liminary communication

ARBON MONOXIDE DISSOCIATION REACTION OF
5-C5H5)2Mo2(CO)6 WITH DIPHENYLACETYLENE

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Received November 3rd, 1980)

ummary

Kinetic studies of the reaction of $(h^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with diphenyl-
acetylene show that it involves successive dissociation of two CO ligands
before reaction with C_2Ph_2 but this dissociative reaction is considerably slower
than the completely reversible homolytic fission of the complex that occurs
concurrently without leading to any product.

Reactions of alkynes with metal—metal bonded carbonyls have reveived
remarkably little kinetic study [1] in spite of the wide and interesting range of
products obtained. It has been speculated that photochemical reactions of
$Cp_2Mo_2(CO)_6$ ($Cp = h^5\text{-}C_5H_5$) with alkynes go via initial photo-induced homo-
lytic fission into $CpMo(CO)_3$ radicals [2] and it has also been suggested that
homolytic fission is the initial step in the thermal reactions [3]. Our studies of
the reaction of $Cp_2Mo_2(CO)_6$ with reagents capable of scavenging the radicals
formed by thermal homolytic fission [4] suggest that reactions with alkynes
proceeded via a different path and we report here a detailed kinetic study of
the reaction with dephenylacetylene in decalin.

Reactions at 145°C proceed cleanly to form $Cp_2Mo_2(CO)_4(C_2Ph_2)$ as the
only observable product. It was characterized by elemental analysis and mass
spectroscopy. When $[C_2Ph_2] = 0.1\text{—}0.7\ M$ yields were generally 70—90% as
measured by IR spectroscopy at the end of the kinetic runs. The rate of the
reaction is accelerated when N_2 is bubbled through the solution and it appears
that reaction is retarded by the CO released. The kinetics were therefore
followed under defined atmospheres of CO when good pseudo-first-order
rate plots were obtained. The dependence of the values of k_{obs} on $[C_2Ph_2]$
suggests that two paths are followed, one (path A) involving an increase in
rate with increasing $[C_2Ph_2]$ to a limiting value and the other (path B)

TABLE 1

VALUES OF THE RATE CONSTANTS k_a (lim) AND k_b FOR THE REACTION OF C_2Ph_2 WITH $Cp_2Mo_2(CO)_6$ IN DECALIN AT 144.8°C. $[Cp_2Mo_2(CO)_6] = (3-16) \times 10^{-4} M$; $[C_2Ph_2] = 0.1-0.7$ i
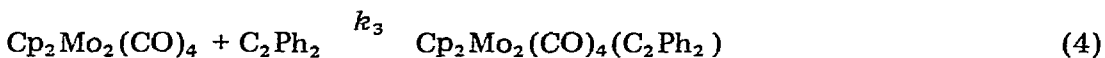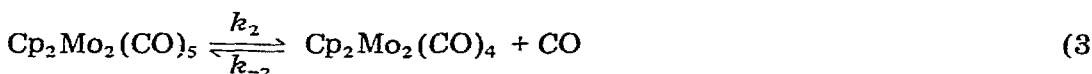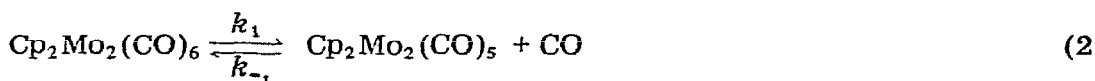
CO^a (%)	$10^4 k_a$ (lim) (s^{-1})	$10^4 k_b$ $(M^{-1} s^{-1})$	No. of runs
5.0	28.5	34.0	5
15.0	17.7	45.0	8
25.0	11.5	47.8	9
40.0	6.0	59.7	9
100.0	2.7	39.8	7

^{a} In CO/N_2 mixtures.

involving first-order dependence on $[C_2Ph_2]$ up to high concentrations. The limiting rate for path A is reached when $[C_2Ph_2] \gtrsim 0.1 M$ and above this concentration the reaction follows eq. 1 very closely. Values of k_a (lim) and

$$k_{obs} = k_a \text{ (lim)} + k_b[C_2Ph_2] \tag{1}$$

k_b are given in Table 1. The value of k_a (lim) decreases with increasing [CO] and the mechanism shown in eq. 2—4 is therefore suggested. This is closely analogous to that found for reaction of C_2Ph_2 with $Co_2(CO)_6(P-n-Bu_3)_2$ when

$$Cp_2Mo_2(CO)_6 \xrightleftharpoons[k_{-1}]{k_1} Cp_2Mo_2(CO)_5 + CO \tag{2}$$

$$Cp_2Mo_2(CO)_5 \xrightleftharpoons[k_{-2}]{k_2} Cp_2Mo_2(CO)_4 + CO \tag{3}$$

$$Cp_2Mo_2(CO)_4 + C_2Ph_2 \xrightarrow{k_3} Cp_2Mo_2(CO)_4(C_2Ph_2) \tag{4}$$

dissociation of two ligands also has to occur before addition of C_2Ph_2 is possible [1,5]. The corresponding rate equation is shown in eq. 5. At high $[C_2Ph_2]$ k_a will approach a limiting value given, after inversion, by eq. 6. A

$$k_a = \frac{k_1 k_2 k_3 [C_2Ph_2]}{k_{-1}k_{-2}[CO]^2 + k_{-1}k_{-3}[CO][C_2Ph_2] + k_2 k_3 [C_2Ph_2]} \tag{5}$$

$$1/k_a \text{ (lim)} = 1/k_1 + (k_{-1}/k_1 k_2)[CO] \tag{6}$$

plot of $1/k_a$ (lim) against [CO] is shown in Fig. 1 where excellent agreement with behaviour predicted by the mechanism is observed.

Another important feature of this reaction is that the yield of $Cp_2Mo_2(CO)_4$-(C_2Ph_2) decreases with decreasing temperature so that it is is negligible at 110°C. The value of k_a (lim) is then independent of [CO]. Since the product is thermally very stable under these conditions we conclude that the reason for the decreasing yield is that $Cp_2Mo_2(CO)_5$ can be attacked by C_2Ph_2 in a way that leads to eventual decomposition rather than product, and that the activation energy for this attack is considerably less than that for dissociation of the second CO ligand. Under these conditions k_a (lim) will be a measure of
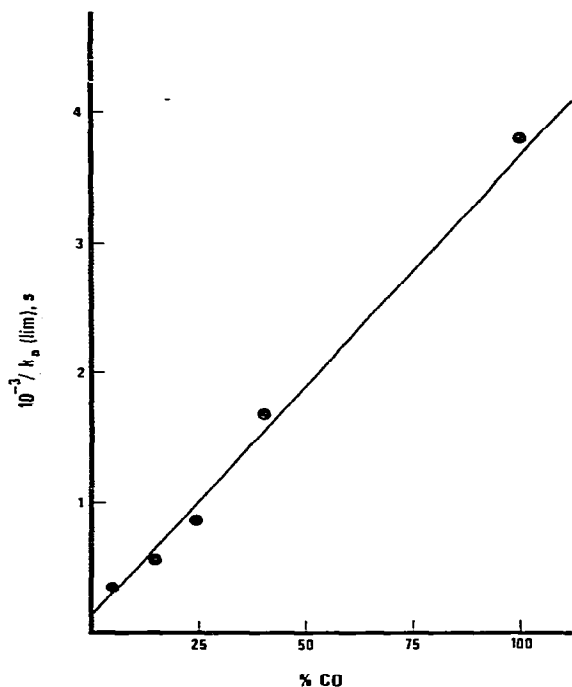
Fig. 1. Dependence of the limiting rate constant for path A on the proportion of CO in CO/N_2 atmospheres above the reacting solutions.

k_1. The values of k_1 found in this way or from the intercept of the plot in Fig. 1 are both much less than the rate constant for homolytic fission of the Mo—Mo bond [4]. Thus the values of k_1 at 110 and 145°C are 7×10^{-5} and ca. 10^{-2} s^{-1}, respectively, as compared with rate constants 2×10^{-3} and ca. 10^{-1} s^{-1} for homolytic fission [4]. During the relatively slow formation of $Cp_2Mo_2(CO)_4(C_2Ph_2)$ in high yield at 145°C under an atmosphere of CO homolytic fission, and its reverse, are occurring ca. 10^3 times for each event leading to $Cp_2Mo_2(CO)_4(C_2Ph_2)$.

The mechanism corresponding to path B is not so well defined and k_b does not vary systematically with [CO]. However, it cannot involve attack by C_2Ph_2 on $Cp_2Mo_2(CO)_5$ (because the values of k_b would have to be inversely proportional to [CO]) and it is probably similar to the corresponding path found for reaction of C_2Ph_2 with $Co_2(CO)_6(P-n-Bu_3)_2$ [5].

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