_\sigma(D_{3h}) = 2A'_1 + A'_2 + E'$; if we follow the usual procedure and use first the s , p_x , p_y and p_z orbitals for the σ bonds, we must also use the d_{z^2} orbital to form the apical bonds. This leaves us with the two degenerate pairs $d_{xy}, d_{x^2-y^2}$ and d_{xz}, d_{yz} as the four highest levels, which have to accommodate the remaining six electrons leading to an orbitally degenerate ground state (Fig. 2). Since such a situation is not allowed, the trigonal bipyramid has to be only slightly distorted in order to lift the degeneracy by losing its three-fold symmetry axis. The point group is then C_{2v} which allows the conservation of symmetry for the reaction (Fig. 3).

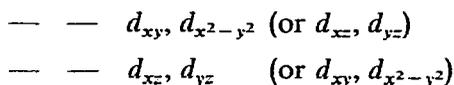


Fig. 2.

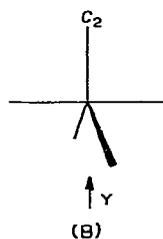


Fig. 3.

The representations are then $F_{\sigma}(A) = 2A_1 + B_1 + E$ and $F_{\sigma}(B) = 3A_1 + B_1 + B_2$. It is difficult, without detailed calculations, to suggest the right ordering of the levels, but here again we shall first use the s , p_x , p_y and p_z orbitals for σ bonding, the fifth orbital being probably $d_{x^2-y^2}$ in (A) and d_{yz} in (B). The question to be answered is, however, that of the relative arrangement of the other orbitals. Crude application of the electrostatic method, which often yields results in fair agreement with MO calculations, leads to the hypothesis that the highest empty (and electrophilic) orbital is the d_{z^2} in both cases. Both species differ thus in the symmetry of the highest occupied level; for (A), we suggest the degenerate pair d_{xz} , d_{yz} and for (B) the d_{xy} orbitals*.

The difference between the (A) and (B) structures is then that the highest occupied levels in (A) have π symmetry, whereas in (B) the nucleophilic orbital has δ symmetry, with respect to the main axis in both cases. These results are summarised in Fig. 4.

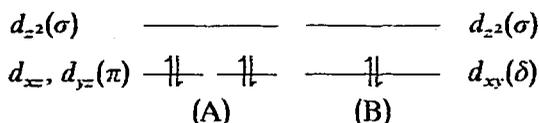


Fig. 4

It appears that (A) has the right orbitals for head-on bonding with σ -donor/ π -acceptor ligands, and (B) for lateral bonding with unsaturated systems having σ -donor properties and an empty anti-bonding orbital in the xy plane (such as acetylene). There is thus no orbital symmetry "selection rule" which would lead to a sharp distinction between both species, and their different behaviours must thus be ascribed to more specific concepts such as nucleophilicity of the various attacking ligands. Since CO reacts with (B) these results do suggest, however, that the process might be a lateral approach to give a π -bonded ligand which rapidly rearranges to the normal σ bonded structure.

EXPERIMENTAL

Products

Chromium hexacarbonyl (Strem Chemicals Inc.) was sublimed twice. Cyclohexane for U.V. (Fluka A.G.) was used for all the flash experiments.

Methylcyclohexane and isopentane (Hopkin & Williams Ltd) were purified by stirring with an equal volume of a mixture (1/1) of concentrated HNO_3 and H_2SO_4 during 12 h; after conventional treatment, distillation gave material free from aromatics.

Low-temperature experiments

The low-temperature experiments were performed by a few minutes' irradiation (with a high pressure mercury arc) of a 10^{-4} M $\text{Cr}(\text{CO})_6$ solution in a 1/1 mixture of methylcyclohexane and isopentane, previously cooled at 77°K; the absorption spectra at 77°K and at progressively higher temperatures were recorded on a Cary 14 spectrophotometer.

* It might be argued that the empty orbital in (B) is not d_{z^2} but d_{xy} . This would not change the main features of the symmetry arguments which are used here:

Flash experiments

The flash experiments were performed with a Northern Precision Company Ltd. apparatus; a Tektronix 545 B oscilloscope coupled with a Unicam SP 500 monochromator provided the detection.

The solutions were degassed by freeze-pump-thaw cycles (10^{-4} mm) and used as such or equilibrated with CO, N₂ or H₂ by stirring thoroughly for 1/2 h. The results are summarized in Table 1.

TABLE 1
DECAY RATE CONSTANTS OF (A) AND (B)

[Cr(CO) ₆] ($\times 10^5 M$)	Wavelength (nm)	Flash intensity (kV; μF)	CO (atm)	$k_1(A)^a$ (sec ⁻¹)	$k'_1(B)^b$ (sec ⁻¹)
7.7	490	8; 4	0	190	
7.7	440	8; 4	0	173	
9.0	550	8; 4	0	166	
9.0	490	8; 4	0	166	
9.0	520	8; 4	0	161	
8.4	490	8; 4	1	205	
8.4	440	8; 4	1		9.2
2.3	490	15; 8	1	173	
2.3	440	15; 8	1		11.5
7.1	490	8; 4	1	166	^c
2.3	490	15; 4	0.5	161	^c
8.3	490	9; 4	0.2	122	^c
9.0	490	9; 8	0.2	177	2.8
9.0	490	9; 8	1	253	10.1

^a k_1 from 2.3 log ($D_t - D_\infty$) vs. time at 490, 520 and 550 nm, or from 2.3 log ($D_\infty - D_t$) vs. time at 440 nm.

^b k'_1 from 2.3 log D_t vs. time. ^c The pseudo-unimolecular rate constant k'_1 was not measured in these cases.

The unimolecular decay constants were calculated using plots of 2.3 log ($D_\infty - D_t$) versus the time, the D_∞ value being the pseudo-constant optical density measured after 30 msec on a 10 msec time-scale.

For accurate measurement of the bimolecular rate constant for recombination of transient (B) with CO, low Cr(CO)₆ concentrations and very high-intensity flashes should have been used, so as to give 100% conversion throughout the reaction cell. Unfortunately, under such conditions, a side-reaction (leading perhaps to lower coordination complexes through biphotonic processes⁵) seems to alter the general reaction scheme.

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