Photochemistry of Tricarbonyl(cyclo-octatetraene)iron

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Summary Tricarbonyl(cyclo-octatetraene)iron undergoes a rapid photochemical conversion into pentacarbonyl (cyclo-octatetraene)di-iron and cyclo-octatetraene in high yield; hexacarbonyl(cyclo-octatetraene)di-iron is also rapidly photochemically converted into pentacarbonyl(cyclo-octatetraene)di-iron.

THE photochemistry of tricarbonyl(cyclo-octatetraene)iron [(cot)Fe(CO)$_3$] (**1**) has been widely studied.[1,2] Initial photochemical studies of this complex led to the conclusion that the compound, under certain conditions, can be recovered unchanged in 80% yield after u.v. irradiation for 20 h in the presence of oxygen.[1] Other investigations[2] were centred around the irradiation of (**1**) in the presence of other reagents, which themselves had potential photochemical activity.

We now report that [(cot)Fe(CO)$_3$], when irradiated in deoxygenated hexane, does, itself, undergo a photoreaction in high yield and is rapidly and cleanly converted into [(cot)Fe$_2$(CO)$_5$], (**2**) and cyclo-octatetraene (cot) according to equation (1). Additionally, we have found that (**1**) is rapidly destroyed when it is irradiated in the presence of oxygen in hexane solution.†

In a typical experiment, (**1**) (0·202 mmol), dissolved in

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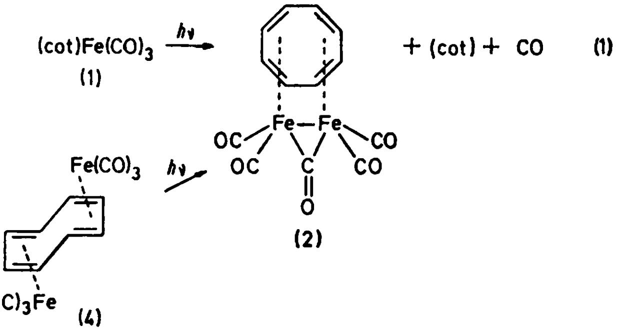
† After irradiation for 5 h of (**1**) (30 mg) in hexane solution through which oxygen was continuously bubbled, only (cot) and iron oxides were recovered. A trace of (**1**) was present in solution as determined by i.r.

dry n-hexane (15 ml), was irradiated under an argon atmosphere.‡ Work-up of the reaction mixture consisted of cooling the solution to room temperature and filtration to remove the product, (**2**), which was shown to be homogeneous by t.l.c. In this way, yields of (**2**) greater than 65% (based on Fe) were obtained in less than 3 h of irradiation.§ The yield of (**2**) was essentially unchanged regardless of the reaction temperature ($-30°$ to $+60°$) or of irradiating wavelength (full arc, Pyrex, or > 360 nm). The identity of product (**2**) was confirmed by comparison of its i.r. and mass spectra with authentic material.[1,3] That (cot) was produced was demonstrated by i.r. and g.l.c. comparison with authentic material.

We have also observed that $[(\mathrm{cot})\mathrm{Fe_2(CO)_6}]$, (**3**), when irradiated for a short time in hexane under an argon atmosphere, results in the formation of high yields of (**2**). Thus (**3**) could be an important photoproduct of (**1**) in a sequence in which any binuclear complexes initially produced, with the exception of (**2**), are rapidly converted thermally[3] or photochemically into (**2**). In an attempt to observe this postulated formation, in quantity, of binuclear complexes of empirical formula $[(\mathrm{C_8H_8})\mathrm{Fe_2(CO)_6}]$, a solution of (**1**) was irradiated, as above, for 8 min. Crystals of (**2**) were removed from the reaction mixture by filtration, and solvent was removed from the filtrate *in vacuo*. The crystalline residue was analysed by mass spectrometry, but only a trace of product with empirical formula $[(\mathrm{C_8H_8})\mathrm{Fe_2(CO)_6}]$ was detected. Unfortunately, the structure of this compound could not be determined due to the small amount of material that was produced.

The results of these photochemical studies are especially noteworthy in that, when $[(\mathrm{cot})\mathrm{Fe(CO)_3}]$ is irradiated, no appreciable amount of (**3**), the least sterically hindered binuclear (cot) complex, is produced. Apparently, (**3**) is not produced in quantity even when the low conversion studies described were performed. However, when (**1**) is heated with excess of iron pentacarbonyl, (**3**) is produced in yields ten times higher than is (**2**).[1] If a co-ordinatively unsaturated iron complex, $(\mathrm{cot})\mathrm{Fe(CO)_2}$, is the primary photoproduct[4] of $[(\mathrm{cot})\mathrm{Fe(CO)_3}]$, then the complex isolated may be formulated as the product of attack of the most nucleophilic species in solution upon this unsaturated intermediate. This implies that the iron(0) of another molecule of $[(\mathrm{cot})\mathrm{Fe(CO)_3}]$ is far more nucleophilic toward the unsaturated species in an *inter*molecular fashion than are either of the non-co-ordinated double bonds of $(\mathrm{cot})\mathrm{Fe(CO)_2}$, *intra*molecularly.



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‡ Unless the reaction mixture was cooled in a bath, the solvent was heated to reflux by the heat of the 450 W Hanovia lamp.

§ The solution was saturated with (**2**) after irradiation for only 8 min.

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