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COMMUNICATION

Teflon AF-2400 mediated gas–liquid contact in continuous flow methoxycarbonylations and in-line FTIR measurement of CO concentration†

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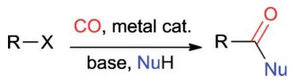
We report on the development of a continuous flow process for the palladium catalysed methoxycarbonylation of aryl, heteroaromatic and vinyl iodides and an aryl bromide using a Teflon AF-2400 based Tube-in-Tube reactor to mediate the selective permeation of carbon monoxide into solution at elevated pressures. The low volume of pressurised gas within the reactor (5.6 mL) offers the potential for an enhanced safety profile compared to batch processes. We also present preliminary results for the use of *in situ* FTIR to measure solution concentrations of carbon monoxide and demonstrate the use of a second reactor to effect the removal of carbon monoxide from the flow stream.

The carbonyl group is integral to many of the key bond forming reactions of organic synthesis.[1] Its success is dependent upon the availability of methods to access carbonyl substrates, of which the transition metal-mediated insertion of carbon monoxide (CO) is one of the most efficient (Scheme 1).[2]



Scheme 1 General transition metal-catalysed carbonyl insertion reaction.

This atom-economical process combines the ready availability of CO, the ability to drive reactions to completion through pressurisation, and ease of workup (as the excess reagent is a gas), making this transformation particularly attractive to synthesis chemists. However, there still exists a general reluctance to use CO gas in research laboratories, and there are good reasons for this. The concerns relate to the pressurised containment, toxicity and flammable nature of this reactive gas input. As such the safe and scalable use of CO and other gases within laboratory synthesis programmes represents an unmet need. Flow chemistry (in which the substrates/reagents are continuously pumped through a relatively low volume reaction zone so that only a very small fraction of the total is exposed to the reaction conditions at any one time) has emerged as a new paradigm of chemical synthesis which offers several advantages to batch chemistry. This is particularly true for reactions involving hazardous/unstable intermediates and reagents and/or extreme reaction conditions (*e.g.* high temperature or pressure).[3] This being the case, flow chemical methods should overcome some of the obstacles to the broader application of CO-mediated carbonylation as a useful synthetic transformation. The majority of recent developments in gas–liquid phase contact under flow conditions involve 'segmented flow',[4] in which the gas and the liquid are in two separate phases. The reaction rate, which is partly determined by the concentration of dissolved gas, is therefore dependent on the morphology of the biphasic system (segment size, interfacial area *etc.*). Control and prediction of this morphology (which depends on factors including solvent/gas pressure and flow rate, geometry of the mixing junction *etc.*) is by no means trivial and many of the existing methods aimed at increasing the mixing of gas and liquid phases, although involving some interesting engineering developments,[5] are often technically quite complex and require fabrication techniques which are beyond the means of most synthesis laboratories. Seeking a simpler, more accessible and more controllable means of achieving gas–liquid contact, we conceived the use of gas-permeable polymer membranes in flow synthesis. We have previously reported on the use of the amorphous fluoropolymer Teflon AF-2400[6] as a particularly effective method of delivering ozone (in oxygen),[7] carbon dioxide[8] or hydrogen[9]

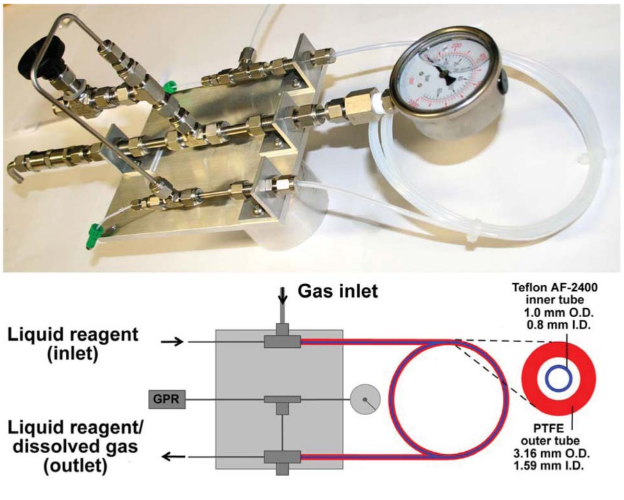


Fig. 1 The concentric tubular (Tube-in-Tube) gas-liquid reactor.

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to a continuous (liquid) flow stream in a controlled and efficient manner.

Here, we report our initial findings on the use of a gas–liquid flow reactor employing Teflon AF-2400 in a concentric tubular design for palladium catalysed methoxycarbonylation reactions and we also discuss preliminary results from the use of an in-line FTIR flow-cell to measure concentrations of CO in the solutions so generated. In this reactor (Fig. 1),[10] the liquid stream is directed through the inner Teflon AF-2400 membrane tubing and CO gas fills the outer tubing (standard PTFE). **CAUTION**!!: *This reactor is a prototype and not fully tested for safety! All reactions involving pressurised gas should be carried out in an efficient fumehood with adequate safety systems in place capable of handling an unexpected rupture and/or ignition. Carbon monoxide is highly toxic. This is made worse by the odourless and tasteless nature of the gas. Excess carbon monoxide released was directed into the exhaust of the fumehood. Carbon monoxide monitoring equipment was used inside and outside the fumehood at all times*! The Teflon AF-2400 (3.8 m, 1.91 mL) and the outer PTFE tubing are separated by stainless steel T-pieces, allowing the liquid and gas stream to be independently introduced into the reactor with accurate control of flow rate and pressure for each input. This maximises membrane surface area, ensuring efficient permeation of CO and, as the volume of gas occupying the reactor at any given instance does not exceed 4.56 mL (1.2 mL of gas per meter of tubing, which can be tailored by simply modifying the length of tubing), the hazards, risks and precautionary measures associated with the use of traditional high-pressure batch equipment are largely circumvented. The study was initiated by evaluating the methoxycarbonylation of *m*-iodotoluene (**1a**) using the flow arrangement shown in Fig. 2. Vapourtec R2/R4 units were used in conjunction with a Knauer 100 pump but any other commercially available flow synthesis platform could also be used. Substrate (**1a**) and triethylamine were premixed and loaded into a PEEK sample loop, a second loop was filled with the palladium acetate and the ligand xantphos.

The reagent streams were pumped at a rate of 0.1 mL min^{-1} and united at a T-piece, then combined with a third CO-enriched stream from the gas–liquid reactor. This is an alternative configuration to those described in our earlier work with these reactors, as the substrate/catalyst does not pass through the Tube-in-Tube device which now acts purely as a means to inject gas into the flow stream. A 100-psi (6.9 bar) back-pressure regulator was installed after the gas–liquid reactor to prevent out-gassing of the dissolved CO. The presence of this back-pressure regulator is vital to ensure that the gas–liquid stream remains a homogeneous solution, thus avoiding segmented flow. The combined flow streams were then directed into the heating coils and a QP-TU (polymer supported thiourea) cartridge was incorporated to scavenge the palladium from the product stream. Shown in Table 1 are the conversions obtained in several experiments where conditions were varied according to flow rates, CO pressure, and heating coil length and temperature. The initial conditions (entry 1) gave only a low 18% conversion. Increasing the ratio of CO enriched solvent stream led to a dramatic increase to 73% conversion (entry 2). Increasing the total volume (and therefore residence time) of the heating coils increased the conversion to 86%. It was found that decreasing the amount of the relatively expensive xantphos ligand (to just over stoichiometric with respect to the Pd) gave the same conversion (entry 4). Increasing the CO pressure to 10 bar led to a slightly increased conversion of 90% (entry 6). Lowering the temperature gave a corresponding reduction in conversion (entry 5).

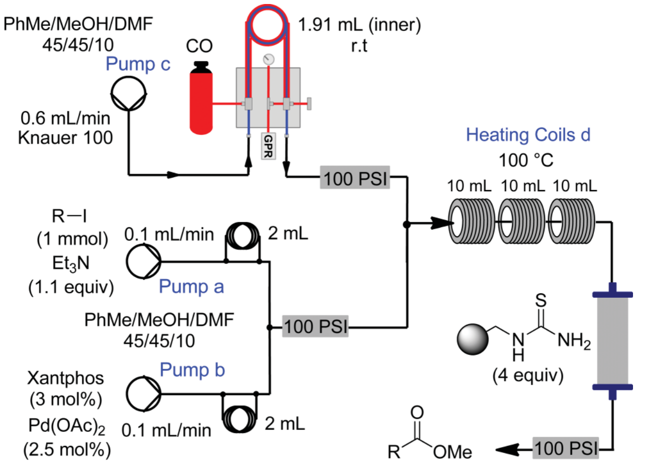


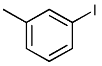
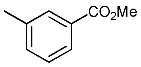
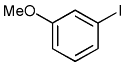
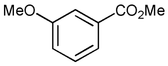
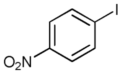
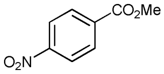
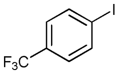
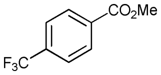
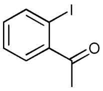
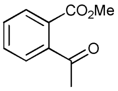
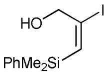
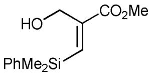
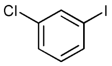
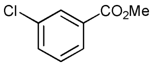
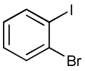
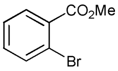
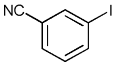
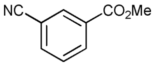
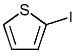
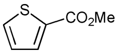
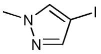
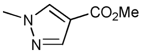
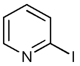
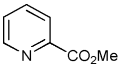
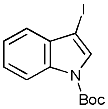
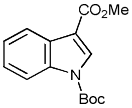
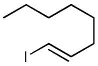
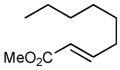
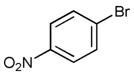
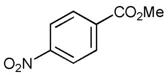
Fig. 2 A schematic of the optimised gas-flow reactor configuration involving a third solvent stream.

Using the conditions from Table 1, entry 4, we then evaluated the scope of the process. As the fact that the swaged joints between the PTFE outer tubing and stainless steel connectors in the Tube-in-Tube reactor/injector are non-standard (normally joints are made between like materials) we decided, due to the high toxicity and odourless nature of CO, to carry out preparative reactions initially at 7 bar. For some later reactions, when we were now confident that the interconnects were robust, we used pressures of up to 15 bar where required but with the added precaution that the main gas cylinder was used only periodically to charge an intermediate 'reservoir' section of high-pressure hose tubing, the volume of which was sufficient to maintain constant pressure for several hours. These manifolds have now been used with other gases at pressures of up to 35 bar without incident. The results of the methoxycarbonylation reactions of a series of aryl/alkenyl iodides and an aryl bromide are shown in Table 2. Electron-deficient aryl iodides **3a**, **4a**, **7a** and **9a** afforded the corresponding

Table 1 Results for investigation of reaction conditions for the conversion of **1a** to **1b**

Entry	Pd(II)/L mol (%)	CO (bar)	Pump a = b (mL min^{-1})	Pump c (mL min^{-1})	Coils d total (mL)	Coils d (°C)	Conv. %
1	2.5/5	7	0.1	0.1	20	100	18
2	2.5/5	7	0.1	0.6	20	100	73
3	2.5/5	7	0.1	0.6	30	100	86
4	2.5/3.0	7	0.1	0.6	30	100	86
5	2.5/3.0	7	0.1	0.6	30	70	80
6	2.5/3.0	10	0.1	0.6	30	100	90

Table 2 Results of continuous flow methoxycarbonylations

Entry	Substrate (a)	Product (b)	Solvent[a]	Yld[b]/(Conv.[c])
1			A	70/(85)
2			A	63/(78)
3			A	81/(95)[d]
4			A	88/(95)
5			A	(11)[e]
6			A B	38/(95)[f] 83/(100)[g,h]
7			A	93/(95)
8			B	69/(77)[h,i,j]
9			A	72/(90)
10			A	71/(85)
11			A B	43/(60)[e] 65/(73)[h,j]
12			B	62/(88)[h,j]
13			B	62/(100)[j]
14			B	81/(100)[i,k]
15			B	72/(94)[h,i,j,l] 77/(90)[h,i,j]

[a] A = PhMe : MeOH : DMF 45 : 45 : 10, B = dioxane : MeOH 1 : 1. [b] isolated yield after column chromatography on silica gel. [c] conversion based on signals from product and starting material in ^{1}H NMR spectrum of crude product material (no reference compound was added). [d] Substrate and base were introduced in DMF. [e] Rapid Pd(0) precipitation observed. [f] Reaction performed at 50 °C, side products observed. [g] Reaction performed at 25 °C, 15 bar CO, no xantphos, 5 mol% Pd(OAc)$_2$. [h] No thiourea cartridge used. [i] 5 mol% Pd(OAc)$_2$/6 mol% xantphos used. [j] 15 bar CO used and 30 mol% hydrazine (from 1.0 M THF solution) added. [k] reaction performed at 25 °C, 15 bar CO. [l] reaction performed at 120 °C.

methyl esters with high conversions and high isolated yields, while yields and conversions for electron-rich aromatic iodides **1a** and **2a** were more moderate. The *ortho*-keto substrate **5a** resulted in low conversion, perhaps due to catalyst deactivation, evidenced by significant visible Pd black formation. With the exception of the reactive vinyl iodide **6a**, all of the methoxycarbonylations proceeded cleanly without the formation of unwanted by-products and within short reaction times (37 min in heating coils).

While the thiophene **9a** reacted cleanly under these conditions, affording the product in good conversion and yield, the pyrazole **11a** gave only modest conversion and low yield.

After a brief screen of solvents and additives, we found that using a 1 : 1 mixture of dioxane : methanol with the addition of 30 mol% hydrazine (1.0 M THF solution)[11] at an increased CO pressure of 15 bar led to an improvement in the yield of **11b** (65%). We used these conditions for the reaction of two further nitrogenous heterocycles, **12a** and **13a**, which both afforded products in 62% yield. We found that with **12a** the use of the polymer supported thiourea cartridge led to poor recovery, perhaps due to the resin binding to the product, and for this reaction this was removed. Interestingly, we found that the sensitive vinyl silane product **6a** was unstable to both the thiourea resin and the presence of the xantphos ligand during the reaction and, when these were removed and the reaction carried out at 15 bar CO pressure at room temperature, a much improved 83% yield of the product was isolated. The *E*-vinyl iodide **14a** also reacted more smoothly at room temperature with quantitative conversion to the product **14b** which was recovered in high yield.

We have also begun to investigate the alkoxycarbonylation of the less active but potentially more useful aryl bromides. Focussing on 4-nitro-bromobenzene, we found that using the dioxane–MeOH system with 30 mol% hydrazine and twice the catalytic loading gave a 77% isolated yield of product (90% conversion). A higher conversion could be obtained with a higher reaction temperature (120 °C) but only at the expense of yield, presumably due to side reactions (entry 15). The 2-bromo-iodobenzene **8a** reacted cleanly and selectively at the iodo position only. Further investigation with aryl and heteroaryl bromides in our laboratory is ongoing.

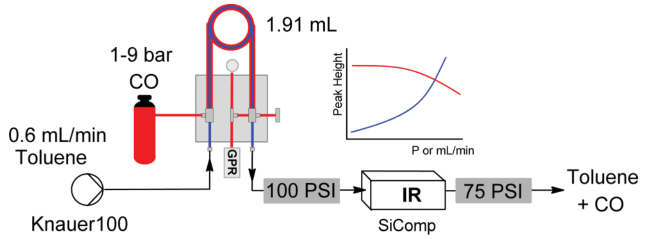


Fig. 3 Flow configuration for in-line real-time FTIR CO monitoring.

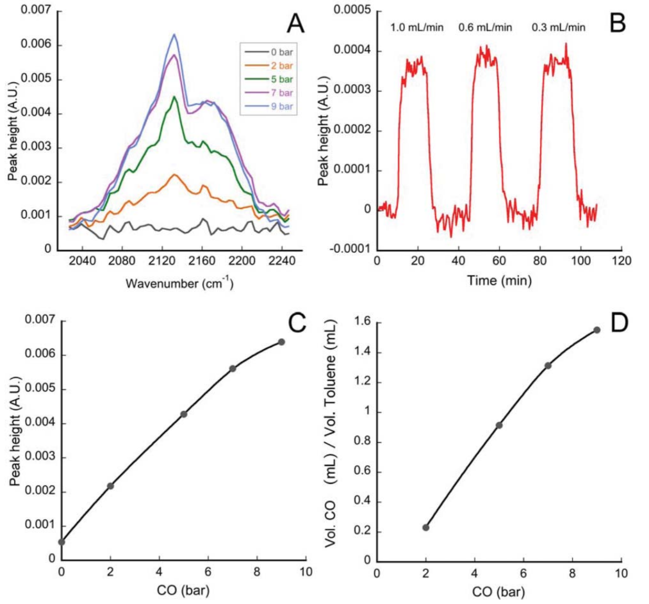


Fig. 4 (a) Intensity of the CO stretching frequency at 2133 cm^{-1} against pressure at constant flow rate (0.6 mL min^{-1}; 2, 5, 7, 9 bar of CO; 0 bar is without CO); (b) Real time, in-line monitoring of dissolved CO in toluene at various flow rates with constant pressure of CO (7 bar of CO; 1.0, 0.6, 0.3 mL min^{-1}); (c) average peak height from A against CO pressure; (d) A plot of volume of CO (mL) degassed per volume of toluene (mL) using the gas burette measurements.

It is noteworthy that the corresponding batch reactions of these and similar substrates can often require significantly longer reaction times (12–24 h *vs.* 37 min) in addition to CO pressure.[12] This is perhaps attributable to the very high effective surface-area : volume ratio provided by the Teflon AF-2400 membrane which leads to rapid dissolution of CO into the solvent.[13] In order to gain quantitative insight into the uptake of CO into the solvent stream as a function of pressure and flow rate, we sought a means of measuring the solution concentration of the gas in flow and conjectured that the distinctive IR absorption of CO might be used for this purpose. To assay this possibility an in-line real-time FTIR experiment was performed,[14] monitoring the intensity of the dissolved CO IR stretching frequency[15] at 2133 cm^{-1} using a ReactIR$^{\text{TM}}$15 unit fitted with a silicon (SiComp) flow probe (Fig. 3).[16] In these experiments, CO was dissolved in toluene and this flow stream was then directed to the input of the flow probe. The inclusion of a back-pressure regulator before the probe was necessary to ensure that the liquid stream pressure did not exceed 8 bar (the current maximum pressure tolerance of this cell is 10 bar). Initially, the influence of CO pressure on the intensity of the peak at 2133 cm^{-1} was examined using a constant flow rate (0.6 mL min^{-1}) (Fig. 4a). The peak intensity of this spectral region clearly shows a dependence on applied CO pressure, which results in increased CO dissolution.

As shown in Fig. 4c, a plot of the relative peak intensity at 2133 cm^{-1} against CO pressure increases linearly prior to approaching approximately 9 bar of CO. Separately, a gas burette was used to measure the volume of CO, which evolved from the solvent on depressurisation of the gas–liquid stream to ambient pressure.

The volume of CO collected per unit volume of toluene at 0.6 mL min^{-1} as a function of applied CO pressure is shown in Fig. 4d. A similar dependence on pressure was observed for the gas burette and IR measurements (Fig. 4c and 4d), demonstrating that the burette measurements can be used to quantify the intensities in the IR experiments and that the IR intensity is a true reflection of the CO concentration. With a view to determining the concentration of dissolved CO over a range of flow rates, additional in-line IR monitoring experiments were undertaken. The preliminary results are shown in Fig. 4b, in which the dissolved CO IR stretching frequency at 2133 cm^{-1} (in toluene) was monitored in real time at 7 bar CO (solvent flow rates 0.3, 0.6 and 1.0 mL min^{-1}).

The approximately equal peak intensity indicates that the concentration of CO in the solvent stream is independent of flow rates below 1.0 mL min^{-1} suggesting that (at these flow rates and with this length of Teflon AF-2400 tubing) the level of CO in solution has reached saturation for this pressure. With a broader data set in terms of pressure, AF-2400 length, flow rate, temperature and solvent, it should be possible to accurately predict the concentration of CO (and other IR visible gases) in solution. This would also help to determine the minimum length of Teflon AF-2400 length required to achieve saturation under the respective conditions. We are currently developing this proof-of-concept into a fully automated system which will provide both extensive permeation/solubility data as well as real-time monitoring of reaction parameters. We,[9] and others,[17] have shown that these emerging small-dimension continuous flow methods of obtaining thermodynamic and kinetic gas-solubility data potentially offer real benefits in comparison to traditional static methods which often require more specialist apparatus and much longer equilibration times.[18]

Finally, to further develop the possibility of multi-step continuous flow reaction sequences, in which downstream processes may not be compatible with unreacted CO, we investigated the possibility of removing excess dissolved gas by using a second gas–liquid reactor unit in which dissolved CO was extracted by applying a vacuum around the inner AF-2400 tube (Fig. 5). In this configuration, the second reactor (0.5 mL) was placed immediately after the first reactor, in which CO was injected (at 5 bar). The ReactIR was used to monitor the CO peak (2133 cm^{-1}) with the applied vacuum (10 mbar). At 10 mbar vacuum, the CO peak was not visible in the IR spectrum, suggesting that all the CO had been removed.

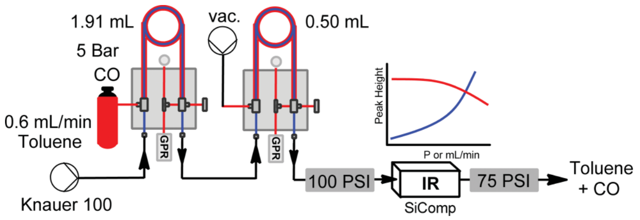


Fig. 5 CO gas removal by a second gas–liquid reactor with applied vacuum (10 mbar).

Conclusions

The use of Teflon AF-2400 to mediate gas–liquid contact in a simple concentric Tube-in-Tube configuration allows the continuous flow palladium catalysed methoxycarbonylation of aryl iodides to be carried out in an efficient and reliable manner. The fact that only a small volume of this toxic and flammable gas is pressurised at any one time greatly enhances the safety profile of the process. The in-line IR measurement of gas concentration, calibrated by gas burette measurements, shows promise as a powerful and convenient monitoring tool for gas–liquid flow chemistry which should lend itself to automation and may find use in a broader scope of applications where the real-time quantification of gas concentration in liquids is required. Further development of this system is currently underway in our laboratories.

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