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Fluoride effect on the palladium–phenanthroline catalyzed carbonylation of nitroarenes to carbamates

Michela Gasperini, Fabio Ragaini*, Sergio Cenini, Emma Gallo and Simone Fantauzzi

Università degli Studi di Milano, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, ISTM-CNR, via Venezian 21, 20133 Milano, Italy

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Fluorides promote the palladium–phenanthroline catalyzed carbonylation of nitroarenes to carbamates. The effect is more evident on the rate of the reaction at short reaction times, but a positive effect on selectivity is also observed under certain conditions. The effect is observed even under conditions under which chloride inhibits the reaction. Tetraethylammonium is a better countercation than sodium. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: fluoride; carbonylation; homogeneous catalysis; nitroarenes; palladium; carbamates

INTRODUCTION

The carbonylation of organic nitro compounds is a process of great potential synthetic and industrial interest, since many products can be obtained from nitro compounds and CO, including isocyanates, carbamates and ureas.[1–3] Ureas and carbamates are important final products and intermediates in the synthesis of pesticides and fertilizers, and mono- and diisocyanates are important intermediates in the manufacturing of pesticides, polyurethane foams, plastics, synthetic leather, adhesives and coatings.

The classical method for the production of isocyanates requires the intermediate reduction of the nitro compound to amine, followed by reaction with phosgene. However, phosgene is a very toxic and corrosive material. Very recently (summer 2006), a large plant producing toluenediisocyanate (TDI) was shut in Italy mainly because of the pressure from the local population and authorities against the use of phosgene close to a populated area. Thus it is not surprising that an enormous effort has been applied to the development of phosgene-free routes to isocyanates. Among these, the catalytic carbonylation of nitro compounds, particularly of aromatic ones, represents one of the most interesting alternatives, but the direct carbonylation of nitro compounds to the corresponding isocyanates has proved to be a difficult reaction. However, in the presence of an alcohol, carbamates can be obtained more easily and with a high selectivity [equation (1)]:

$$\mathrm{ArNO_2 + ROH + 3\,CO \xrightarrow{cat.} ArNHCOOR + 2\,CO_2} \qquad (1)$$

Diarylureas are intermediately formed during the reaction in many cases and carbamates are formed by their alcoholysis reaction only at a later stage.[4–11] Both carbamates and ureas are important industrial products themselves, but can also be thermally cracked to the corresponding isocyanates, thus providing a phosgene-free route to these important intermediates.[12–15]

In recent years the catalytic system based on palladium–phenanthroline complexes has emerged as the most active and promising for possible industrial application.[16–51] We have much improved the activity of this catalytic system in the production of carbamates by the addition of phosphorus acids.[46–48] Very recently, we investigated the effect of small amounts of chloride anion on this reaction.[11] Contrasting effects had been previously reported in the literature.[21,25] We have shown that chloride can indeed act both as a promoter or an inhibitor depending on the reaction conditions. The promoting effect was proposed to be due the formation of anionic palladium(0) species of the kind $[\mathrm{Pd(Phen)Cl}]^-$ (Phen = 1,10-phenanthroline), which can probably reduce nitroarenes more efficiently than neutral complexes (Scheme 1). The inhibiting effect, on the other hand, can quite confidently be attributed

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*Correspondence to: Fabio Ragaini, Università degli Studi di Milano, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, ISTM-CNR, via Venezian 21, 20133 Milano, Italy.
E-mail: fabio.ragaini@unimi.it
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to the formation of $Pd(Phen)Cl_2$, which is notoriously very little soluble and inactive as a catalyst for the carbonylation reaction.

In recent years, an increasing number of metal-catalyzed processes have been found to be promoted by fluoride ion.[52,53] The complex $Pd(Phen)F_2$, corresponding to the inactive species generated with other halides, is not known and attempts made by our group to synthesize it by reactions analogous to those suitable for $Pd(Phen)Cl_2$ failed. Although it is possible that other synthetic approaches may result in the isolation of this difluoride complex, it is also evident that it is not formed easily[54] (complexes of the kind PdL_2F_2 have been isolated only where L_2 is a chelating alkyl phosphine). This suggested to us that fluoride may have a similar promoting effect to chloride, without showing the inhibiting effects of the latter. In this paper we report the results of our study.

RESULTS AND DISCUSSION

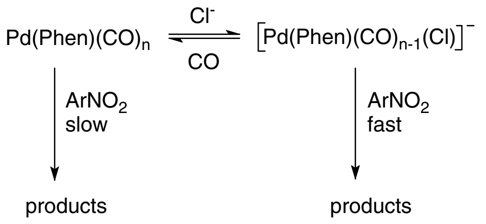
In our previous study on the effect of chloride on the palladium–phenanthroline carbonylation of nitroarenes we investigated the synthesis of both diarylureas and carbamates.[11] While both positive and negative effects had been found for urea synthesis, only negative effects had been found for carbamates. However, the synthesis of carbamates is more important from an industrial point of view and in this work we decided to focus on this reaction.

First we investigated the carbonylation of nitrobenzene to methyl phenylcarbamate [Ar = Ph, R = Me in equation (1)]. We employed conditions very close to those previously optimized by us for this reaction,[46,47] but worked at a lower CO pressure (60 instead of 100 bar) in order to better differentiate the results avoiding reaching too high conversions.

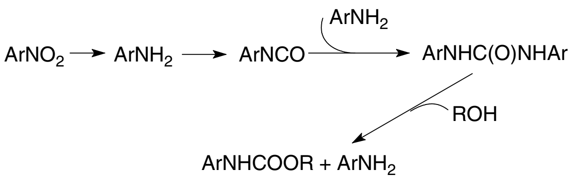
Before commenting on the results, it must be recalled that we have previously shown[46,47] that under the conditions here investigated the main reaction pathway requires the intermediate reduction of the nitroarene to aniline (Scheme 2). The latter is then carbonylated to phenylisocyanate, which is trapped by excess aniline to generate diphenylurea. Only at the end is the urea alcoholyzed by methanol to generate the carbamate. The last reaction is not fast even at high temperature and significant urea accumulation is observed during the reaction, although its amount tends to decrease as the reaction approaches completion.

The rate-determining step of the cycle, under these experimental conditions, is aniline carbonylation and this reaction is accelerated by the presence of acids, most notably phosphorus acids such as phosphoric or phenylphosphonic acids. If no aniline is added to the reaction mixture, an induction period is observed that is needed for its generation. Thus it is convenient to add a small amount of aniline from the beginning. The aniline amount at the end of the reaction may be larger or smaller than the initially charged one, depending on the experimental conditions. Apart from the intermediately formed urea, the other byproducts of the reaction are azo- and azoxybenzene. The results of the experiments made on nitrobenzene as substrate are reported in Table 1.

From a comparison between reactions run in the absence or in the presence of fluoride, it immediately emerges



Scheme 1.



Scheme 2.

Table 1. Effect of fluoride on the carbonylation of nitrobenzene to methyl phenylcarbamate[a]

Run	$[Et_4N][F]$–Pd mol ratio	*t* (h)	$PhNO_2$ converted (%)[b]	PhNHCOOMe selectivity (%)[c]	PhN(O)=NPh selectivity (%)[c]	PhN=NPh selectivity (%)[c]	PhNHC(O)NHPh selectivity (%)[c]
1	—	1	33.6	86.7	1.8	1.9	9.6
2	8.2	1	43.2	83.4	1.4	1.5	13.7
3	—	2.5	84.3	84.3	1.5	2.9	11.3
4	8.2	2.5	96.9	86.6	1.3	2.5	9.6

[a] Experimental conditions: catalyst $[Pd(Phen)_2][BF_4]_2 = 1.4$ mg, 2.2×10^{-3} mmol, mol ratios $PhNO_2$–$PhNH_2$–H_3PO_4–Phen–Pd = 7500 : 200 : 682 : 100 : 1, 2,2-dimethoxypropane = 0.5 ml, $P_{CO} = 60$ bar, $T = 175\,°C$, in methanol (15 ml).

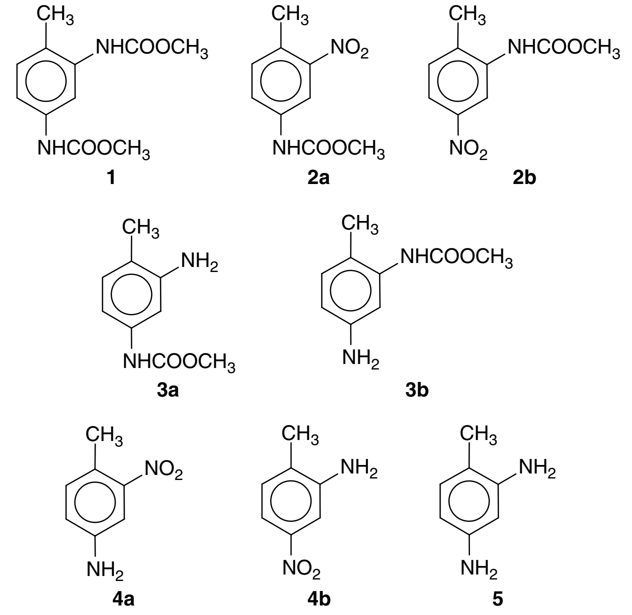
[b] Calculated with respect to the initial $PhNO_2$.

[c] Calculated with respect to the converted $PhNO_2$. The amount of aniline at the end of the reaction was indistinguishable from the initially added one.

that fluoride affects the reaction mainly by accelerating it. A slight positive effect on selectivity is also observed at longer reaction times. Note that the slightly worse apparent selectivity in carbamate after the one hour run is due to the accumulation of more diphenylurea, a consequence of the faster reaction. In principle, fluoride may also promote the reaction by stabilizing the catalytic system against deactivation. However, the fact that a high acceleration effect is observed for short reaction times, when deactivation is surely negligible,[46,47] indicates that a direct promotion of the reaction must be present. A possible stabilization effect is not evidenced by the data in Table 1. This point will be further considered when dealing with the carbonylation of 2,4-dinitrotoluene.

Encouraged by these positive results, we also extended the study of the fluoride effect to the more industrially important carbonylation of 2,4-dinitrotoluene. From this compound, formation of two intermediate nitrocarbamates, two aminocarbamates, two nitroanilines, 2,4-diaminotoluene (Scheme 3) and a virtually unlimited number of ureas, azo- and azoxyarenes is possible.

We had previously solved the problem of the independent quantification of all compounds shown in Scheme 3,[48] although ureas and azo derivatives could not be quantified. In this case, several amines can be added as promoters. Nitrotoluidine **4b** had been earlier found to be the most efficient and the conditions employed for the reported reactions (Table 2) are identical to those previously optimized for these substrates.[48] Note that dinitrotoluene reacts at a much faster rate than the intermediate nitrocarbamates **2**. Thus dinitrotoluene will be almost completely consumed before dicarbamate **1** is formed in appreciable amounts. It follows that dinitrotoluene conversion is an useful index of reaction rate only at short reaction times, whereas the selectivity in **1** and **2a, b** must be considered at longer reaction times or under more efficient conditions.



Scheme 3.

From a comparison of runs 1 and 2 in Table 2 it immediately emerges that the addition of five equivalents of fluoride with respect to palladium to the catalytic system accelerates the reaction even more markedly than in the case of nitrobenzene, the conversion increasing from 57.4 to 100%. Note that, under identical experimental conditions, chloride inhibits the reaction already at a 0.5 Cl^-—Pd ratio.[11] Increasing the fluoride amount up to 8.2 equivalents (run 4) further increased the reaction rate (compare the amount of **1** formed) but a further increase led to a less efficient promotion and with 20 equivalents the results are essentially indistinguishable from those in the absence of fluoride (compare runs 1 and 7). The fact that the best results were obtained at the same F^-—Pd ratio initially employed for nitrobenzene is fortuitous, but it should be realized that the results obtained between 7.5 and 10 equivalents of fluoride are very close to the experimental reproducibility.

When the reaction time is increased to 3.5 h (runs 8 and 9), all intermediate products are almost completely converted both in the absence and in the presence of fluoride. No appreciable benefit is observed in this case and the selectivity in dicarbamate is even slightly lower when fluoride is present.

One of the problems previously found when carbonylating dinitrotoluene is that the catalytic system deactivates more quickly than in the case of simple nitroarenes. Whereas a Turn Over Number (TON) up to 10^5 could be obtained in the case of nitrobenzene, the catalytic activity decreased even before 5000 equivalents of dinitrotoluene (corresponding to 10^4 nitro groups) had been completely converted. Although this number is anyway remarkable and quite higher than any other TON previously reported for this substrate, it is not ideal for an industrial application. In order to see if fluoride was also able to retard catalyst deactivation, we performed two reactions at a higher catalytic ratio (runs 10 and 11). The results are essentially indistinguishable whether fluoride is present or absent.

During our studies on the promotion by [Et_4N][Cl] of the $Ru_3(CO)_{12}$-catalyzed carbonylation of nitrobenzene, we had found that Et_4N^+ slowly decomposes during the reaction time to afford triethylamine and that the latter plays a role in the catalytic reaction at high conversions.[9,10] To see if better results could be obtained with an 'indestructible' countercation, we also examined the promoting activity of sodium fluoride. The results (Table 2, runs 12–15) parallel those obtained with the tetraethylammonium countercation, but are slightly inferior. Since the amount of triethylamine possibly formed under the present conditions is much lower than that formed in the $Ru_3(CO)_{12}$-catalyzed reaction and that an acid is also present now that is absent in the ruthenium case, it is unlikely that the better results obtained with Et_4N^+ with respect to Na^+ are due to triethylamine formation. We consider it more likely that a tighter ionic couple between sodium and fluorine is responsible for the lower promoting

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Table 2. Effect of fluoride on the carbonylation of 2,4-dinitrotoluene to dimethyl 2,4-toluenedicarbamate (**1**)[a]

Run	Fluoride source	F^-—Pd mol ratio	t (h)	Dinitrotoluene – Pd mol ratio	Dinitrotoluene converted (%)[b]	**4b** converted (%)[c]	**1** selectivity (%)[d]	**2a** selectivity (%)[d]	**2b** selectivity (%)[d]	**3a** selectivity (%)[d]	**3b** selectivity (%)[d]
1	—	—	1	2920	57.4	36.0	2.1	32.4	31.8	—	—
2	$[Et_4N][F]$	5	1	2920	100	69.3	13.4	34.0	24.2	0.7	0.7
3	$[Et_4N][F]$	7.5	1	2920	100	79.4	18.0	29.4	22.0	0.1	0.9
4	$[Et_4N][F]$	8.2	1	2920	100	75.6	19.7	32.2	24.3	1.1	1.0
5	$[Et_4N][F]$	8.75	1	2920	100	76.9	18.0	30.7	22.9	1.0	0.9
6	$[Et_4N][F]$	10	1	2920	100	74.8	17.2	32.4	25.6	1.3	1.1
7	$[Et_4N][F]$	20	1	2920	57.5	5.8	3.5	38.6	42.3	0.4	0.7
8	$[Et_4N][F]$	8.2	3.5	2920	100	100	71.7	2.8	—	2.6	0.7
9[f]	—	—	3.5	2920	100	100	77.6	1.1	—	2.6	0.8
10	$[Et_4N][F]$	8.2	3.5	5840[e]	97.5	100	21.7	28.2	20.6	0.4	0.4
11	—	—	3.5	5840[e]	100	100	19.4	27.4	19.6	0.5	0.5
12	NaF	5	1	2920	98.9	64.7	8.7	38.3	28.6	0.2	0.3
13	NaF	8.2	1	2920	100	65.8	12.7	36.6	25.2	0.9	0.9
14	NaF	11	1	2920	95.2	53.2	5.2	36.7	28.3	<0.1	<0.1
15	NaF	15	1	2920	82.5	62.9	5.5	41.8	32	<0.1	<0.1

[a] Experimental conditions: catalyst $[Pd(Phen)_2][BF_4]_2 = 3.2$ mg, 5.0×10^{-3} mmol, mol ratios **4b**–phenylphosphonic acid–Phen–Pd =400 : 330:32 : 1, 2,2-dimethoxypropane = 1.0 ml, $P_{CO} = 100$ bar, $T = 170\,°C$, in MeOH (20 ml).

[b] Calculated with respect to the initial dinitrotoluene.

[c] Calculated with respect to the initial **4b**.

[d] Calculated with respect to the sum of reacted **4b** and dinitrotoluene.

[e] MeOH = 30 ml.

[f] Data from Gasperini *et al.* 48.

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activity of NaF. Note that solubility is surely not an issue here, because even at the higher F^-—Pd ratio employed, the amount of NaF corresponds to just 3.15 mg and this amount is completely soluble in the employed amount of methanol even at room temperature. Indeed, to avoid the problem of precisely weighing very small amounts of fluorides, we prepared stock solutions of both fluorides in methanol and measured the require promoter amount by volume.

CONCLUSIONS

In this work, we have found that fluoride is an efficient promoter for the palladium–phenanthroline-catalyzed carbonylation of nitroarenes to carbamates. The effect is observed even under conditions in which chloride inhibits the reaction and is more evident in the case of the industrially important 2,4-dinitrotoluene. Fluoride addition mostly affects the reaction rate and may allow shorter reaction times, which are an important issue when dealing with very large amounts of materials. On the other hand, small and variable effects on the selectivity and no stabilization effect on the catalytic system are observed. The last two points are probably connected. Previous studies on catalyst deactivation during the carbonylation of dinitrotoluene had led to the conclusion that the most likely explanation for the observed deactivation is that some organic compounds are formed during the reaction which interact with the palladium catalyst and decrease its reactivity.[48] If fluoride does not alter the selectivity of the reaction, it probably also does not prevent the formation of the inactivating byproducts.

The reason for the promoting efficiency of fluoride is not known at the moment. Although it is tempting to suggest that the same explanation proposed and partially supported[11] for the promoting effect of chloride is also operating here (Scheme 1), it should be noted that this explanation accounts for the accelerating effect only if the nitroarene activation step is rate determining in the catalytic cycle. However, under the conditions employed in the present study, this is surely not the case for nitrobenzene, since the kinetics of the reaction has been shown to be zero order in this substrate,[46,47] and is very unlikely to hold even for dinitrotoluene. Thus a different explanation must be found for the accelerating effect of fluoride. At the moment, too many possibilities and too little experimental data are available to make a sound proposal and we prefer to avoid any completely unsupported speculation.

EXPERIMENTAL

General procedure

All solvents were dried by standard procedures, distilled and stored under dinitrogen before use. Phenanthroline monohydrate was dried by dissolving it in CH_2Cl_2 and drying the resulting solution with Na_2SO_4. The solution was then filtered, evaporated *in vacuo*, and the obtained phenanthroline was stored under a dinitrogen atmosphere. Dry Phen can be quickly weighed in the air without problems, but long storage in an undried atmosphere converts it quantitatively to the monohydrate. $[Pd(Phen)_2][BF_4]_2$,[21] was synthesized as reported in the literature. Nitrobenzene was purified by shaking with 10% H_2SO_4, washing with water, and drying with Na_2SO_4, followed by distillation under dinitrogen and storage under an inert atmosphere. Aniline was distilled and stored under dinitrogen before use. 2,4-Dinitrotoluene was recrystallized from methanol to remove the water present in the commercial product. The anhydrous product was stored under dinitrogen. Nitrotoluidine **4b** was purified by sublimation. All other reagents were commercial products and were employed as received. HPLC analyses were performed on a Hewlett Packard series 1050 chromatograph. Gas chromatographic analyses were performed on a Dani 8610 capillary gas chromatograph (see later for details on the analysis conditions).

Catalytic reactions

In a typical catalytic reaction, all the reagents except for the solvent and fluoride (which was added as a stock solution in methanol) were weighed in a glass liner. See captions to Tables 1 and 2 for reagents amounts and experimental conditions. The liner was placed inside a Schlenk tube with a wide mouth under dinitrogen and was frozen at −78 °C with dry ice, evacuated and filled with dinitrogen, after which the solvent (and the fluoride solution if required) was added. After the solvent was also frozen, the liner was closed with a screw cap having a glass wool-filled open mouth which allowed gaseous reagents to exchange, and then was rapidly transferred to a 200 ml stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO was then charged at room temperature at the required pressure and the autoclave was immersed in an oil bath preheated at the required temperature; the autoclave took about 15 min to fully equilibrate at the final temperature. At the end of the reaction the autoclave was cooled with an ice bath and vented. In the case of carbonylation reactions of nitrobenzene, the products were analyzed by gas chromatography (PS 255 column, naphthalene as the internal standard). For dinitrotoluene reactions, the products were analyzed by HPLC (RP_{18} column, methanol–water 55 : 45 as eluent, benzophenone as the internal standard; for 2,4-dinitrotoluene, **1, 2a, b**,and **3a, b**) and gas chromatography (PS 255 column, naphthalene as the internal standard; for **4a, b** and **5**). Response factors for both GC and HPLC analyses had been determined in previous works[47,48] by injection of known amounts of the pure compounds.

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