The Comparative Photochemical Behaviour of Dibenzenechromium and Benzenetricarbonyl Chromium

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Photochemical Ligand Exchange

In comparison with (CeH₆)Cr(CO)₃, (CeHe²Cr₂ is relatively light stable. The major part of the light energy absorbed by (CeH₆)Cr leads neither to its decomposition or ligand exchange, nor can it be transferred to common low energy triplet acceptors. Internal dissipation of energy, either by rapid conversion to the ground state or by rapid reversible isomerization, must be an important process.

In the case of (CeH₆)Cr(CO)₃, the main pathway to the previously reported light-induced exchange of benzene involves an intermediate which is suggested to be (benzene)-dicarbonylchromium (1) and not a one-step dissociation of the excited molecule, to give Cr(CO)₃ and benzene. 1 is also of major importance for the exchange of CO.

Benzenetricarbonyl chromium (BTC) is known to be photo-chemically labile and to undergo facile light-induced exchange of both benzene and carbon monoxide: this has been demonstrated using ¹⁴C-labelled benzene and carbon monoxide. On the other hand, the only published work on the photochemistry of dibenzenechromium (DBC) appears to be its photoreaction with alkyl chlorides to give (C₂H₅)₂CrCl⁻ and hydrocarbons and a comparison of its photochemical reactivity in cyclohexane solution with that of other metallocones. Light-induced decompositions of (C₂H₅)₂Cr⁺(DBC⁺) in aqueous solution yields DBC and benzene as well as Cr₂²⁺ and Cr³⁺.

Our interest in DBC was to investigate the effect of coordination on the photochemistry of benzene and to explore the possibility of exchanging the coordinated benzene of (C₂H₅)₂Cr for other aromatic ligands.

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No ligand exchange could be detected by mass spectroscopy after 2 h irradiation (313 nm, 550 nm or unfiltered light from high pressure Hg arc) of DBC(0.6-1.0 × 10⁻¹ M) in C₆D₆ or C₆D₆/cyclohexane solution. Some C₂H₆ was however detected in the solvent after irradiation, amounting to approximately 10% DBC decomposition; this was accompanied by the formation of some precipitate. No decomposition occurred in the dark during 48 hours at 20 °C.

BTC behaved quite differently however, and under comparable conditions 70% of the (CeH₆)Cr(CO)₃ underwent photoinduced exchange of the benzene in C₆D₆ solution. In this case decomposition was very slight. In a further experiment, two samples of BTC (0.5 × 10⁻¹ M) in C₆D₆ were prepared by flushing with argon and with carbon monoxide, respectively. After irradiation through a pyrex glass filter for 1 h, the samples contained 6.9% and 0.9% (CeD₆)Cr(CO)₃, respectively: the addition of carbon monoxide had thus considerably suppressed the benzene exchange process. Further no Cr(CO)₆ could be observed, hence ruling out the conceivable reaction of Cr(CO)₃ with CO:
In cyclohexane solution BTC undergoes rapid light induced decomposition to release benzene and to yield a grey-green solid, which was not further investigated. Carbon monoxide reduces this decomposition substantially and $^{13}$CO is rapidly incorporated into BTC. In contrast CO does not affect the slow decomposition of DBC under the same conditions.

Light-induced (313 nm) ligand exchange in BTC has been further investigated in the presence of $^{13}$CO and/or C$_6$D$_6$ with argon and cyclohexane as the alternative atmosphere and medium respectively. The resultant mixtures were analysed by mass spectrometry and although some difficulty was experienced in exact reproducibility from experiment to experiment, it was evident that incorporation of C$_6$D$_6$ was strongly suppressed by CO whereas that of $^{13}$CO was little affected by benzene. This suggests that (arene)Cr(CO)$_2$ (1) may also be a precursor in the exchange of the aromatic ligand as well as the CO exchange. In particular the results would argue against the competition of the arene and CO for a species such as (tetrahapto-benzene) tricarbonyl chromium for which structure 2 is conceivable, although stepwise deco-ordination of benzene has been suggested for thermal S$_2$N$_2$ reactions of arene tricarbonyl chromiums and molybdenums. In the thermal substitution reactions it is always the aromatic ligand which is replaced.

The measured quantum efficiency for CO exchange with 313 nm radiation was in accord with that (0.72) reported by Wrighton and Haverty: the efficiency of arene exchange is approximately one sixth of this value.

The described photochemical stability of dibenzenechromium, which contrasts that of BTC, finds its parallel in the thermal reactivity difference of these two compounds. Thermal exchange of benzene in DBC for another aromatic ligand is only observed in the presence of catalysts, while that in BTC is easily brought about by simply heating the reactants. We have not been able to provide any evidence for an intermediate in the process of deactivation of electronically excited DBC. We considered that it might be possible to trap an intermediate such as 3 with powerful ligands (L). Attempts with CO, dimethylfumarate and dimethylmaleate were unsuccessful. However, an intramolecular S$_2$N$_2$ reaction involving an attack of the uncoordinated double bond in 4 and a concomitant elimination of L cannot be ruled out. A very rapid backreaction of 3 to DBC could provide another explanation for the failure of the trapping experiments: the same argument would also stand for an intermediate such as 5.

Use of maleic anhydride (MA) as a trap for 3 was also checked, but solutions of the complex and the anhydride (MA) reacted in the dark to yield an orange paramagnetic complex having a UV spectrum indicative of DBC$^+$ ($\lambda_{max}$ at 271 nm and 333 nm). Strong Lewis bases are known to yield violet black 1:1 complexes with DBC and these are formulated as DBC$^+$ salts of radical anions. Although the composition of the present orange complex was relatively variable, such results as given in the experimental section were more consistent with the complex, having a 2:1 rather than a 1:1 ratio of MA to DBC: 2:1 complexes of a seemingly similar type have been reported for nickelocene.

The possibility of fast benzene valence bond isomerization as a path of radiationless deactivation also has to be considered. For example formation of 6 may result on irradiation of DBC but this would be expected to undergo facile exchange of the aromatic ligand and this was not observed. Further, elimination of the substituted benzvalene should occur on irradiation of di(p-xylene)chromium, and thereby result in the production of isomeric xylenes: this however was found not to be the case.

Attempts were made to check for intermediates from these photolyses by irradiation of DBC and
BTC in a 50:50 methylecyclohexane/isopentane glass at 77 K. This technique, however, proved to be inapplicable as both DBC and BTC aggregate on cooling the solution. Cooling of a $10^{-3}$ M solution of BTC, produced crystals. At lower concentrations the absorption band ($\lambda_{\text{max}}$ at 316 nm at 20 °C) shifted to shorter wavelengths ($\lambda_{\text{max}}$ at 306 nm at $-160$ °C): the shorter wavelength band ($\lambda_{\text{max}}$ at 262 nm) also shifted and was obscured by intense tail-end absorption. Similarly with DBC, the absorption spectrum showed marked changes ($\lambda_{\text{max}}$ from 307 nm at 20 °C to 302 nm at $-165$ °C, and the appearance of strong structureless absorption between 200 and 300 nm). Braterman has reported aggregation on cooling solutions of the analogous $\pi$-cyclopentadienyl tricarbonyl manganese.$^{14}$

On flash photolysis of a $5 \times 10^{-4}$ M cyclohexane solution of (CeH$_6$)$_2$Cr, no transients could be detected and the solution was recovered essentially unchanged after photolysis. These results suggest either, that if isomers such as 3 or 6 are formed, they do not absorb sufficiently strongly in the visible region of the spectrum or that their lifetime is less than 5 µsec. Alternatively, it is possible that the excited state of DBC undergoes rapid radiationless deactivation without any change in its chemical nature.$^{15}$

Transients could, however, be observed on flash photolysis of a $10^{-5}$ M cyclohexane solution of BTC. Immediately after the flash, a weakly absorbing species was recorded which reacted further within the first millisecond to form a second transient species and this absorbed throughout the visible spectrum ($\lambda_{\text{max}}$ at approx. 500 nm). The concentration and rate of reaction of these species were essentially unaffected by the presence of $1.1 \times 10^{-1}$ M benzene in the solution, but the species are strongly quenched if the solution was saturated under one atmosphere of CO: the optical density at 497 nm 100 µs after the flash was then reduced to 15% of that in the absence of CO. While these studies are insufficient to allow an unambiguous identification of the transient species observed, it is probable that the first species observed is (benzene)Cr(CO)$_3$, and that in the presence of added CO we are observing the combination of this with CO to reform BTC. The nature of the second species is at present uncertain and more detailed experiments would have to be carried out before one could differentiate between possibilities such as dimers, isomers, or complexes with trace solvent impurities, by analogy with the case of Cr(CO)$_6$.$^{16}$

DBC is isoelectronic with ferrocene and a comparative study of their photochemistry should be of interest. In agreement with the results of Borrell and Henderson$^{3}$ we have found that DBC is quite light stable and similar in this respect to ferrocene. Ferrocene is however an efficient quencher of triplet excited ketones and aromatic hydrocarbons, even of those with a triplet energy lower than 160 kJ mol$^{-1}$. Further ferrocene is known to sensitize cis-trans-isomerisation of stilbene and of piperylene, and to promote the dimerisation of isoprene.$^{18}$ We have found that while DBC does not sensitize any of the above reactions, it is capable of quenching the fluorenone triplet excited state at a diffusion controlled rate.$^{19}$

**Conclusions**

In comparison with (CeH$_6$)$_2$Cr(CO)$_3$, (CeH$_6$)$_2$Cr is relatively light stable. The major part of the light energy absorbed by (CeH$_6$)$_2$Cr leads neither to its decomposition or ligand exchange, nor can it be transferred to common low energy triplet acceptors. Internal dissipation of energy, either by rapid conversion to the ground state or by rapid reversible isomerization, must be an important process. By analogy with ferrocene and ruthenocene$^{17, e}$ it is possible that the species merely undergoes symmetrical expansion in passing from the ground state to the excited state.

In the case of (CeH$_6$)$_2$Cr(CO)$_3$, the main pathway to the previously reported light-induced exchange of benzene involves an intermediate which is suggested to be (benzene)dicarbonylchromium (1), and not a one-step dissociation of the excited molecule, to give Cr(CO)$_3$ and benzene$^{15}$: 1 is also of major importance for the exchange of CO.
We hope that our observations will catalyse further studies of arene chromium complexes to get a better understanding of the intimate mechanisms of their photo reactions. A search for possible wavelength effects would be especially desirable.

**Experimental**

(C$_6$H$_5$)$_2$Cr and (C$_6$H$_5$)$_2$Cr(CO)$_3$ were prepared by reported procedures$^{30,31}$. After repeated sublimation, weak fluorescence of BTC samples was removed and that of DBC samples was reduced. Spectroscopic data were as reported in the literature, with the exception of the UV spectrum of (C$_6$H$_5$)$_2$Cr. When purified, this species showed as well as the band with $\lambda_{\text{max}}$ at 307 nm, a previously unreported shoulder at 392 (e $\simeq 1000$ 1xmol$^{-1}$ cm$^{-1}$) and a deepened valley at 250 nm (e $\simeq 100$ 1xmol$^{-1}$ cm$^{-1}$).

All steady state experiments reported here were carried out in well-dried argon degassed cyclohexane or benzene. We have, however, attempted to use other solvents as reaction media for the irradiation. (C$_6$H$_5$)$_2$Cr is only slightly soluble in methanol, acetonitrile and acetone: while admission of trace amounts of air to suspensions of DBC in these solvents apparently increased the solubility, spectral data clearly showed that this was due to the formation of DBC$^+$ ($\lambda_{\text{max}}$ at 270 nm and 333 nm). Irradiations of such solutions produced green-grey solids and a colourless solution containing at least 80% of the originally complexed benzene.

Steady state irradiations were carried out using a water-cooled high pressure mercury lamp (Philips HPK 125 W). The exchange experiments with $^{13}$CO (isotopic purity 90.9% from Merck, Sharp and Dohme, Canada) and C$_6$D$_6$ were performed in SOLIDEX tubes (fitted with a 3-way stopper) of 15 cm length and 1 cm i.d. at a fixed 6 cm distance from the lamp. Products were analysed by mass spectrometry with an ATLAS CH5. For experiments with monochromatic light, the beam was passed through a Bausch-Lomb high intensity monochromator. Samples were contained in a conventional 1 cm Suprasil cell, fitted with a Teflon stopper, adapted so that the sample could be flushed with argon and sample transfer accomplished under argon. All experiments were carried out at room temperature.

Flash photolysis experiments were carried out on the previously described apparatus$^{32}$. Samples were degassed by the reported procedure$^{16}$.

**Reaction of dibenzenechromium with maleic anhydride**

2 ml of a saturated solution of DBC in dry and argon degassed benzene were added to 1 ml of a saturated benzene solution of maleic anhydride. An orange solid precipitated, which was washed with dry and argon degassed ether (2 x 5 ml) and dried in vacuo. Thereafter the product was handled in air. Its paramagnetism prohibited a $^1$H-NMR investigation. According to the elemental analysis, addition of 2 moles maleic anhydride to 1 mol DBC and 1 mol H$_2$O had occurred.

(C$_6$H$_5$)$_2$Cr · C$_6$H$_5$O$_3$ (306.3)

Calcd C 62.70 H 4.61 Cr 16.99

(C$_6$H$_5$)$_2$Cr · 2(C$_6$H$_5$O$_2$) (404.3)

Calcd C 59.41 H 3.99 Cr 12.86

(C$_6$H$_5$)$_2$Cr · 2(C$_6$H$_5$O$_2$) + 2 H$_2$O (440.4)

Calcd C 54.60 H 4.58 Cr 11.82

(C$_6$H$_5$)$_2$Cr · 2(C$_6$H$_5$O$_2$) + 1 H$_2$O (422.4)

Calcd C 56.87 H 4.30 Cr 12.31

Found C 56.16 H 4.35 Cr 11.60

Found C 56.14 H 4.31

Mol. weight found [crysc. in (CH$_3$)$_2$SO]: 437

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7 The trivial mechanism of traces of air or moisture promoting oxidation to form the (C$_6$H$_5$)$_2$Cr$^+$ ion, which is subsequently photolyzed yielding benzene inter alia$^4$ cannot be totally discounted, since the complete absence of such ubiquitous impurities can never be assured. However in this case, the ion would be present in very low concentration as its solubility in very dry cyclohexane is very low.

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