Selective Formation of Propyne by Protonation of an Allyl Complex

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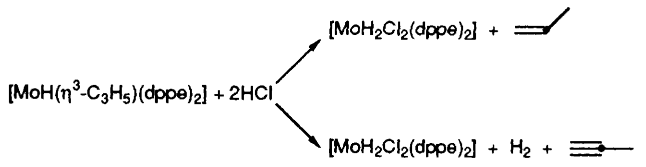
Treatment of $[MoH(\eta^3\text{-}C_3H_5)(Ph_2PCH_2CH_2PPh_2)_2]$ with a large excess of anhydrous HCl in tetrahydrofuran rapidly yields $[MoH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$ and propyne, at lower concentrations of acid, propene is formed; the mechanism of these reactions has been established by detailed kinetic studies and product analyses.

We have been investigating the activation of coordinated small molecules, such as dinitrogen,[1] hydrogen[2,3] and unsaturated hydrocarbons,[4] towards protonation. One aspect of our work on the protonation of unsaturated hydrocarbons focuses on defining the factors which discriminate between the formation of different hydrocarbons at various acid concentrations.[5] Herein we report the novel reaction shown in Scheme 1,[†] in which protonation of $[MoH(\eta^3\text{-}C_3H_5)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in thf (thf = tetrahydrofuran) gives rise to propyne. That is, an alkene complex can be protonated to form an alkyne!



Scheme 1

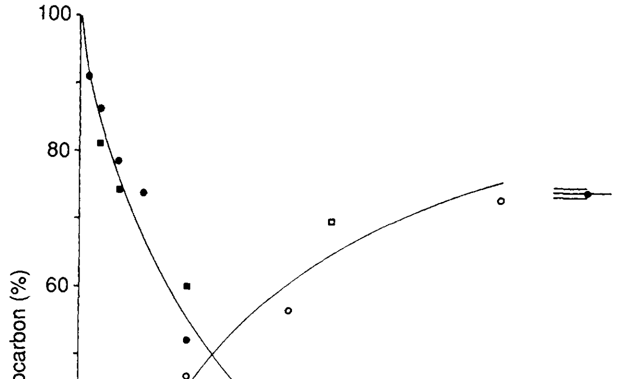


Fig. 1 Hydrocarbon composition from the reaction of $[MoH(\eta^3\text{-}C_3H_5)(dppe)_2]$ with HCl in thf at 25.0 °C. Data points correspond to $[Mo]_o$ = 1.0 mmol dm^{-3}, [HCl] = 0–200 mmol dm^{-3}: propene (●), propyne (○); $[Mo]_o$ = 0.125–2.0 mmol dm^{-3}, [HCl] = 30.0 mmol dm^{-3}: propene (■), propyne (□). Curves drawn are those defined by eqn. (2). For the meaning of $[Mo]_o$ and $[Mo]_e$ see footnote §.

The composition of the hydrocarbon mixture formed at various concentrations of $[MoH(\eta^3\text{-}C_3H_5)(dppe)_2]$ and HCl is shown in Fig. 1. Two features of these data are important. First, under all conditions, quantitative and rapid[‡] release of the coordinated 'C_3 fragment' is observed, and secondly the composition of the hydrocarbon mixture depends on the ratio, [HCl]/[Mo], and not on the absolute concentrations of either HCl or the complex.

In order to understand how each of these hydrocarbons is produced the reaction has been studied by stopped-flow spectrophotometry monitoring the absorbance changes of the molybdenum species. Upon mixing $[MoH(\eta^3\text{-}C_3H_5)(dppe)_2]$

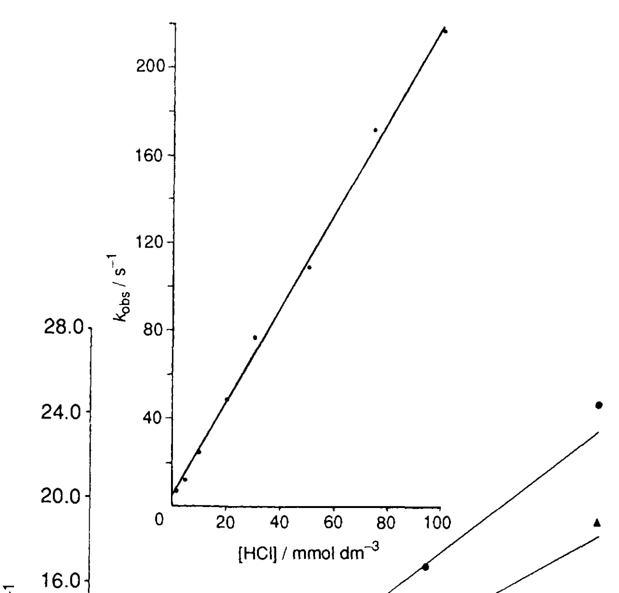
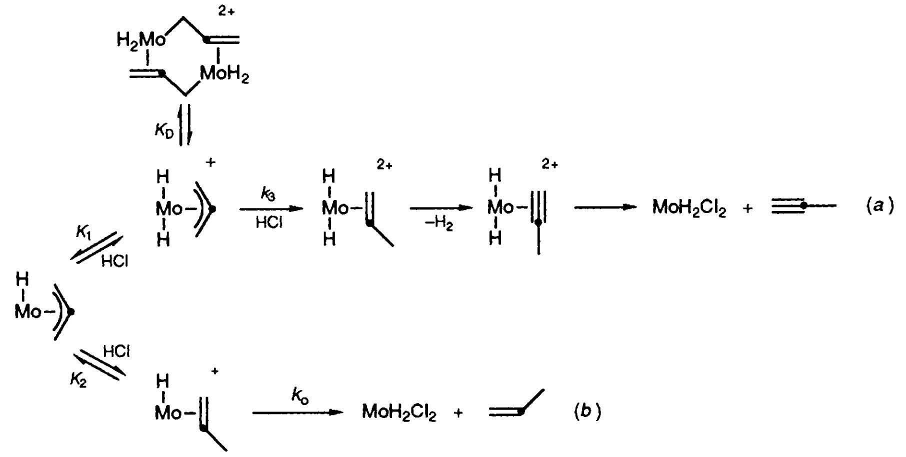


Fig. 2 Kinetic data for the reaction between $[MoH(\eta^3\text{-}C_3H_5)(dppe)_2]$ and HCl in thf at 25.0 °C. Data points correspond to $[Mo]_o$ = 0.5 mmol dm^{-3} (■); $[Mo]_o$ = 0.125 mmol dm^{-3} (▲); $[Mo]_o$ = 0.03 mmol dm^{-3} (●). Lines drawn are those defined by eqn. (1). Insert shows the linear dependence on the concentration of HCl over an extended concentration range, $[Mo]_o$ = 0.10 mmol dm^{-3}.

[†] The reaction product, $[MoH_2Cl_2(dppe)_2]$ was identified by its characteristic $^{31}P\{^1H\}$ NMR spectrum [δ −71.1(t), −99.7(t), $^2J_{P,P}$ 10.0 Hz *vs.* $P(OMe)_3$] and ^1H NMR spectrum [δ −4.5(quintet), $^2J_{P,H}$ 45 Hz, Mo–H *vs.* $SiMe_4$].[6] The hydrocarbons were determined by GLC using a Poropak Q column operating at 130 °C, and calibrated with authentic samples of propene and propyne.

[‡] A time-course experiment for the production of the hydrocarbons showed that in the reactions with HCl quantitative yields of propene and propyne are present in the gas phase within 5 min at 25.0 °C. Whereas in the absence of acid less than 8% of the available propene is formed in 1 h.



Scheme 2 Phosphine ligands omitted for clarity

and an excess of HCl in thf there is a rapid, small decrease in absorbance [complete within the dead-time of the apparatus (2 ms)], followed by a large absorbance–time decay, which at [HCl] = 20 mmol dm^{-3} (for instance) is complete within 0.2 s, to yield the products. The kinetics of the slow stage are illustrated in Fig. 2, and the derived rate law is shown in eqn. (1). The kinetic data and the product composition are

$$\frac{d[MoH_2Cl_2(dppe)_2]}{dt} = \left\{(4.3 \pm 0.2) + \frac{(3.8 \pm 0.3) \times 10^3\,[HCl]}{1 + (1.0 \pm 0.3) \times 10^4\,[Mo]_e}\right\}[Mo]_o \quad (1)$$

consistent with the mechanism shown in Scheme 2.§ In this mechanism, initial rapid protonation of [MoH(η^3-C_3H_5)(dppe)$_2$] gives an equilibrium mixture of [MoH$_2$(η^3-C_3H_5)(dppe)$_2$]$^+$ and [MoH(η^2-MeCH=CH$_2$)(dppe)$_2$]$^+$ together with some starting material, by competitive protonation at the metal and the allyl ligand. It is the equilibrium formation of these two cations which is responsible for the initial absorbance decrease observed on the stopped-flow apparatus. Subsequently the reaction can proceed *via* two pathways. At low concentrations of HCl the dominant route is that involving dissociation of propene from [MoH(η^2-MeCH=CH$_2$)(dppe)$_2$]$^+$ [pathway (*b*)], $k_0 = 4.3 \pm 0.2$ s^{-1}, but at higher acid concentrations the acid-dependent route [pathway (*a*)] contributes to the overall reaction rate. This latter pathway involves further protonation of [MoH$_2$(η^3-C_3H_5)(dppe)$_2$]$^+$ [$k_3 = (3.8 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1}] and results ultimately in the evolution of propyne and dihydrogen. It is likely that the propyne formation from [MoH$_2$(η^3-C_3H_5)(dppe)$_2$]$^+$ involves generation of [MoH$_2$(η^2-MeC≡CH)(dppe)$_2$]$^{2+}$ *via* the 14-electron species, [Mo(η^2-MeCH=CH$_2$)(dppe)$_2$]$^{2+}$, in which the metal is so coordinatively-unsaturated that it abstracts hydrogen atoms from the coordinated propene.

The kinetics of the acid-dependent pathway are complicated by the dimerisation process shown in Scheme 2, with $2K_D = (1.0 \pm 0.3) \times 10^4$ dm^3 mol^{-1}. The exact nature of the dimeric species is not entirely clear, and cannot be defined from these mechanistic studies. However, we propose that the dimer is formed as a consequence of the η^3-allyl ligand rearranging to an η^1-allyl species and, in order to maintain a closed-shell configuration, the metal centres dimerise.

Chloride ion has no effect on either the kinetics or the hydrocarbon distribution in the concentration range, [(PBu$_4$)Cl] = 0.05–5.0 mmol dm^{-3}. Using the kinetic data, the hydrocarbon composition shown in Fig. 1 can be simulated, and in particular the characteristic dependence on the ratio, [HCl]/[Mo] is a natural consequence of this mechanism. Inspection of the mechanism permits derivation of eqn. (2),

$$\frac{[MeC{\equiv}CH]}{[MeC{\equiv}CH] + [MeCH{=}CH_2]} = \frac{k_3[HCl]}{k_3[HCl] + 2k_0K_D(K_2/K_1)[Mo]_e} \quad (2)$$

which describes the propyne proportion of the total hydrocarbon mixture.¶ Using the established values of k_3, k_o and K_D the hydrocarbon composition shown in Fig. 1 can be best fitted when $K_2/K_1 = 10$.

Thus, at low concentrations of acid the reaction proceeds predominantly by the pathway (*b*) shown in Scheme 2, and any [MoH$_2$(η^3-C_3H_5)(dppe)$_2$]$^+$ formed is ultimately converted to [MoH(η^2-MeCHCH$_2$)(dppe)$_2$]$^+$ and hence to propene. Only at high acid concentrations can [MoH(η^3-C_3H_5)(dppe)$_2$]$^+$ be protonated to form [MoH$_2$(η^2-MeCHCH$_2$)(dppe)$_2$]$^{2+}$ and from thereon is irreversibly committed to the formation of propyne. It is only the occurrence of the dimerisation process which gives rise to the molybdenum dependence on this hydrocarbon product distribution.

This analysis shows that protonation of the allyl complex, [MoH(η^3-C_3H_5)(dppe)$_2$] gives essentially quantitative yields of propyne at high concentrations of acid; with propene being produced preferentially only at relatively low acid concentrations. How general this type of reaction is remains to be seen,

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§ The rate law for the formation of products from the initially formed equilibrium mixture of [MoH$_2$(η^3-C_3H_5)(dppe)$_2$]$^+$ and [MoH(η^2-MeCHCH$_2$)(dppe)$_2$]$^+$ is shown in eqn. (3) where [Mo]$_o$ is the total

$$\frac{-d\{[MoH_2(\eta^3\text{-}C_3H_5)] + [MoH(\eta^2\text{-}MeCHCH_2)]\}}{dt} = \left\{k_0 + \frac{k_3[HCl]}{1 + 2K_D[Mo]_e}\right\}[Mo]_o \quad (3)$$

concentration of molybdenum in the system and [Mo]$_e$ is the equilibrium concentration of the monomeric species [MoH$_2$($\eta^3$$C_3H_5$)(dppe)$_2$]$^+$ present, calculated using the value, $K_D = 5 \times 10^3$ dm^3 mol^{-1}. The value of K_D was estimated from an iterative 'best fit' analysis of the data in Fig. 2.

¶ This expression is readily derived[7] by considering the kinetics for the propyne- and propene-formation from [MoH($\eta^3$$C_3H_5$)(dppe)$_2$]; eqns. (4) and (5), respectively, for definition of [Mo]$_o$ and [Mo]$_e$

$$\frac{d[propyne]}{dt} = K_1k_3[HCl]^2[Mo]_o/(1 + 2K_D[Mo]_e) \quad (4)$$

$$\frac{d[propene]}{dt} = K_2k_0[HCl][Mo]_o \quad (5)$$

see footnote §.

but this study indicates that alkyne formation from an alkene is favoured when protonation of an electron-rich metal, and subsequent evolution of dihydrogen are facile.

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