Journal of Organometallic Chemistry, 54 (1973) C33–C36

Preliminary communication

The kinetics and mechanism of the thermal reaction between iron pentacarbonyl and iodine in n-hexane

GERARD R. DOBSON, ROBERT T. JERNIGAN and PING-TZU CHANG

Department of Chemistry, North Texas State University, Denton, Texas 76203 (U.S.A.)

(Received February 21st, 1973)

SUMMARY

The mechanism of the thermal oxidative elimination reaction between iron pentacarbonyl and iodine in n-hexane to afford *cis*-$Fe(CO)_4I_2$ is inferred to involve the successive formation of 1/1 and 1/2 "adducts" of iron pentacarbonyl and iodine; each adduct ultimately yields the observed product through loss of carbon monoxide. A common mechanism can encompass the observed kinetic behavior for both octahedral and trigonal bipyramidal metal carbonyl substrates.

The reaction of iron pentacarbonyl with iodine to yield the octahedral, *cis*-$Fe(CO)_4I_2$ product is a representative example of an oxidative elimination reaction, a widely observed reaction type among metal carbonyls and derivatives[1]. While a few kinetic studies of this class of reaction have recently been reported[2], these have not included investigations of trigonal bipyramidal substrates nor halogens as oxidizing agents, although, for the reaction of iron pentacarbonyl with halogens, low temperature infrared studies have demonstrated the presence of reaction intermediates which were variously formulated and whose identity differed with the solvent employed in the synthesis[3,4].

The study of the kinetics and mechanism of this thermal reaction ($X_2 = I_2$) in n-hexane has been undertaken employing stopped flow kinetic techniques. Initial studies under pseudo first order reaction conditions (at least a ten-fold excess of I_2) were monitored at 410 nm. The reaction was found to be photochemical as well as thermal at 25.0 ± 0.1°. The contribution of the photochemical path to the overall rate was eliminated by means of a shutter placed between the visible source and the observation cell. The initial transmittance observed after the shutter was opened at some time, *t*, after the solutions were mixed thus could be related to the extent to which the thermal (dark) reaction had proceeded up to that time. Pseudo first order (k_{obs}) plots of $\ln(A_t - A_\infty)$ *vs.* *t* were found to be linear after an initial induction period. From a plot of k_{obs} *vs.* $[I_2]$ for the linear

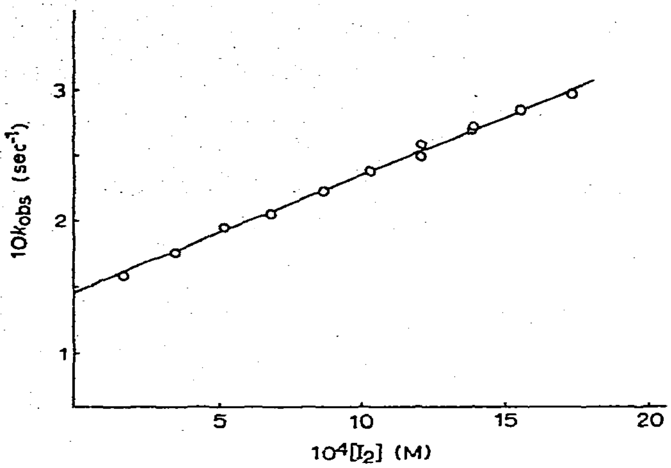

Fig. 1. Plot of k_{obs} *vs.* $[I_2]$ for reaction of $Fe(CO)_5$ with I_2 in n-hexane at 25.0°.

portions of the k_{obs} plots (Fig. 1) were extracted the rate constants, $k_b = 1.45 \times 10^{-1} \pm 2 \times 10^{-3}$ sec^{-1} and $k_c = 9.04 \times 10^1 \pm 1.4 M^{-1} \cdot$sec^{-1}.

Several lines of evidence suggested the initial induction period observed for the k_{obs} plots to arise through the rapid formation of an intermediate of stoichiometry $Fe(CO)_5 \cdot I_2$, which would be analogous to intermediates proposed in other kinetic studies of oxidative elimination reactions[2]. This intermediate could then decay via the two competing paths governed by k_b and k_c to afford the observed product:

$$\begin{tikzcd}
Fe(CO)_5 + I_2 \arrow[r, "k_a"] & Fe(CO)_5 \cdot I_2 \arrow[dl, "k_b" ', "-CO"] \arrow[dr, "k_c" ', "+I_2"] & \\
cis\text{-}Fe(CO)_4 I_2 & & Fe(CO)_5 \cdot 2I_2 \arrow[ll, "{-CO,\ -I_2}" ']
\end{tikzcd} \tag{1}$$

The rate law derived from the linear portions of the k_{obs} plots cannot correspond to the decay of the substrate since CO-exchange studies have shown the rate of carbonyl dissociation from $Fe(CO)_5$ to be very slow at room temperature[5]. If the first intermediate formed is one of those observed in the low-temperature infrared studies[3,4], carbonyl dissociation from it would be expected to be more facile than from $Fe(CO)_5$, since the carbonyl stretching absorptions observed for these intermediates were in all cases at higher energy than are those reported for $Fe(CO)_5$. Higher $\nu(CO)$ would indicate weaker OC—Fe π-bonding in the intermediate.

The rate law predicted by the mechanism (1) for the step governed by k_a (first order in I_2 and $Fe(CO)_5$) was confirmed by kinetic studies under pseudo first order conditions (large excess of $Fe(CO)_5$) chosen so as to inhibit steps subsequent to k_a. The

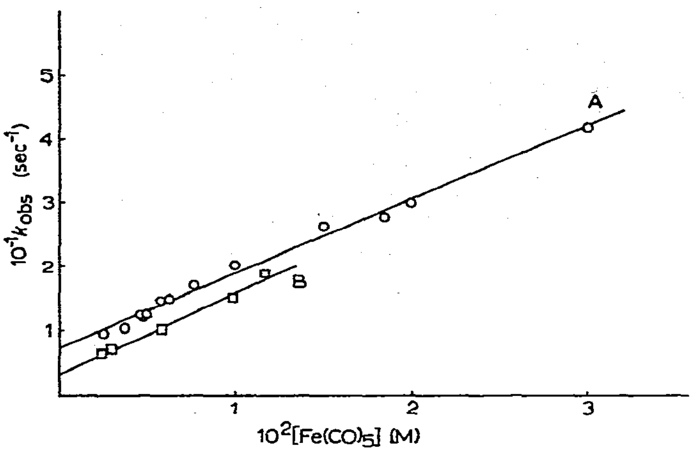

Fig. 2. Plots of k_{obs} *vs.* [Fe(CO)$_5$] for reaction of Fe(CO)$_5$ with I_2 in n-hexane at 25.0° at different visible source powers. A. at 36.6 watts; B. at 27.5 watts.

reaction, monitored at 475 nm, was too fast to employ the shuttering technique, and thus plots of k_{obs} *vs.* [Fe(CO)$_5$] were obtained at two different source intensities; these plots (Fig. 2) are observed to be parallel, with intercepts which differ with the intensity of the light source. This observation suggests the path dependent only upon the concentration of iodine to be photochemical, probably involving the initial formation of iodine radicals[6]. In contrast, the invariance of the slopes of these plots with source intensity indicates the bimolecular path to be thermal. From the slopes of the k_{obs} *vs.* [Fe(CO)$_5$] plots at two source intensities were obtained the second order rate constants, $k_a = 1.17 \times 10^3 \pm 35\,M^{-1}\cdot\text{sec}^{-1}$ and $1.28 \times 10^3 \pm 74\,M^{-1}\cdot\text{sec}^{-1}$ at 25.0 ± 0.1°.

The observed overall rate law, together with those determined for the oxidative elimination reactions of substituted octahedral metal carbonyl complexes with various oxidizing agents[2] can be encompassed within an overall mechanism involving the formation of 1/1 and 1/2 "adducts" of the substrate and oxidant, the differing stereochemistries of the substrates notwithstanding.

The relative magnitudes of the rate constants are consistent with the formation of an intermediate of stoichiometry $Fe(CO)_5 \cdot I_2$ at low temperature. Moreover, the synthesis of the species studied by Farona and Camp was effected in hydrocarbon solvent[4], and thus it is probable that it is the kinetically observed intermediate. On the basis of its infrared spectrum, and conductivity data which demonstrated it to be molecular, Farona and Camp favored a seven-coordinate, pentagonal bipyramidal or capped octahedral structure, but the present observation that it is further susceptible to associative attack argues against this proposal. Octahedral metal carbonyls and derivatives of the first row transition metals are markedly less susceptible to reaction via associative paths than are those of the second and third transition series, an effect attributed to differences in the atomic sizes of the metal atoms[7]; it would thus appear highly improbable that seven-coordinate iron could undergo facile attack. It appears more likely that the intermediate is six-coordinate, perhaps of distorted capped trigonal bipyramidal or other irregular geometry, in light of the complexity of its carbonyl stretching spectrum in solution at low temperature[4].

ACKNOWLEDGEMENTS

The financial support of this research by the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund is gratefully acknowledged. We thank Professor Kenneth R. Ashley, East Texas State University, for valuable comments.

REFERENCES

1 W. Hieber and G. Bader, *Ber. Deut. Chem. Ges. B*, 61 (1928) 1717; K. Noack, *Helv. Chim. Acta*, 45 (1962) 1847.
2 J.W. McDonald and F. Basolo, *Inorg. Chem.*, 10 (1971) 492; R.T. Jernigan and G.R. Dobson, *Inorg. Chem.*, 11 (1972) 81; M.N. Memering, A. Moradi-Araghi and G.R. Dobson, *J. Coord. Chem.*, in press.
3 K. Noack, *J. Organometal. Chem.*, 13 (1968) 411.
4 M.F. Farona and G.R. Camp, *Inorg. Chim. Acta*, 3 (1969) 395.
5 D.F. Keeley and R.E. Johnson, *J. Inorg. Nucl. Chem.*, 11 (1959) 33.
6 J. Zimmerman and R.M. Noyes, *J. Chem. Phys.*, 18 (1950) 658.
7 See, *e.g.*, R. Kummer and W.A.G. Graham, *Inorg. Chem.*, 7 (1968) 310, and R.J. Angelici, *Coord. Chem. Rev.*, 3 (1968) 273.