

Microwave-enhanced ruthenium-catalysed atom transfer radical additions

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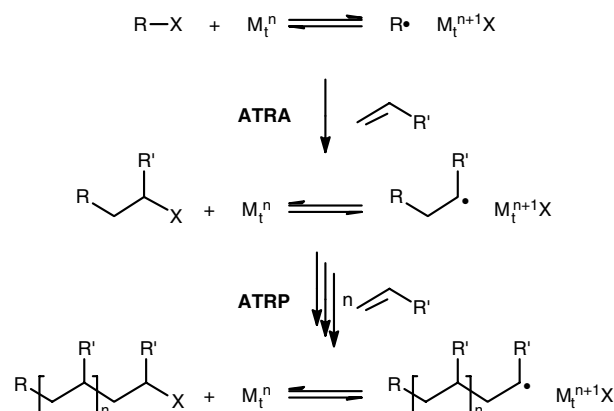
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Abstract—The first monomode microwave-assisted atom transfer radical additions (ATRA) of carbon tetrachloride to various olefins were successfully performed, affording the adducts with almost quantitative yields in less than 10 min at 160 °C.
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Known for more than half a century, the Kharasch reaction is an effective method for the formation of carbon–carbon bonds.¹ This process consists in adding a polyhalogenated alkane to an alkene and requires either a radical initiator—as in the original Kharasch reaction—or a transition metal catalyst. The latter really emerged in the mid-1990s when it was extended to olefin polymerisation, the so-called atom transfer radical polymerisation (ATRP), discovered by Sawamoto² and Matyjaszewski.³ Because of the similarities between both transformations (Scheme 1), the metal-catalysed Kharasch reaction was then named as atom transfer radical addition (ATRA). ATRP is currently an area of utmost interest in polymer chemistry⁴ and it is well established that knowledge from ATRA should be especially useful for understanding ATRP.

Several transition metal complexes have been described to catalyse both processes. Amongst them, copper- and ruthenium-based catalysts are nowadays the most popular ones.⁴ In particular, we have reported in recent years that $[\text{RuCl}(\text{Cp}^\#)(\text{PR}_3)_2]$ ($\text{Cp}^\#$ is the cyclopentadienyl ligand or a derivative thereof),⁵ $[\text{RuCl}_2(=\text{CHPh})\text{L}_2]$ ⁶ and $[\text{RuCl}_2(p\text{-cymene})\text{L}]$ ⁷ complexes displayed high catalytic performance.⁸

On the other hand, since 1986, when Gedye⁹ and Giguere¹⁰ published their first articles on microwave-assisted

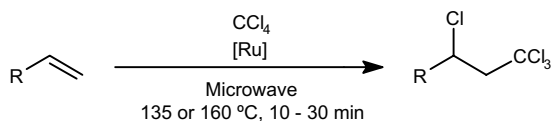


Scheme 1. Commonly accepted mechanism for ATRA and ATRP reactions.

syntheses in household microwave ovens, there has been a steadily growing interest in this research field.¹¹ In recent years, indeed, a plethora of publications have shown that microwave heating is an efficient tool in organic synthesis to enhance the effectiveness of the reactions, but surprisingly enough only a limited number of examples of radical reactions has been reported.¹² In particular, to the best of our knowledge, there is only one paper on Kharasch additions accelerated by microwaves. Thus, using a domestic microwave oven for the copper-catalysed addition reactions of tetrachloromethane and ethyl trichloroacetate with styrene, a 3 to 21-fold increase of the reaction rate was observed compared to classical heating.¹³ As part of our ongoing research programme on microwave-assisted

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Scheme 2. Kharasch addition of carbon tetrachloride to olefins.

transformations,^{14,15} we now wish to report that the Kharasch addition can be dramatically accelerated under single-mode microwave irradiation (Scheme 2).

The study began with the more challenging, non-activated case of 1-decene, a sluggish substrate in Kharasch chemistry, together with carbon tetrachloride as a reaction partner. $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes were elected as (pre)catalysts, because they proved to be moderately active in this field. Previous experiments^{7f} demonstrated that very long reaction times (at least 200–300 h) were necessary for complete conversion of the substrate at 60 °C, using a thermostated oil bath as the heating source (Supplementary Fig. S1). As expected, when the same experiments were conducted at 85 °C, the conversions were faster, yet relatively slow since 50–150 h were still required for the reaction to proceed to completion.

In a typical microwave experiment, a mixture of $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complex, 1-decene and carbon tetrachloride in toluene was irradiated using a CEM Discover reactor at a maximum power of 150 W, and monitored by GC using dodecane as internal standard. Two reaction conditions were chosen, either 135 °C for 30 min, or 160 °C for 10 min.

Examination of the results summarised in Table 1 clearly demonstrates that microwave irradiation at 160 °C for 10 min is a highly efficient protocol for the Kharasch addition. Excellent yields were indeed obtained with most of the $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes under investigation. Microwave irradiation at 135 °C for 30 min was, however, slightly less efficient and more time was required to complete each reaction. Under both conditions, all $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes proved to be—almost—equipotent catalysts for the test reaction, with the exception of the electron-poor $[\text{RuCl}_2(p\text{-cymene})(\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3)]$ complex,^{7f} which displayed a significantly lower activity. Additional experiments indicated that $[\text{RuCl}_2(\text{PPh}_3)_3]$ catalysed reactions, first reported by Nagai et al.¹⁶ and then applied to a variety of synthetically useful reactions,¹⁷ were also dramatically accelerated under microwave irradiation, albeit to a lesser extent than in the presence of $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ complexes (Table 1). On the other hand, several control experiments were conducted to assess the actual role of the catalyst, in particular, given the high temperatures employed. As expected, no reaction occurred in the absence of a catalyst, even under extended reaction times with heating to 160 °C.

To optimise the conditions, we next studied the combined effects of temperature and reaction time (Figs. 1 and 2).

Table 1. Addition of carbon tetrachloride to 1-decene catalysed by various ruthenium complexes^a

| | 1-Decene conversion ^b (%) / Kharasch addition ^b (%) | | |
|--|--|--------------------|--------------------|
| | Δ , ^{c,d} | MW, ^{c,e} | MW, ^{c,e} |
| | 85 °C | 135 °C | 160 °C |
| | 30 h | 30 min | 10 min |
| No catalyst | <1/<1 | <1/<1 | 1/<1 |
| $[\text{RuCl}_2(p\text{-cymene})(\text{PAr}_3)]$ | | | |
| Ar: $p\text{-C}_6\text{H}_4\text{OCH}_3$ | 89/89 | 88/87 | 92/92 |
| $p\text{-C}_6\text{H}_4\text{CH}_3$ | 79/78 | 90/90 | 95/95 |
| C_6H_5 | 67/66 | 88/87 | 92/91 |
| $p\text{-C}_6\text{H}_4\text{F}$ | 59/58 | 90/87 | 96/96 |
| $p\text{-C}_6\text{H}_4\text{Cl}$ | 45/44 | 79/77 | 95/95 |
| $p\text{-C}_6\text{H}_4\text{CF}_3$ | 64/63 | 54/54 | 85/84 |
| $[\text{RuCl}_2(\text{PPh}_3)_3]$ | 91/83 | 67/65 | 70/61 |

^a Reaction conditions: Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures, distilled and kept under nitrogen at –20 °C.

^b Conversions and yields based on GC using dodecane as internal standard.

^c The catalyst (0.03 mmol) was dissolved in toluene (1 mL) and subsequently added through a septum to the solution of 1-decene (9 mmol), CCl_4 (13 mmol), dodecane (0.25 mL) in toluene (3 mL).

^d The reaction was performed using a thermostated oil bath.

^e The reaction mixture (2 mL) was introduced in a 10 mL microwave reaction vial and irradiated in a microwave reactor CEM Discover at a maximum power of 150 W.

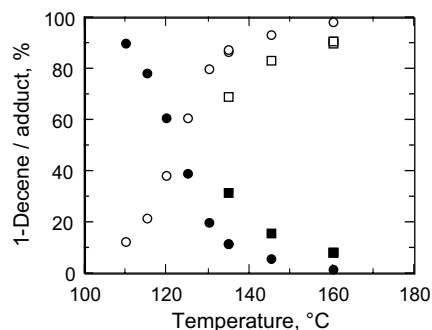


Figure 1. Optimisation of reaction conditions: time and temperature effects on the microwave-assisted addition of CCl_4 to 1-decene catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)_3]$; 10 min runtime (■, □) or 30 min runtime (●, ○); 1-decene (■, ●), Kharasch adduct (□, ○). The reaction conditions are the same as in Table 1.

Below 160 °C, the reaction was incomplete with significant amounts of 1-decene remaining (Fig. 1). At 135 °C, increasing the run time from 10 to 30 min improved the conversion from 68% to 87%, and at 145 °C the conversion increased from 85% to 94%. At 160 °C and above, the products were greater than 97% pure as judged by GC. Thus, the optimal combination of yield and conversion was determined to be 160 °C, for 30 min. At 135 °C, however, the conversion never reached completion (Fig. 2), seemingly because of the competitive decomposition of the catalyst. Indeed, although in the beginning $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ was completely soluble in the reaction mixture at ambient temperature, a brownish solid appeared on the wall of the reaction vial after microwave irradiation and cooling to room temperature.

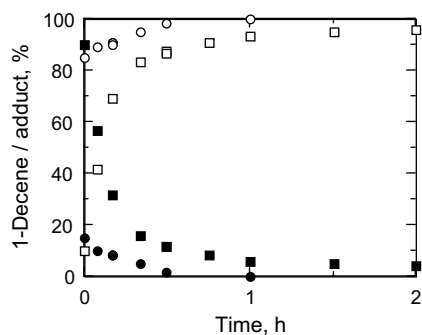


Figure 2. Optimisation of reaction conditions: time and temperature effects on the microwave-assisted addition of CCl_4 to 1-decene catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$; temperature: 135 $^\circ\text{C}$ (■, □) or 160 $^\circ\text{C}$ (●, ○); 1-decene (■, ●), Kharasch adduct (□, ○). The reaction conditions are the same as in Table 1.

For comparison, Kharasch addition of CCl_4 to decene was also conducted using a thermostated oil bath under otherwise identical conditions (concentration, temperature, etc.), except that the reactions were performed in sealed tubes, which were immersed in the oil bath at 160 $^\circ\text{C}$. Examination of Figure 3 clearly demonstrates that microwave irradiation is superior to conventional heating. Indeed, under microwave conditions, decene conversions were as follows: 92%, 95% and 99% for run-times of 10, 20 and 30 min, respectively, against 37%, 70% and 85% for conventionally heated reactions.

In Figure 3, it is also observed that the origin is not intercepted in the plot of substrate conversion against time (see also Supplementary Fig. S4 for the $\ln([S]_0/[S]_t)$ vs time plot). Thus, experiments performed for 0 min revealed already 1-decene conversions of 10% and 85% for the reaction temperatures of 135 and 160 $^\circ\text{C}$, respectively (Supplementary Fig. S6). This effect was confirmed for other substrates, such as 1-hexene (Supplementary Fig. S5). For the sake of understanding, it is worth mentioning first that the CEM Discover microwave instrument is programmed so as $t = 0$ when the desired temperature is attained and not—as expected—when irradiation starts. The phenomenon described above is therefore related to the time that the microwave reactor takes to reach the desired reac-

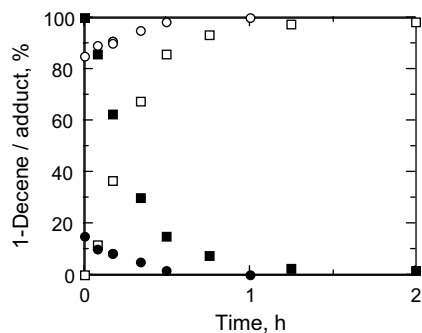


Figure 3. Comparison between microwave heating and conventional heating for the addition of CCl_4 to 1-decene catalysed by $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ at 160 $^\circ\text{C}$; microwave heating (●, ○), conventional heating in an oil bath (■, □); 1-decene (●, ■), Kharasch adduct (○, □). The reaction conditions are the same as in Table 1.

tion temperature.^{15,18} We found that the conversions were negligible at temperatures lower than 120 $^\circ\text{C}$ after a reaction time of 0 min, so that the reactions performed at 135 and 160 $^\circ\text{C}$ for 0 min, in fact, were exposed to longer reaction times above 120 $^\circ\text{C}$. These times (as obtained from the data of the experimental set-up) were 25 and 115 s for the reaction temperatures of 135 and 160 $^\circ\text{C}$, respectively (Supplementary Fig. S7). On the other hand, when the Kharasch additions were performed under conventional heating, the reactions started with the immersion of the sealed tube in the oil bath. The conversion was obviously zero at time $t = 0$. In addition, a short induction period was observed (Fig. 3 and Supplementary Figs. S4 and S5), which can be simply explained by the time needed for the heat to be transferred to the reaction medium. In light of these results and taking into account the temperature problems inherent to both methods, it is likely that microwave irradiation and conventional heating are equipotent protocols, thereby ruling out the so-called ‘microwave effect’. However, compared to conventional heating, microwave irradiation is much more convenient, providing a fast and direct heating of the reactants at the desired temperature.

It is also worth noting that our results do not confirm previous works. In a comparable study, indeed, using a domestic multimodal microwave oven instead of a monomodal microwave reactor, Adámek reported quite significant microwave acceleration with respect to that achievable under conventional heating protocols.¹³ Interestingly, as stated very recently by Rannard and co-workers²⁰ in all atom transfer radical reactions (ATRA and ATRP) reported to date, ‘rate enhancements have only been observed when employing laboratory-modified domestic multimodal microwave ovens, where the heating rate and profile are inconsistent and irreproducible. In the case of reactions performed in monomodal microwave reactors, for which the microwave power is more focused and the temperature is accurately monitored, no, or very little, rate enhancement is observed’.²⁰

The microwave conditions from Figures 1–3 were identified as the preferred reaction conditions and were then utilised for the Kharasch addition of CCl_4 to a diverse set of olefins using two readily available catalysts, $[\text{RuCl}_2(p\text{-cymene})(\text{PPh}_3)]$ (1) and $[\text{RuCl}_2(\text{PPh}_3)_3]$ (2) (Table 2).

1-Hexene was first employed and, surprisingly enough, this substrate proved to be less reactive than 1-decene whatever the heating system may be. Again, microwave irradiation at 160 $^\circ\text{C}$ for 10 min was clearly superior to conventional heating at 85 $^\circ\text{C}$ for 30 h (Supplementary Figs. S5 and S8). The most striking results, however, were found with highly polymerisable alkenes, such as styrene and methyl methacrylate. Thus, with $[\text{RuCl}_2(\text{PPh}_3)_3]$ as the catalyst, the standard conditions furnished full conversion of styrene together with low yield of the Kharasch adduct (34%). On the contrary, when the same reaction was performed under microwaves, complete conversions were accomplished within

Table 2. Addition of carbon tetrachloride to representative olefins catalysed by [RuCl₂(*p*-cymene)(PPh₃)] (**1**) and [RuCl₂(PPh₃)₃] (**2**)^a

| Substrate | Catalyst | Substrate conversion ^b (%) / Kharasch addition ^b (%) | | |
|---------------------|----------|--|--|--|
| | | <i>A</i> , ^{c,d} 85 °C 30 h | MW, ^{c,e} 135 °C 30 min | MW, ^{c,e} 160 °C 10 min |
| 1-Hexene | 1 | 40/23 | 74/74 | 81/81 |
| | 2 | 69/63 | 54/53 | 56/56 |
| Styrene | 1 | 62/58 ^f | 100/92 | 99/85 |
| | 2 | 100/34 ^f | 100/96 | 99/83 |
| Methyl methacrylate | 1 | 87/43 | 99/92 | 100/80 |
| | 2 | 100/52 | 93/81 | 100/77 |
| Butyl acrylate | 1 | 96/54 | 100/58 | 100/51 |
| | 2 | 99/46 | 95/50 | 98/52 |

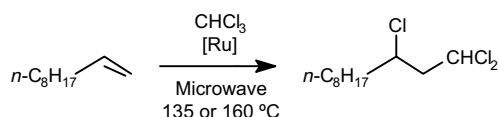
^{a–c} The reaction conditions are the same as in Table 1.^f 60 °C, 30 h.

a short time and the product was formed in high yields (85–95%). It is also noteworthy that the yields were higher at 135 °C than at 160 °C, revealing thereby the occurrence of side reactions. The latter were identified as mainly oligomerisation/polymerisation of the substrate, as indicated by the GPC trace of the reaction mixture.

A similar phenomenon was evidenced with methyl methacrylate (Supplementary Fig. S9). Under conventional heating, indeed, the yields culminated at 50% at complete conversion of the substrate, whereas under microwave heating at 135 °C the Kharasch addition reached 90%, confirming thereby the beneficial effect of microwaves both on the rate¹⁹ and the outcome of the reaction. On the contrary, with *n*-butyl acrylate—another highly polymerisable substrate—recourse to microwaves did not improve the process compared to conventional heating.

With the encouraging results obtained, our next goal was to extend this protocol to the reaction between two very sluggish partners in Kharasch chemistry, that is, chloroform and 1-decene (Scheme 3).

As expected, the Kharasch addition was extremely slow under conventional heating at 85 °C. The yield, indeed, did not exceed 20% after 300 h of reaction (Table 3 and Supplementary Fig. S11). By contrast, the reaction was much faster under microwave irradiation at 160 °C and around 60% conversion was reached after 5 h when [RuCl₂(*p*-cymene)(PPh₃)] was used as catalyst (Supplementary Fig. S12). [RuCl₂(PPh₃)₃], on the other hand, was less active, affording the desired adduct in 26% yield under the same experimental conditions, presumably because of the low solubility of the complex in the reaction medium. Details of the complex' solubility in the course

**Scheme 3.** Kharasch addition of chloroform to 1-decene.**Table 3.** Addition of chloroform to 1-decene catalysed by [RuCl₂(*p*-cymene)(PPh₃)] (**1**) and [RuCl₂(PPh₃)₃] (**2**)^a

| Reaction conditions | Substrate conversion ^b (%) / Kharasch addition ^b (%) | |
|---------------------------------|--|--------------|
| | (1) | (2) |
| <i>A</i> , 85 °C ^{c,d} | 100 h | 13/12 |
| | 300 h | 22/21 |
| MW, 135 °C ^{c,e} | 1 h | 13/13 |
| | 5 h | 26/26 |
| MW, 160 °C ^{c,e} | 1 h | 39/38 |
| | 5 h | 59/59 |

^{a–c} The reaction conditions are the same as in Table 1.

of the Kharasch addition and the applied conditions (high temperature, high pressure), however, are unknown due to the opaqueness of the reaction chamber of the microwave reactor.

In summary, we have developed an efficient method for the ruthenium-catalysed Kharasch reaction using microwave irradiation. This procedure is straightforward and high yielding, even with some highly polymerisable substrates, such as styrene and methyl methacrylate, an advantage over conventional protocols.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.029.

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