Volume 27
Number 7
April 6, 1988

Inorganic Chemistry

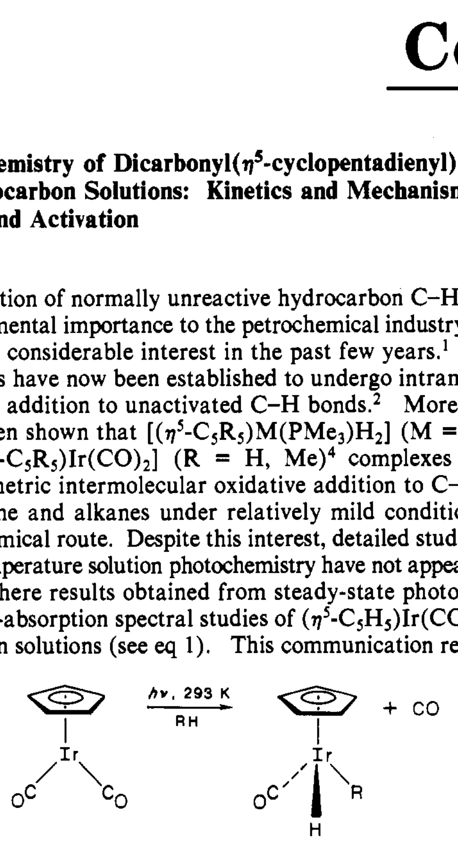
© Copyright 1988 by the American Chemical Society

Communications

Photochemistry of Dicarbonyl(η^5-cyclopentadienyl)iridium in Hydrocarbon Solutions: Kinetics and Mechanism of C–H Bond Activation

Sir:

Activation of normally unreactive hydrocarbon C–H bonds is of fundamental importance to the petrochemical industry and has attracted considerable interest in the past few years.[1] Several molecules have now been established to undergo intramolecular oxidative addition to unactivated C–H bonds.[2] More recently it has been shown that $[(\eta^5\text{-}C_5R_5)M(PMe_3)H_2]$ (M = Rh, Ir)[3] and $[(\eta^5\text{-}C_5R_5)Ir(CO)_2]$ (R = H, Me)[4] complexes undergo stoichiometric intermolecular oxidative addition to C–H bonds of benzene and alkanes under relatively mild conditions via a photochemical route. Despite this interest, detailed studies of the room-temperature solution photochemistry have not appeared. We describe here results obtained from steady-state photolysis and transient-absorption spectral studies of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in hydrocarbon solutions (see eq 1). This communication reports the first available quantum yields and absolute rate data for C–H bond activation of a hydrocarbon following photoexcitation of a metal complex. Evidence presented indicates that the mechanism of C–H bond activation in solution does not involve initial CO dissociation from the photoexcited metal complex.



(1)

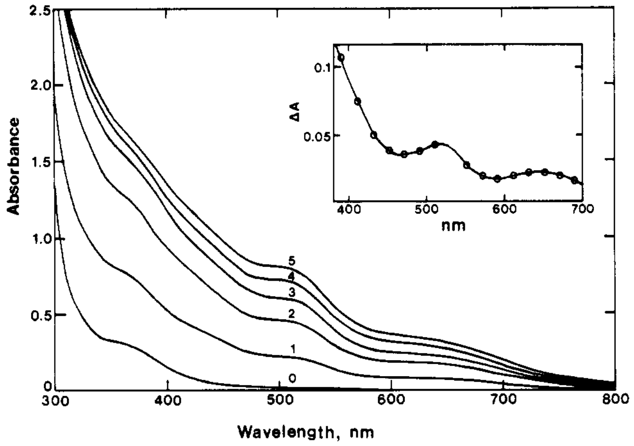


Figure 1. Electronic absorption changes accompanying the 366-nm photolysis (time invervals in hours) of 2.2×10^{-3} M $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in N_2-purged benzene at 293 K. Inset depicts photoproduct spectrum obtained in transient-absorption experiment following 353-nm excitation of 3.8×10^{-3} M $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in benzene at 293 K.

Table I. Quantum Yields (ϕ) for the Conversion of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ to $(\eta^5\text{-}C_5H_5)Ir(CO)(H)(R)$ Products in Various N_2-Purged Hydrocarbon Solvents at 293 K

RH	ϕ^a	RH	ϕ^a
benzene	0.030	*n*-pentane	0.014
toluene	0.026	cyclohexane	0.010
n-heptane	0.015	isooctane	0.006

[a] Reported values estimated to be accurate to ±10%; excitation wavelength is 366 nm.

The spectral sequence observed accompanying the 366-nm photolysis with a 200-W Hg lamp of 2.2×10^{-3} M $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in N_2-purged spectroscopic grade benzene at 293 K is illustrated in Figure 1. This reaction apparently proceeds without interference from secondary photoprocesses, as evidenced by the clean spectral progression to product. We interpret the UV–vis spectral changes to be consistent with oxidative addition of the d^8 Ir(I) complex to form a d^6 Ir(III) species. IR spectral changes recorded during photolysis are also in accordance with conversion of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ [2040 (s) cm^{-1} (ν_{CO}), 1972 (s) cm^{-1} (ν_{CO})] to $(\eta^5\text{-}C_5H_5)Ir(CO)(H)(C_6H_5)$ [2148 (w) cm^{-1} (ν_{IrH}), 2003 (s) cm^{-1} (ν_{CO})].[4]

Quantum efficiency (ϕ) values have been determined in several solvents, and these are shown in Table I; the magnitudes of these values reflect the relative selectivity of the photoexcited $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ complex for the intermolecular activation of hydrocarbon C–H bonds. These quantum yields indicate that the aromatic solvents are activated more efficiently than the aliphatic molecules and strongly imply that the C–H bond activation of

---

(1) (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (c) Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725. (d) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (e) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (f) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 10. (g) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; p 206. (h) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

(2) For example, see: (a) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446. (b) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (c) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59. (d) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (e) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728. (f) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (g) Clark, H. C.; Goel, A. B.; Goel, S. *Inorg. Chem.* **1979**, *18*, 2803. (h) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.

(3) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; **1983**, *105*, 3929. (b) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686.

(4) (a) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

0020-1669/88/1327-1121$01.50/0

Table II. Quantum Yields (ϕ) for the Conversion of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ to $(\eta^5\text{-}C_5H_5)Ir(CO)(H)(C_6H_5)$ in Perfluorobenzene at 293 K[a]

$[C_6H_6]$, M	ϕ[b]	ϕ[c]	$[C_6H_6]$, M	ϕ[b]	ϕ[c]
0.001	0.0056	0.0059	0.10	0.021	0.020
0.005	0.0093	0.0090	0.25	0.027	
0.01	0.013		0.50	0.029	0.028
0.025	0.017	0.015	11.3[d]	0.030	
0.05	0.018				

[a] Reported values estimated to be accurate to ±10%; excitation wavelength is 366 nm. [b] N_2-purged solutions. [c] CO-saturated solutions ($\sim 10^{-2}$ M in dissolved CO concentration; see ref 7). [d] Neat benzene solvent.

these hydrocarbons is facilitated by π-interaction. This observation contrasts with a previous report stating that insertion into the C–H bonds of ethylene by a $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)$ intermediate does not involve prior formation of a π-complex.[5] Furthermore, the exceptionally low yield that we have obtained for isooctane (see Table I) suggests that steric factors may be important in the C–H bond activation mechanism; this is concordant with theoretical considerations using an extended Hückel approach.[6]

Significantly, in neat perfluorobenzene no reaction was observed to take place over an 8-h period of irradiation, thus establishing an inert solvent for this system. Quantum yields for C–H bond activation of benzene are dependent on the concentration of benzene in perfluorobenzene and are listed in Table II. A plot of ϕ versus $[C_6H_6]$ is shown in Figure 2; the data exhibit a linear dependence at low $[C_6H_6]$ and reach a saturation limit at high $[C_6H_6]$. These results imply that the rate-limiting step of the C–H bond activation is a bimolecular process involving the association of the benzene molecule with the metal complex. The mechanistic schemes (A and B) in eq 2–8 are consistent with the above experimental observations (S = perfluorobenzene).

$$(\eta^5\text{-}C_5H_5)Ir(CO)_2 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Ir(CO)_2{}^* \qquad (2)$$

mechanism A

$$(\eta^5\text{-}C_5H_5)Ir(CO)_2{}^* \xrightarrow{k_1,\ S} (\eta^5\text{-}C_5H_5)Ir(CO)(S) + CO \qquad (3)$$

$$(\eta^5\text{-}C_5H_5)Ir(CO)(S) \xrightarrow[CO]{k_2} (\eta^5\text{-}C_5H_5)Ir(CO)_2 + S \qquad (4)$$

$$(\eta^5\text{-}C_5H_5)Ir(CO)(S) \xrightarrow[C_6H_6]{k_3} (\eta^5\text{-}C_5H_5)Ir(CO)(H)(C_6H_5) + S \qquad (5)$$

mechanism B

$$(\eta^5\text{-}C_5H_5)Ir(CO)_2{}^* \xrightarrow{k_1,\ S} (\eta^3\text{-}C_5H_5)Ir(CO)_2(S) \qquad (6)$$

$$(\eta^3\text{-}C_5H_5)Ir(CO)_2(S) \xrightarrow{k_2} (\eta^5\text{-}C_5H_5)Ir(CO)_2 + S \qquad (7)$$

$$(\eta^3\text{-}C_5H_5)Ir(CO)_2(S) \xrightarrow[C_6H_6]{k_3} (\eta^5\text{-}C_5H_5)Ir(CO)(H)(C_6H_5) + CO + S \qquad (8)$$

Quantum yields have also been measured for C–H activation of benzene in perfluorobenzene solutions saturated with CO (ca. 10^{-2} M),[7] and the data are included in Table II. Importantly, these results illustrate that there is little, if any, effect of added CO on ϕ, even when [CO] is approximately 10-fold greater than $[C_6H_6]$. This observation does not support the mechanism involving initial CO dissociation from the photoexcited complex (mechanism A). The data are, though, consistent with a hapticity change ($\eta^5 \to \eta^3$) (mechanism B) where varying CO concentration would not be expected to significantly affect the reaction efficiency. This mechanism for the solution photochemical reaction of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ contrasts with a reported CO dissociation process determined from matrix-isolation studies,[8] but in a low-temperature matrix the $\eta^5 \to \eta^3$ mechanism may be greatly suppressed.

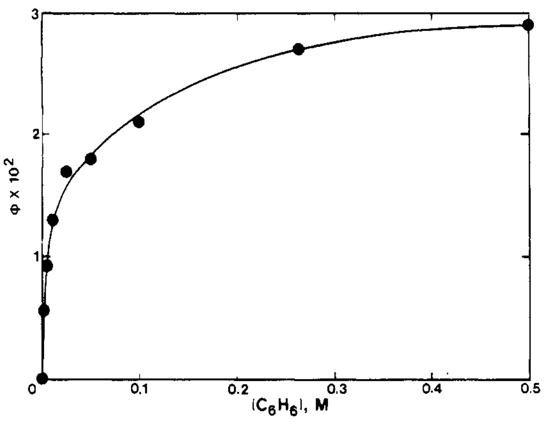


Figure 2. Dependence of observed quantum yield (ϕ) on benzene concentration for the 366-nm photolysis of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in N_2-purged perfluorobenzene at 293 K.

Preliminary laser flash photolysis experiments have also been carried out. Excitation of 3.8×10^{-3} M $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in N_2-purged benzene at 293 K with the third harmonic line of a Korad Nd-glass laser (353 nm, 20-ns pulse width)[9,10] produces an absorbance change immediately following the laser pulse that is depicted in the inset of Figure 1. No further absorbance changes were observed. These absorption features closely match those obtained in the steady-state photolysis experiment, and it is concluded that $(\eta^5\text{-}C_5H_5)Ir(CO)(H)(C_6H_5)$ has been formed within the 20-ns laser pulse. Thus, a lower limit for $k_{app} = (4.4 \pm 0.9) \times 10^6\ M^{-1}\ s^{-1}$ (where $k_{app} = k_{obsd}/[C_6H_6]$) can be estimated for the C–H bond activation of benzene. Any transient produced following photoexcitation is very short-lived and rapidly scavenged by the solvent molecules present (neat benzene at 293 K is 11.3 M). Similar transient-absorption behavior was observed in neat cyclohexane solutions. Further time-resolved experiments are ongoing and will be reported in due course.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank A. S. Lee for assistance with initial experiments and Prof. A. W. Adamson for use of the Nd-glass laser and transient-absorption equipment.

Registry No. $(\eta^5\text{-}C_5H_5)Ir(CO)_2$, 12192-96-0; benzene, 71-43-2; toluene, 108-88-3; *n*-heptane, 142-82-5; *n*-pentane, 109-66-0; cyclohexane, 110-82-7; isooctane, 26635-64-3; perfluorobenzene, 392-56-3.

Department of Chemistry
University Center at Binghamton
State University of New York
Binghamton, New York 13901

David E. Marx
Alistair J. Lees*

Received June 18, 1987

---

(5) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

(6) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(7) The saturated concentrations of CO in C_6H_6 and C_7H_{16} have been determined to be 8.26×10^{-3} and 1.87×10^{-2} M, respectively: Lawson, D. D. *Appl. Energy* **1980**, *6*, 241.

(8) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1181.

(9) Details of the transient absorption apparatus have been previously described: (a) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381. (b) Fukuda, R.; Walters, R. T.; Mäcke, H.; Adamson, A. W. *J. Phys. Chem.* **1979**, *83*, 2097.

(10) Approximately 1.1×10^{-4} M $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ undergoes photodissociation following this excitation. This value has been determined from the laser pulse energy, irradiated volume, absorbance, and quantum yield of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in the transient-absorption experiment.