

Comments on Reactions of Oxide Derivatives of Uranium with Hexachloropropene to give UCl₄

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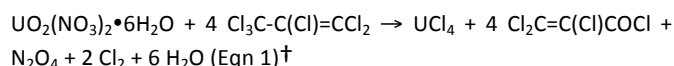
We report that U₃O₈, UO₂(NO₃)₂•6H₂O, and UO₂Cl₂ react with hexachloropropene (HCP) to give UCl₄ in 60, 100, and 92% yields, respectively, and report a protocol to recycle the HCP. This renders the preparation of UCl₄ more accessible and sustainable. 2,5-Dichlorohexachlorofulvene has been identified as a significant by-product from these reactions.

In recent years there has been a resurgence of non-aqueous uranium chemistry.¹ Such advances rely on the straightforward availability of robust halide starting materials, which are the reagents of choice for introducing new ligand-sets to uranium. For non-aqueous uranium chemistry, straightforward routes to halide starting materials are important because these reagents are not commonly commercially available and must be produced 'in-house'. Apart from uranium(III) triiodide² and uranyl(VI) dichloride,³ perhaps the most commonly used uranium halide starting material is uranium(IV) tetrachloride (UCl₄), or solvated derivatives.⁴ The latter of these three key starting materials is nowadays prepared by the action of hexachloropropene (HCP) on uranium(VI) trioxide (UO₃), since the reaction of carbon tetrachloride on uranium oxides is inconvenient and challenging to undertake on a regular basis. This produces emerald green, solvent-free UCl₄ in high yield. The uranium oxide U₃O₈ has sometimes been mentioned in the literature as being a suitable starting material for the reaction with HCP.⁵ One of us routinely makes UCl₄ by this route in yields of typically 60%.

The UCl₄ produced by the UO₃/HCP route is easily isolated by filtration/washing and is an attractive reagent because the chlorides tend to stabilise the tetravalent state of uranium during reactions, thus suppressing undesirable redox side-reactions. However, the production of UCl₄ from HCP is not without its problems. The reaction initiates *via* a vigorous radical reaction that produces an exotherm in an already very hot (ca 200 °C) HCP

solution that requires a very long path length condenser to contain, along with brief removal from heat, which in itself requires extra manipulation that may precipitate an accident. In response to this, various variations have been devised, including the portion-wise addition of UO₃ to hot HCP.^{4d} In principle this circumvents the violent exotherm *via* a series of much smaller reaction events and can be very effective. However, we note the efficacy of the latter depends on the quality of the UO₃, and we have found on occasion that particularly wet samples of UO₃ have an induction period. This can risk the build up of unreacted UO₃, which then suddenly reacts producing an exotherm that might immediately escape out of the flask side arm from which the UO₃ is being introduced. Thus, a safer method can occasionally be turned into a more dangerous one in an unpredictable manner. Increasingly, the use of the UO₃/HCP reaction is also becoming problematic simply because of the difficulties of obtaining UO₃, and HCP is becoming increasingly expensive. However, in contrast to the restrictions of UO₃, uranyl nitrate UO₂(NO₃)₂ is historically widely available in most universities, and is also still commercially available. We therefore considered whether UO₂(NO₃)₂, usually available as UO₂(NO₃)₂•6H₂O, could find a role in the production of UCl₄, and set out to determine whether it could replace UO₃ in this regard.

Here, we show that UO₂(NO₃)₂•6H₂O can indeed be substituted for UO₃ in two ways to produce UCl₄. We also report that the HCP can be recycled after fractional distillation - thus mitigating to some extent the cost of this expensive reagent - and that the use of recycled HCP results in a much reduced exotherm in subsequent UO₃/HCP reactions with no reduction in yields. Lastly, we describe the identification of one of the by-products of this reaction, namely 2,5-dichlorohexachlorofulvene, and report on its reactivity towards a range of substrates.



Encouraged by the fact that U₃O₈ can be converted to UCl₄ by HCP, following the original method,⁴ UO₂(NO₃)₂•6H₂O and HCP were mixed in a 1 litre round bottom flask equipped with three condensers stacked in-line. The mixture was heated to reflux at which point an exotherm was observed. Briefly removing heat allowed the exotherm to subside then heating was resumed. The exotherm was accompanied by the formation of a brown gas, presumably N₂O₄, and it should be noted it is more vigorous than

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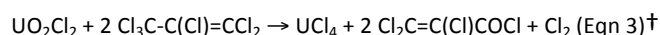
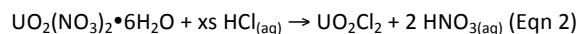
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† Whilst equations 1 and 3 balance, they do not acknowledge the formation of 1 whose formation most likely originates from unknown sub-stoichiometric radical reactions.

Electronic Supplementary Information (ESI) available: Experimental details and proposed mechanism for the formation of C₆Br₆ from 1. See DOI: 10.1039/x0xx00000x

the 'normal' exotherm with UO_3 . Apart from the vigorous exotherm, there is no evidence to suggest any side reactions of the N_2O_4 with the HCP, or the chlorine that is in principle concomitantly formed, and as described below the yield remains excellent. It should also be noted that although chlorine is classically proposed as one of the reaction byproducts,⁴ we have not observed any obvious chlorine gas evolution and the equation as proposed in Eqn 1, whilst balanced, does not acknowledge the formation of **1** (see below). In terms of the exotherm, in this regard the reaction offers no improvement over the use of UO_3 , but where UO_3 is not available $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ now provides an alternative, more readily available precursor to UCl_4 . Soon after the exotherm the formation of a yellow precipitate is observed, which may well be UO_2Cl_2 *en route* to UCl_4 . As heating is continued this yellow precipitate dissolves and is eventually replaced by the formation of UCl_4 . Once the reaction is complete (overnight reflux), the UCl_4 can be isolated by the usual filtration and washing steps with dichloromethane to afford UCl_4 in quantitative yield. This offers a modest increase in yield, since we usually observe yields of *ca* 95% when UO_3 is used.



Since the observation of a yellow precipitate suggested the formation of UO_2Cl_2 , and the exotherm was found to be quite violent, which may be associated with the liberation of NO_3^- and its conversion to N_2O_4 , we investigated the use of UO_2Cl_2 directly. UO_2Cl_2 may be prepared from the reaction of aqueous HCl on UO_3 ; however, to provide a route to UCl_4 where UO_3 may not be available but $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is plentiful we focussed on the use of the latter. Accordingly, we treated $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with an excess of 12M HCl to give a clear yellow solution, then removed all volatile materials under vacuum to give a yellow solid, Eqn 2. The large excess of HCl ensures complete conversion of the nitrate to chloride. Treatment of the product of Eqn 2 with HCP following the standard protocol results in the formation of UCl_4 in yields averaging 92% after work-up, Eqn 3. Although this route requires an extra step of HCl treatment, this can be done quickly, and an exotherm is still observed, it is significantly less vigorous than for Eqn 1. This may reflect the fact that two chlorides are already installed at uranium by this method and we also note the absence of evolution of any brown gas by this route. As for equation 1, whilst balanced equation 3 does not acknowledge the formation of **1**, and chlorine gas evolution has not been obviously observed.

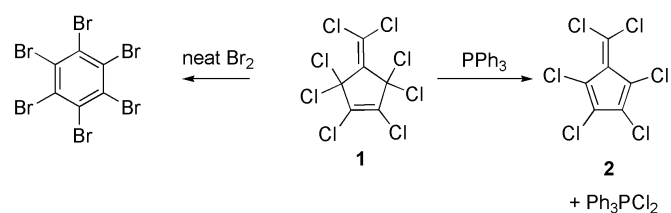
In an age of growing environmental concerns, chlorinated solvents are increasingly becoming restricted in their use and supply, and in this regard HCP is no exception. The price of HCP has risen dramatically in recent years and a 2.5 litre bottle of HCP can easily cost *ca* fifty times that of the equivalent volume of tetrahydrofuran. Original preparations of UCl_4 make no mention of recycling HCP, and given that the commonly employed ratio of UO_3 to HCP is 10 g to 100 ml (a 1:23 molar ratio), it is not sustainable to use and discard 100 ml of HCP per 10 g reaction. We therefore considered it worthwhile to assess the recyclability of HCP since only a small molar fraction should be consumed during the preparation of UCl_4 .

The HCP mother liquor is usually filtered away from the UCl_4 precipitate and collected in a flask. We have found that fractional distillation of the HCP mother liquor at reduced pressure affords three fractions. Distillation at 10 mbar and 35–36 °C affords the first

low-boiling fraction, adjustment to 10 mbar and 46–48 °C affords the second fraction, and finally distillation at 6 mbar and 69–71 °C affords the third fraction. The latter fraction is found by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy to be essentially pure HCP which can be recycled for future use (90 ml recovered from 200 ml of HCP). Indeed, interestingly we find that the use of recycled HCP results in reactions with UO_3 or UO_2Cl_2 with significantly reduced or absent exotherms. This is certainly desirable from a safety perspective, though we recommend that reactions are still closely monitored through the induction period as a precaution. Importantly, there is no reduction in the respective yields of UCl_4 when the recycled HCP is used, irrespective of whether UO_3 , $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, or UO_2Cl_2 are used and the HCP can be recycled several times. NMR spectroscopic analysis of as-supplied HCP usually reveals, in addition to the three resonances attributable to HCP, a fourth resonance. We have been unable to identify this compound and note that it is not separable by distillation in the first instance, but we find that after reaction to produce UCl_4 and distillation it is absent. It is tempting to speculate that this species may have a role to play in the exotherm, but we cannot unequivocally state this to be the case on the basis of the evidence to hand. The first two fractions to distill out appear to be acid chlorides but we have not pursued their characterisation any further.

Once the first three fractions of the HCP mixture are distilled away, which represents the majority of the material, a small oily residue remains. This material crystallises when stored at room temperature. Alternatively, standing of the HCP/dichloromethane washings from the work-up of the UCl_4 affords colourless crystals of the same material. We analysed this material and found it to be the 2,5-dichlorohexachlorofulvene compound $\text{Cl}_2\text{C}=\text{C}(\text{CCl}_2\text{CCl}_2)_2$ (**1**). This compound formally arises from the combination of two HCP molecules that have each lost two Cl atoms, one from the 1- and 3-positions and in the other from the 2- and 3-positions. The identity of this compound was confirmed by X-ray crystallography as **1** has previously been structurally characterised from a radical-induced cyclisation reaction of perchloro-hexatriene.⁶

The isolation of **1** is surprising, because the reaction of HCP with uranium oxides is usually rationalised on the basis of producing acid chloride by-products and chlorine, whereas there is no oxygen incorporation in **1**. Instead, Cl atoms have been removed, possibly generating radicals which would account for the formation of **1** and the widely accepted radical nature of the initiation of the UO_3/HCP reaction.



Scheme 1. Reactions of **1** to give **2** and C_6Br_6 .

With **1** in hand we briefly surveyed its reactivity, in part to confirm its formulation, Scheme 1 (see below and the ESI for further details). We reasoned that **1** could be readily converted to the hexachlorofulvene derivative **2** with concomitant release of Cl_2 , so that **1** may be classed as a 'bottleable' source of chlorine. Thus, reaction of **1** with the halide-trap PPh_3 in refluxing toluene affords quantitative conversion to Ph_3PCl_2 (by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, $\delta_{\text{p}} = -45 \text{ ppm}^7$). Upon cooling, colourless crystals deposit in the NMR tube and these were confirmed by X-ray crystallography to be

the known hexachlorofulvene compound **2**.^{7,8} We also briefly explored the reactions of **1** and **2** towards the dienes butadiene and cyclopentadiene but no reactions occur, which may be attributed to steric blocking, though the lack of reactivity may also be attributable to a mis-match between frontier orbital HOMO-LUMO energies of these dienes and dieneophiles. Compound **1** reacts with KMnO_4 to afford a complex mixture of products that we have been unable to conclusively identify. However, surprisingly, **1** does not react with bromine water, a classic test for the presence of alkenes, but it does react slowly with neat Br_2 over a few weeks to afford red crystals in almost quantitative yield that were identified as hexabromobenzene (see the ESI for full details).

To summarise, whereas most of the literature regarding the production of UCl_4 has previously focussed on the use of UO_3 and hexachloropropene, this work confirms that U_3O_8 , $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and UO_2Cl_2 provide alternative uranium oxide sources to prepare UCl_4 . Given the general difficulties in sourcing UO_3 this could provide valuable alternatives to preparing one of the most important uranium starting materials, UCl_4 . We have also shown that the hexachloropropene may be recycled, thus mitigating to some extent the expensive nature and sustainability of this increasingly difficult to source reagent. This work has also identified a previously unrecognised chloro-fulvene reaction product from the reductive chlorination of uranium oxides by hexachloropropene, which affords insight into the complex chemistry that operates in these reactions, and the fulvene itself exhibits some interesting chemistry.

Experimental

Preparations

UCl_4 . Method A: UCl_4 was prepared by an adaptation of the literature methods⁴ substituting U_3O_8 for UO_3 . Portionwise addition of U_3O_8 (5 g, 5.94 mmol) to hexachloropropene (50 ml) at high temperatures afforded firstly a red solution, and over the period of 8-10 hrs green UCl_4 precipitated. After filtration, the UCl_4 was refluxed in freshly distilled SOCl_2 overnight. The SOCl_2 was removed *in vacuo* and the residue washed with copious dichloromethane and dried *in vacuo* to yield UCl_4 as a green solid (1.24 g, 55%). **Method B:** $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (20 g, 39.8 mmol) and hexachloropropene (200 ml) were placed in a 1 litre round bottom flask equipped with 3 condensers stacked in line and a nitrogen supply. The mixture was heated to reflux accompanied by a violent exotherm and the liberation of a brown gas. The flask was lifted away from the heat momentarily to allow the exotherm to subside then heating was resumed overnight. As the reaction progresses a yellow precipitate forms which then redissolves and over the period of 8-10 hrs UCl_4 precipitates as a green solid. The solids were collected by filtration, washed with copious dichloromethane and dried *in vacuo* to yield UCl_4 as a green solid (15.11 g, 100%). **Method C:** $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (20 g, 39.8 mmol) was dissolved in concentrated aqueous 12M HCl (100 ml) in a 1 litre round bottom flask to give a clear yellow solution. The mixture was evaporated to dryness and the resulting yellow solid was suspended in hexachloropropene (200 ml). The flask was equipped with 3 condensers stacked in line and a nitrogen supply. The mixture was heated to reflux until the exotherm was observed, heat was removed to allow the exotherm to subside then the reaction was heated overnight. During the course of the reaction the yellow solid dissolves and green UCl_4 is precipitated. The solids were collected by filtration, washed with copious dichloromethane and dried *in vacuo* to yield UCl_4 as a green solid (13.91 g, 92%).

Recycling HCP. After the overnight reflux to make UCl_4 from methods B or C the green-brown liquor (~200 ml) was filtered into a clean 500 ml round bottom flask. Using a single length vacuum-jacketed Vigreux distillation apparatus and an ice cooled receiving flask the distillation was commenced. The first two fractions collected at 35-36 °C and 10 mbar and 46-48 °C and 10 mbar and were isolated as clear colourless liquids and were discarded. The fraction collected at 69-71 °C and 6 mbar was neat hexachloropropene and was isolated as a clear colourless liquid (90 ml, 45 %). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) for hexachloropropene: δ 131.9, 127.2, 92.7 ppm.

1. Compound **1** crystallises from cooling of the residue that remains after the HCP distillation. Alternatively, slow evaporation of the dichloromethane washings from any of the oxide preparations affords **1** as large colourless crystals. $^{13}\text{C}\{^1\text{H}\}$ NMR (155 MHz, CDCl_3) for **1**: δ 137.1, 135.9, 135.0, 81.4 ppm. FTIR ν (cm^{-1}) for **1**: 1638, 1602 (s, C=C), 1208 (s, C-Cl), 1166, 934, 797, 659, 628 (s, C-Cl).

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