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Deuterium labelling evidence for a hydride mechanism in the formation of methyl propanoate from carbon monoxide, ethene and methanol catalysed by a palladium complex

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Received 12th February 2002, Accepted 5th March 2002
First published as an Advance Article on the web 21st March 2002

Reaction of ethene with CO in CH_3OD in the presence of a catalyst prepared *in situ* from [Pd(DBPMB)(DBA)] (DBPMB = 1,2-bis[(di-*tert*-butyl)phosphinomethyl]benzene, DBA = dibenzylideneacetone) and methanesulfonic acid under conditions of good gas mixing gives a 1 : 1 mixture of $CH_2DCH_2CO_2Me$ and CH_3CHDCO_2Me with no H incorporated into the CH_3OD. If the gas mixing is less efficient, the methyl propanoate has 0–5 D atoms incorporated in the ethyl group, CH_3OD exchanges to give increasing amounts of CH_3OH throughout the reaction and there is a slight increase in the less deuteriated products with reaction time. Significant D incorporation into unreacted ethene is also observed. These results are interpreted in terms of a hydride mechanism with the rates of the individual steps under conditions of good mixing being: reversible H migration to coordinated ethene > CO coordination ≫ C_2H_4 exchange > H/D exchange.

Introduction

The carbonylation of ethene in methanol using palladium based catalysts can lead to polyketones and/or to methyl propanoate (MeP) depending on the choice of phosphine ligand. Originally it was suggested that monodentate ligands gave catalysts selective to MeP, whereas bidentate ligands produced catalysts selective to copolymers.[1] However, more recently it has been demonstrated that this simple relationship does not hold[2] and indeed some of us have shown that complexes derived from palladium precursors and 1,2-bis[(di-*tert*-butyl)phosphinomethyl]benzene (DBPMB) are the most active and selective catalysts for the formation of MeP.[3]

Two possible mechanisms have been proposed. The "carbomethoxy" mechanism involves initial formation of a methoxycarbonyl complex either by migratory insertion of CO into a Pd–OMe bond or by nucleophilic attack of methanol on coordinated CO, followed by coordination and insertion of ethene and methanolysis (Fig. 1). This mechanism has been shown to be plausible for the stoichiometric formation of methyl propanoate in the presence of [Pd(1,3-bis(diphenylphosphino)propane)] complexes. Catalytically the products are poly and oligo ketones, which can also be formed by a carbomethoxy mechanism.[4] It is believed that the carbomethoxy mechanism operates for propyne carbonylation to methyl methacrylate catalysed by Pd complexes of PPh_2py,[5] as well as in copolymeristion of CO and ethene.[1] Some of us have recently shown that it can also operate in the formation of methyl propanoate and methyl propenoate from CO, ethene and methanol catalysed by rhodium complexes containing electron donating β-ketophosphine and related ligands.[6]

The alternative "hydride" mechanism starts with a metal hydride formed by protonation of the palladium centre (a proton source is often, although not always, required for activity). Sequential coordination and insertion of ethene and CO leads to an acyl complex from which methyl propanoate is released by nucleophilic attack of methanol (Fig. 2). The

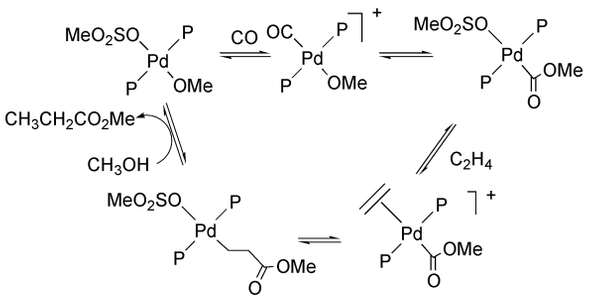

Fig. 1 Carbomethoxy mechanism for the preparation of methyl propanoate from ethene and CO using palladium complexes of unidentate phosphines (*e.g.* P = PPh_3) in methanol in the presence of methanesulfonic acid.[1]

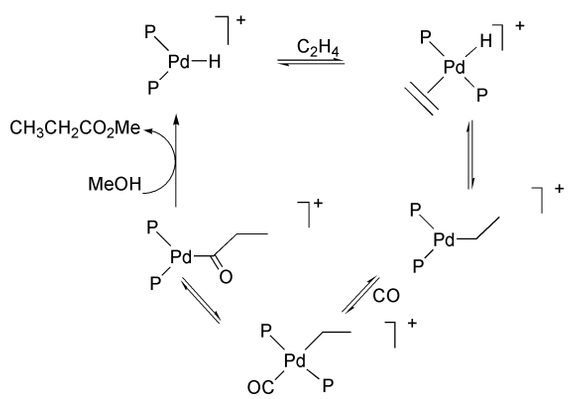

Fig. 2 Hydride mechanism for the preparation of methyl propanoate from ethene and CO using palladium complexes of unidentate phosphines (*e.g.* P = PPh_3) in methanol in the presence of methanesulfonic acid.[1] The vacant sites may be stabilised by coordination of $MeSO_3^-$ or solvent.

hydride mechanism has been shown to operate in copolymerisation of CO and ethene,[1] as well as in the methoxycarbonylation of ethene catalysed by Pd/PPh_3 complexes[7] or in the synthesis of 3-pentanone catalysed by rhodium complexes of triethylphosphine.[8]

Given the extremely high activity and unexpected selectivity for the production of methyl propanoate (MeP) when complexes derived from palladium precursors and DBPMB are activated with acids such as methanesulfonic acid, we were interested in which mechanism might be operating in this case. We, therefore, carried out the reaction in CH_3OD to investigate whether the labelling pattern of the product would give any information. Labelling studies have been used successfully to derive mechanisms for the formation of oligoketones and small amounts of methyl propanoate form CO and ethene,[4] as well as for the formation of 3-pentanone from hydrocarbonylation of ethene[9] or from reaction of ethene with CO and methanol, where the methanol is the source of the extra H atoms.[6,8] A multinuclear NMR study, in which all the possible intermediates were identified, strongly suggests that a hydride mechanism operates for the methoxycarbonylation catalysed by Pd/DBPMB complexes.[10]

Experimental

GCMS data were collected on a Hewlett-Packard HP 6890 gas chromatograph with an HP 5973 mass selective detector. $^{13}C\{^1H\}$ and $^{13}C\{^1H, ^2H\}$ spectra were recorded on a Varian 500 MHz spectrometer operating in the Fourier transform mode. Quantitative analysis of the labelling pattern in the mixtures of $CH_2DCH_2CO_2Me$ and CH_3CHDCO_2Me obtained from reactor A, below, was carried out by integration of a $^{13}C\{^1H\}$ NMR spectrum accumulated with a 10 s pulse delay. Quantitative analysis of the labelled products from reactors B and C was carried out using the parent ion peak in the GCMS since for pure methyl propanoate this consists of a single peak at *m/e* 88. This is flanked by two small peaks at *m/e* 87 and 89 with intensities *ca.* 10% and 4% of that of the major peak. These were ignored in the analysis for the products from reactor B but not from reactor C. The identity of the isotopomers was confirmed by $^{13}C\{^1H, ^2H\}$ NMR spectroscopy.[11]

Mixtures of partially deuteriated ethenes were analysed by GCMS. The spectrum of each isotopomer was calculated based on that of ethene and making the assumptions (i) that loss of H or D from the parent ion or fragment depends only on the number of H or D atoms present, *i.e.* that there is no isotope effect on fragmentation; (ii) that $[M - 2]^+$ in ethene is $[HCCH]^+$ not $[H_2CC]^+$ and (iii) that *Z*- and *E*-CHDCHD give identical fragmentation patterns. The peak at 32 amu arises only from C_2D_4 and that at 31 amu only from C_2D_3H so they were used to calculate the relative amounts of these two isotopomers and their contribution to the peak at 30 amu, which was subtracted from the total, leaving a peak corresponding to all isomers of $C_2D_2H_2$. The relative contributions to the peak at 29 amu from all isotopomers with > 1 D atom were subtracted leaving a peak corresponding to C_2DH_3. In principle a similar process can be repeated to obtain the contribution of the peak at 28 amu from C_2H_4. In practice this is difficult since the loss of 2 H/D atoms from CH_2CD_2 leads only to $[CHCD]^+$, whilst from CHDCHD, $[C_2H_2]^+$, $[C_2HD]^+$ and $[C_2D_2]^+$ are expected in a 1 : 2 : 1 ratio. Since the relative amounts of these isomers are not known, there is ambiguity about the contribution of these to the peak at 28 amu. In practice, we used a simulation program, written in-house, in which the height of each mass spectral peak was calculated knowing the mass spectra of the individual isotopomers and their relative abundance. The amounts for C_2D_4, C_2D_3H and C_2DH_3, calculated as described above were put in and variations were then made in the amounts of the other three isotopomers until the best fit was achieved, always ensuring that the sum of CH_2CD_2 and CHDCHD was what had been calculated as above. An example of the comparison between the measured and simulated spectra is shown in Fig. 3.

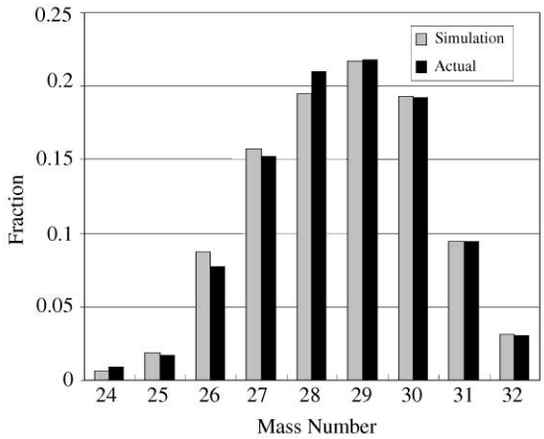

Fig. 3 Experimental (black) and simulated (grey) mass spectra of the mixture of isotopomers of dissolved ethene after 15 min in a reaction carried out in reactor C, stirring at 100 rpm. The values used for the simulation are in the Experimental section. (Note the analysis was carried out several days after the reaction and the D incorporation largely arises from post reaction exchange).

Catalytic experiments

Reactor A. A catalyst solution consisting of CH_3OD (120 cm^3), [Pd(DBPMB)(DBA)] (DBA = dibenzylideneacetone) (30 mg, 4.08×10^{-5} mol) and $MeSO_3H$ (53 μL, 8.2×10^{-4} mol) was prepared under argon and sucked into a stainless steel autoclave (volume 300 cm^3), which had previously been evacuated, fitted with a paddle stirrer. The solution was heated to 80 °C and then the stirrer started (1000 rpm). The autoclave was opened to a supply of ethene/CO (1 : 1) at 10 bar ($t = 0$) and the pressure maintained at 10 bar as the reaction proceeded by feeding the same gas mixture from a supply vessel through a constant pressure valve. Samples were taken through a liquid sampler after 5, 10, 15, 30, 45, 60, 90 and 120 min by removing 5 cm^3 to flush the sampling pipe (for all samples except the first), followed by 5 cm^3 for analysis. The samples for analysis were stored in screw top glass vials in which diffusion of gas between the headspace and the atmosphere could occur. These were analysed by GCMS and all contained only d^1-methyl propanoate. The mass spectrum of the methanol was also measured and shown to be the same in all samples. (The analysis suggests that significant amounts (35%) of MeOH are present, but we have shown that this arises from post reaction exchange). The products were further analysed by $^{13}C\{^1H\}$ and $^{13}C\{^1H, ^2H\}$ NMR[11] spectroscopy and shown to contain both $CH_2DCH_2CO_2Me$ and CH_3CHDCO_2Me.

Reactor B. A glass Buchi designed autoclave, fitted with a magnetic stirrer, was charged *via* syringe with a deep red–orange catalyst solution consisting of CH_3OD (*ca.* 30 cm^3, see Table 1), [Pd(DBPMB)(DBA)] (100 mg, 1.36×10^{-4} mol) and $MeSO_3H$ (44 μL, 6.8×10^{-4} mol). The reaction was then initiated as described above except at 90 °C. After the desired reaction time (Table 1), the reactor was sealed and cooled in a cold water bath. The excess pressure was released, the contents of the autoclave poured into a sample bottle, and the mass of the product solution measured to give the weight gain and hence the yield of methyl propanoate. As with the samples taken from reactor A there was no barrier to exchange between the sample bottle headspace and the atmosphere in this system. The reaction products, pale yellow–green solutions, were analysed as described above and the results are collected in Table 1. GCMS analysis of the methanol showed

Table 1 Results from the carbonylation of ethene in CH_3OD catalysed by [Pd(DBPMB)(DBA)] in the presence of $MeSO_3H$ with slow stirring in reactor B[a]

			Labelling pattern for MeP[d]					
Time/min	MeOD[b]/g	Yield of MeP[c]/mol	d^0	d^1	d^2	d^3	d^4	d^5
5	26.42	0.046	27	37	24	10	2.5	0.4
10	25.63	0.091	29	40	22	8	2	—
15	26.32	0.10	32	42	20	6	1	—
30	26.78	0.19	26	37	25	10	3	—
45	29.92	0.34	30	37	23	9	2	—
60	28.12	0.31	29	37	23	9	2	—

[a] [Pd(DBPMB)(DBA)] (1.36×10^{-4} mol), CH_3SO_3H (6.8×10^{-4} mol), reactor B, 90 °C, $p_{CO} = p_{ethene} = 5$ bar. [b] Charged to reactor. [c] From weight gain during reaction. [d] In the ethyl group.

Table 2 Results from the carbonylation of ethene in CH_3OD catalysed by [Pd(DBPMB)(DBA)] in the presence of $MeSO_3H$ with slow stirring in reactor C[a]

		Labelling pattern for MeP[c]			
Time/min	Yield of MeP[b]/mol	d^0	d^1	d^2	d^3
5	0.024	41	54	5	0
10	0.060	40	54	6	0
15	0.085	39	54	6	1
30	0.26	37	53	9	1
45	0.39	33	54	11	2
60	0.53	30	55	13	2
90	0.75	25	59	13	3
120	0.82	23	61	14	2

[a] [Pd(DBPMB)(DBA)] (6.13×10^{-5} mol), CH_3SO_3H (1.23×10^{-4} mol), reactor C, 100 rpm, 90 °C, $p_{CO} = p_{ethene} = 5.75$ bar. [b] From gas uptake during reaction. [c] In the ethyl group.

that significant amounts of H were incorporated during the reaction.†

Reactor C. A stainless steel autoclave (volume = 2 dm^3) was set up as for reactor A and charged with CH_3OD (300 cm^3, < 5% CH_3OH by GCMS and ^1H NMR) containing [Pd(DBPMB)(DBA)] (45 mg, 6.13×10^{-5} mol) and $MeSO_3H$ (80 μL, 1.23×10^{-3} mol). It was heated to 80 °C and CO/ethene (1 : 1) was added to give a total pressure of 11.5 bar. The paddle stirrer was started (100 rpm), and CO/ethene (1 : 1) fed constantly to maintain the pressure. Liquid samples were taken after 5, 10, 15, 30, 45, 60, 90 and 120 min, as described for reactor A, but were used to fill vials completely. These vials were immediately sealed with air-tight caps, through which GC samples could be withdrawn. This process ensured that post reaction exchange of the methanol with moisture in the air did not occur. This was confirmed by the isotopic analysis of the methanol, which showed no change from that originally charged. After the sample at 15 min, the stirrer was stopped and the headspace gas sampled. The reactor was repressurised and the stirrer restarted. The products were analysed by GCMS and the results are collected in Table 2. The ethene in the gas sample taken from the headspace after 15 min consisted of C_2H_4 (93%), C_2H_3D (6%) and $C_2H_2D_2$ (1%). ‡

A second experiment was carried out under identical conditions except that the stirrer was driven at 1000 rpm for the first 15 min. After the headspace had been analysed, the stirrer was left stopped for 30 min. It was then restarted at 1000 rpm. Samples were taken at the same times as above, but additionally at 150 and 180 min. The composition of the methanol was unchanged during this reaction and the ethene from the headspace was undeuteriated. The methyl propanoate was d^0 14%, d^1 82% and d^2 3.5% throughout the reaction.

Reaction between methyl propanoate and MeOD

The complex, [Pd(DBPMB)(DBA)] (60 mg, 8.2×10^{-5} mol), was added to a 250 cm^3 round bottomed flask in an argon filled glovebox. The flask was removed and degassed CH_3OD (30 cm^3) added followed by methyl propanoate (25 cm^3). The stirred solution was treated with methanesulfonic acid (26.5 μL, 4.1×10^{-4} mol) to from a deep red–orange solution, which was quickly added to a previously degassed autoclave by syringe and pressurised to 6 bar with N_2. The autoclave was closed and heated to 90 °C with stirring for 1 h. The autoclave was cooled, vented and the contents (yellow solution) poured into a sample bottle before samples were transferred into sealed vials of the type used for the products from reactions in reactor C.

GCMS analysis of samples taken before and after heating showed that the methyl propanoate was completely undeuteriated.

Results and discussion

The carbonylation of ethene in MeOD using a catalyst prepared *in situ* from [Pd(DBPMB)(DBA)] and methanesulfonic acid was carried out under four different sets of conditions. In the semi-technical reactor (A), the design ensures excellent mixing of the gases with the liquid, low catalyst concentrations were employed and the temperature was 80 °C. In the laboratory scale reactor (B) the mixing is less efficient, higher catalyst concentrations were used and the reactions were carried out at 90 °C. The main difference is that mass transport across the liquid–gas interface is rate limiting in reactor B (*i.e.* there is CO starvation) but not in reactor A. Reactor C is similar to A, but has a higher volume and the efficiency of mixing was controlled by altering the stirrer speed.

Analysis of the products obtained from reactions carried out in reactor A by mass spectrometry, showed that all of the methyl propanoate was monodeuteriated and that this remained the case throughout the reaction. In addition, the mass spectrum of the methanol did not change during the course of the reaction. Analysing the products by $^{13}C\{^1H\}$ and $^{13}C\{^1H, ^2H\}$ NMR,[11] however, showed that the methyl propan-

† The composition of the solution after 5 min reaction is very similar to that obtained throughout the reaction in reactor A (*i.e.* 35% MeOH, 65% MeOD), again presumably because of post reaction exchange. After the end of the reaction it is 65% MeOH, 35% MeOD. Because of the problems of exchange with atmospheric moisture, we have not used these data, as better data were obtained by rigorous exclusion of air (reactor C).

‡ It is possible to analyse the small amount of dissolved ethene present in each liquid sample. All the samples are similar and this ethene is extensively deuteriated (up to 4 D atoms). A typical example is shown in Fig. 3 (from the sample taken after 15 min). The simulation in this case contained C_2H_4 (8%), C_2H_3D (28%), CHDCHD (33%), CH_2CD_2 (3%), C_2HD_3 (21%) and C_2D_4 (7%). This extensive deuteriation arises from post reaction exchange catalysed by the Pd complex. (Note: the solution phase analyses were carried out many days after the reactions).

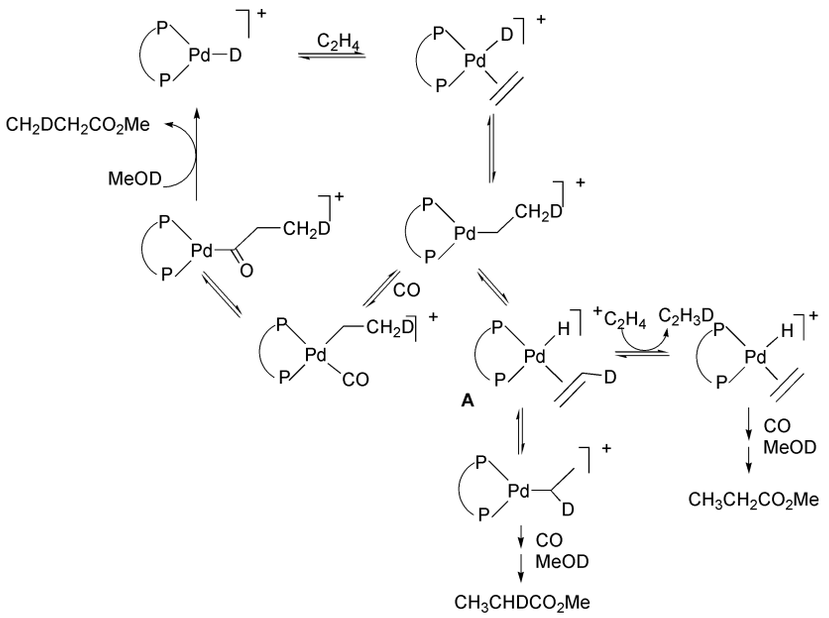

Fig. 4 Proposed hydride mechanism for the formation of d^{0-5}-methyl propanoate from CO, C_2H_4 and CH_3OD catalysed by [Pd(DBPMB)(DBA)] in the presence of $MeSO_3H$ under conditions of CO starvation. Multiply labelled products would arise from Pd–H exchange with MeOD in intermediate **A**. The vacant sites may be stabilised by coordination of $MeSO_3^-$ or solvent. P^P = DBPMB.

oate was present as the two different isotopomers, $CH_2DCH_2CO_2Me$ and CH_3CHDCO_2Me in approximately equal proportions. There were also low levels of $C_2H_5CO_2Me$ (<10%) and $CH_2DCHDCO_2Me$ (<4%). In a separate experiment, it was shown that no exchange of D into methyl propanoate occurs if it is heated in MeOD in the presence of the catalyst at 90 °C for 1 h. Very similar results were obtained for the reaction carried out in reactor C with rapid stirring, although there was slightly more d^0-methyl propanoate§ and it was further shown that the ethene in the gas phase of reactor C after 15 min reaction was completely undeuteriated.

The formation of $CH_2DCH_2CO_2Me$ and CH_3CHDCO_2Me in the catalytic reaction can be explained if a hydride mechanism operates with rapid reversible migration of the hydride to the coordinated ethene molecule and coordination of carbon monoxide occurring at a much higher rate than exchange of Pd–H with MeOD (Fig. 4). It also suggests that coordination of ethene is essentially irreversible since, if it were reversible, significant amounts of $C_2H_5CO_2Me$ would be formed from loss of C_2H_3D from intermediate **A** in Fig. 4, followed by coordination of C_2H_4 to the Pd–H intermediate. Reversible C_2H_4 coordination would also lead to a build-up of C_2H_3D in the gas phase and hence the formation of d^2-methyl propanoate, neither of which is observed.

It is also possible to explain the formation of $CH_2DCH_2CO_2Me$ and $CH_3CH_2DCO_2Me$ using the carbomethoxy mechanism as shown in Fig. 5. It requires that after migratory insertion of the ethene molecule into the Pd–CO_2Me bond there is a reversible β-H abstraction in intermediate **B** to give **C**, in which H migration can occur to either end of the double bond. Methanolysis by MeOD would then lead to the two products observed. Once again, the termination reaction would have to be rapid relative to Pd–H/CH_3OD exchange or multiply deuteriated products would be produced. If the β-H abstraction/insertion process were very rapid compared with methanolysis, and unselective with regard to Markownikoff *vs.* anti-Markownikoff addition, a 1 : 1 ratio of the two d^1 isotopomers would be possible.

§ This undeuteriated methyl propanoate probably arises from the CH_3OH present in the CH_3OD (*ca.* 3%). The higher amount than 3% may be because of an isotope effect favouring H incorporation over D. It may also be that the mixing is not perfect, but if this were the case, D incorporation into the ethene would be expected. This is not observed.

Using reactor B or C under conditions of slow stirring (poor gas transport), rather different results were obtained. In reactor B, the methyl propanoate formed contained 0–5 deuterium atoms, with the proportion of the deuteriated isotopomers remaining almost the same as the reaction proceeded (Table 1). In the reaction carried out in reactor C with slow stirring, a high proportion of d^0 and d^1 together with a smaller amount of d^2-methyl propanoate were formed in the early stages of the reaction with more extensive deuteriation occurring later on (Table 2). Overall, D incorporation was less extensive in the reaction carried out in reactor C than in the one carried out in reactor B. The important observation from the experiment in reactor C with slow stirring was that after 15 min, the ethene in the gas phase contained, in addition to C_2H_4, significant amounts of C_2H_3D (6%) and $C_2H_2D_2$ (1%). (The ethene remaining in solution was much more extensively deuteriated (Fig. 3), presumably because of post reaction exchange, confirming that the catalyst is active for H/D exchange between C_2H_4 and CH_3OD). Given that the autoclave, which contains 300 cm^3 of liquid, has a volume of 2 dm^3 it is possble to calculate that the head space contains 0.35 mol of ethene (1700 cm^3, 5.75 bar, 80 °C). For each molecule of d^0-MeP produced, one molecule of C_2H_3D is released into the gas phase, if the mechanism shown in Fig. 4 is correct. This amounts to 0.033 (39% of 0.085) mol after 15 mins, when the gas phase was analysed. Some of this (0.005 mol) may have been reabsorbed to give the d^2-MeP. Others may be further reacted to give the observed $C_2H_2D_2$, so one might expect to see 7–8% of C_2H_3D in the gas phase. This is slightly higher than the 6% observed, but the assumptions made do not allow us to determine whether this difference is significant.

The carbomethoxy mechanism of Fig. 5 would be able to explain the multiple deuteriation observed in reactor B and slight increase in less deuteriated products as the reaction progresses, if Pd–H/CH_3OD exchange in intermediate **C** becomes rapid with respect to methanolysis, although there is no obvious reason why the reaction rates of these reactions should be affected by gas mixing. It would also be consistent with the formation of C_2H_3D in reactor C if, after H/D exchange in intermediate **C**, the equilibria back to **E** were reversed and exchange of C_2H_3D in **E** occurred for free C_2H_4. The carbomethoxy mechanism cannot, however, explain the formation of large amounts of d^0-methyl propanoate at low reaction times since the termination step must always transfer a

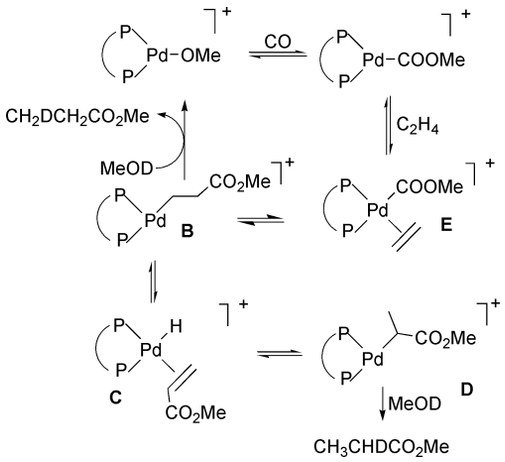

Fig. 5 Carbomethoxy mechanism for the formation of $CH_2DCH_2CO_2Me$ and CH_3CHDCO_2Me from CO, C_2H_4 and CH_3OD catalysed by [Pd(DBPMB)(DBA)] in the presence of $MeSO_3H$ under conditions of good gas mixing. Multiply labelled products, which are obtained under conditions of CO starvation, would arise from reversible exchange between intermediates **B**, **C**, and **D**, with exchange of Pd–H in **C** with MeOD. Note: there is no way of forming d^0-methyl propanoate without significant incorporation of H into the methanol. The vacant sites may be stabilised by coordination of $MeSO_3^-$ or solvent. P^P = DBPMB.

D atom from the CH_3OD to end up on one of the ethyl carbon atoms of the methyl propanoate.

The hydride mechanism of Fig. 4 does, however, allow an explanation of all the data. (We cannot distinguish between the mechanism shown and one in which coordination of ethene precedes protonation. However, other studies have confirmed the order shown in the scheme, although not under catalytic conditions).[10] The rather high percentage of d^0-methyl propanoate formed at the start of the reaction, when the methanol has undergone little exchange and hence cannot provide significant amounts of H to the metal, suggests that under these conditions of lower CO availability, the rate of ethene exchange between intermediate **A** and the gas phase becomes competitive with that of CO coordination. This exchange must, however, be slow compared with the reversible migration of H onto ethene. The formation of multiply deuteriated methyl propanoate in reactor B shows that, when mixing is very poor, H/D exchange between intermediate **A** and the solvent also becomes competitive.

The fact that 87–93% of the products ($\Sigma d^0 + d^1 + d^2$) from the reactions in reactor B and all the products from reactor C with slow stirring can be explained as arising from reactions in which Pd–H/MeOD exchange does not occur suggests that the rates of the various possible reactions of intermediate **A** in this system where CO mass transport is limiting are in the order: H migration > ethene loss > H/D exchange > CO coordination. When CO transport is not rate limiting, under the conditions of reactor A, the order becomes H migration > CO coordination ⩾ ethene loss > H/D exchange. In either case, the rate determining step occurs after the formation of the ethyl group.

Conclusion

We conclude that the formation of methyl propanoate from CO, C_2H_4 and methanol in the presence of a catalyst derived from [Pd(DBPMB)(DBA)] and methanesulfonic acid occurs by a hydride mechanism in which the rate determining step is after the formation of the ethyl complex. The carbomethoxy mechanism cannot be operating in this system.

Acknowledgements

We thank Peter Pogorzelec for technical assistance and the Scottish Higher Education Funding Council for funding the Catalyst Evaluation and Optimisation Service (CATS).

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