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A mechanism for the 'solid–solid' reaction between Mn(CO)₄(PPh₃)Br and solid phosphines

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Abstract

The 'solid-solid' reaction between $Mn(CO)_4(PPh_3)Br$ and solid phosphines at temperatures lower than the reactant melting points is shown to occur in the melt.

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Novel approaches to waste disposal and atom economy are being incorporated into synthetic chemistry [1,2]. The simplest approach to these issues is to perform reactions in the absence of solvents [3,4]. While in principle this appears a trivial solution to an environmental problem, complicating factors relating to diffusion, heat and mass transfer, etc., have to be addressed. These factors may yield different reaction mechanisms and either aid or reduce the activity/selectivity of the process. Little information is available on the competing roles of the chemical reaction and diffusion in the melt. Much work thus needs to be performed to evaluate this synthetic strategy.

Our approach has been to evaluate solventless reactions via a study of well-established organometallic chemistry reactions. Others have investigated solventless chemical reactions by studying organic reactions [3–7].

Recently, we reported that the reaction between $CpM(CO)_3Me$ (M = Mo, W) and PPh₃ occurred in the absence of solvents to yield the CO insertion/Me migration product $CpM(CO)_2(PPh_3)(COMe)$ [8]. This

study revealed that the reaction was well behaved and at low temperature *appeared* to occur in the solid state.

We now wish to report on an extension of our studies to an investigation of the solventless CO substitution reaction of Mn(CO)₄(PPh₃)Br by phosphines [9]. The reaction between Mn(CO)₄(PPh₃)Br and PPh₃ was monitored as a function of reactant ratio (1:1 to 1:10) and temperature in the absence of solvents. Initially, a DSC profile of the mixture was recorded (10 °C min⁻¹) and revealed only the mp of PPh₃ (78 °C) in the region 25-100 °C, suggesting no influence of reagents on each other. Reactants were mixed together without grinding, placed in NMR tubes (under argon) and heated in an oil bath (35-70 °C; below the mp of the individual reactants) at a pre-set temperature. After intervals of time the NMR tubes were removed from the oil bath, cooled, and IR spectra recorded (in CHCl₃). Calibration curves permitted the degree of reaction to be determined. Typical reaction plots were obtained which fitted first order kinetics for the reaction. Visual inspection of the reaction revealed solid at all phases during the reaction and, together with the DSC and kinetic data, suggested a well-behaved solid state substitution reaction. Foil wrapped reaction tubes, reactions in air and varying reactant ratios did not modify the kinetic results.

To further understand the reaction, it was decided to monitor the reaction under an optical microscope. Reactants were mixed together as previously and crystals

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of the mixture placed on a home built glass heating device, calibrated with crystals of known melting point. The device was placed in a dome that was flushed with inert gas, to ensure that the reactions were performed in an inert atmosphere.

To our surprise the reaction between $Mn(CO)_4$ -(PPh₃)Br and PPh₃ was found to commence at 39 °C, a temperature far below that of either of the melting/decomposition points of the reactants (78 °C, PPh₃; 131– 132 °C, $Mn(CO)_4(PPh_3)Br$). An optical microscopy study was then initiated to fully explore this finding and our further investigations revealed the following (see Fig. 1):

- (i) Reaction between Mn(CO)₄(PPh₃)Br and PPh₃ occurred at the interface where the two crystalline materials touched (Fig. 1(a)).
- (ii) At the interface the PPh₃ melted and reacted with 'solid' Mn(CO)₄(PPh₃)Br (Fig. 1(b)).
- (iii) Crystals of both reactants that did not touch, neither melted nor reacted at the reaction temperatures used, i.e., 35–65 °C (Fig. 1(b)).
- (iv) The reaction is thus occurring at about 40 °C below the mp of the reactants; a reaction not detected by DSC data.
- (v) As reaction progressed the consumption of PPh₃ led to crystallisation, giving the appearance of a solid-solid reaction (Fig. 1(c)).
- (vi) IR analysis of the material at the end of the reaction confirmed the formation of *trans*-Mn(CO)₃(PPh₃)₂Br.
- (vii) Reaction between $Mn(CO)_4(PPh_3)Br$ and $P(p-OMePh)_3$ (mp = 150 °C) was monitored by optical microscopy at 65 °C and indicated that the $Mn(CO)_4(PPh_3)Br$ melted and reacted with 'solid'

 $P(p-OMePh)_3$, again at the interface between the touching crystals. If the reactants did not touch, no melting or reaction occurred. The product $Mn(CO)_3(PPh_3)[P(p-OMePh)_3]Br$ was characterised by IR and NMR spectroscopy.

(viii) Thus, melting of either reactant will initiate the reaction.

The above results indicate that the reaction between $Mn(CO)_4(PPh_3)Br$ and PPh_3 , in the absence of solvent, provides substantive data on the mechanism of the 'solid-solid' CO substitution reaction.

When the reactants contact each other at room temperature, no reaction occurs. As the temperature is raised, reaction of interface molecules takes place. Normally, this reaction would proceed to completion. However, there is a complication – the product has a melting point higher than that of the staring materials. As it forms it crystallises from the melt and thus blocks further reaction. This is an important process as it can *limit the reaction even in a well mixed mixture.* Further. reactants that do not touch neither react nor melt and thus secondary processes are required to lead to their reaction. A secondary pathway is provided by reactant diffusion (e.g., PPh₃ has a high vapour pressure and readily sublimes) that permits further reaction. Indeed, we have observed a fall of rate but continued reaction with time towards the end of a reaction. Thus, the kinetics measured are reflective of kinetic reaction control in the melt. The measurement of the initial initiation rate will require techniques with more rapid timescales for analysis.

A remarkable feature of the study is the observation in the DSC of a melting point for reactants in the 1:1 reaction mixture. This finding partly relates to the



Fig. 1. Reaction between $Mn(CO)_4(PPh_3)Br$ and PPh_3 (1:1 ratio, 42 °C) as a function of reaction time: (a) $Mn(CO)_4(PPh_3)Br$ and PPh_3 are seen separately on the RHS of the picture and are seen to touch on the LHS; (b)–(d) reaction of the touching materials can be seen (see arrows), while the separated reactants show no reaction.

heating rate used (10 °C min⁻¹) but even with a 1:10 mixture, or a slower heating rate (1 °C min⁻¹), similar DSC traces are observed. Clearly, DSC data must in future be interpreted circumspectly.

The implications from the reaction are that the reaction is complex. Initial reaction at the reactant-reactant interface could involve a solid-solid reaction. This is then followed by a reaction in the melt and finally reaction will be influenced by reactant diffusion.

A preliminary optical microscopy study of the $CpM(CO)_3Me$ (M = Mo, W) and PPh_3 reaction [9] also indicates reactant *interface* melting prior to reaction to give $CpM(CO)_2(PPh_3)(COMe)$. This suggests that the reaction mechanism described above represents a general reaction type and may be applicable to many other 'solid-state' organometallic reactions [10]. Indeed, our data are consistent with the proposal [5,6] that many reactions previously reported to be solid-solid reactions actually occur in the melt, prior to product crystallisation.

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