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Tracking SF₅I in the Iodopentafluorosulfanylation of AlkynesThi Mo Nguyen,^[a] Claude Y. Legault,^{*[b]} Nicolas Blanchard,^[c] Vincent Bizet,^{*[c]} and Dominique Cahard^{*[a]}^[a] T.M. Nguyen, Dr D. Cahard

CNRS, Univ Rouen Normandie, INSA Rouen Normandie, Normandie Univ, COBRA UMR 6014, INC3M FR 3038

F-76000 Rouen, France

E-mail: dominique.cahard@univ-rouen.fr<https://www.lab-cobra.fr/>^[b] Pr C.Y. Legault

Centre in Green Chemistry and Catalysis, Department of Chemistry, University of Sherbrooke

Sherbrooke, Québec J1K 2R1, Canada

E-mail: claudel.legault@usherbrooke.ca<https://cyl.recherche.usherbrooke.ca/>^[c] Dr N. Blanchard, Dr V. Bizet

Université de Haute-Alsace, Université de Strasbourg, CNRS, LIMA, UMR 7042, 68000 Mulhouse

E-mail: vbizet@unistra.fr<https://bsm.unistra.fr/>

Abstract: In the vibrant field of SF₅ chemistry, SF₅X reagents (X = F, Cl, Br) are at the heart of current investigations in radical pentafluorosulfanylation reactions. Alas! SF₅I is the missing link whose existence has not been reported albeit its potential as SF₅ donor. We herein report the formal addition of the hitherto unknown SF₅I reagent to alkynes by means of a combination of SF₅Cl / KI / 18-crown-6 ether. The exclusive regio- and stereoselective synthesis of unprecedented (*E*)-1-iodo-2-(pentafluoro-λ⁶-sulfanyl) alkenes was achieved. A consensus was reached through computational and mechanistic studies for the realistic formation of SF₅⁻ anion but not SF₅I in solution and the rational involvement of SF₅⁻ and iodine radicals in the iodo pentafluorosulfanylation reaction.

Introduction

The sulfur pentafluoride SF₅ group is one of the rare functional groups in the present-day investigation allowing to broaden out our perspective in organic chemistry. Outstanding physico-chemical properties, unique spatial charge distribution and potential uses in the next generation of fluorochemicals provide the rationale for current frenetic craze.^[1] State-of-the-art construction of SF₅-containing molecules is so far limited to the direct introduction of SF₅ by means of SF₅X (X = Cl, Br) or SF₆ reagents yet hampered by the poor availability of SF₅X^[2] and the notoriously inertness of SF₆^[3] that are serious impediments to global wider development of SF₅ chemistry. Otherwise, literature flourished with reports on building the SF₅ motif from thiols or disulfides under oxidative fluorination to furnish a wide variety of SF₅ (het)aromatic building blocks.^[4] However, this approach was not extended to aliphatic molecules, which are better suited to conduct direct introduction of SF₅.^[5] Free radical chain pentafluorosulfanylation has long been restricted to specialized photochemical processes or to reactions run in steel autoclaves till the major breakthrough by Dolbier and co-workers in 2002 who established the low-temperature Et₃B/O₂ procedure with SF₅Cl.^[6] Two decades after, this method is still the most applied although efforts were directed toward alternative activation modes (amine-borane complexes,^[7] electron donor-acceptor complex,^[8] 20W blacklight compact fluorescent lamp^[9]). It can be noted that in absence of activation, except by natural light, or in the dark the reaction yields are significantly lower.^[3d, 10] While SF₅Cl reacts essentially through free radical chain addition with rare exception leading to chlorofluoro undesired products through ionic species,^[11] its more reactive analogue SF₅Br can produce electrophilic Br⁺ and SF₅⁻ but here again the anion decomposes

into fluoride and SF₄ ending up with bromofluoro products probably via a bromonium bridge.^[12] Rare examples of radical bromo pentafluorosulfanylations were nevertheless reported in steel bomb,^[13] in Pyrex vessel under pressure and sunlamps^[14] or with the aid of triethylborane.^[12c-d, 15] We surmised that amplifying the electronegativity difference in the pseudo-halogen structure SF₅X with the less electronegative halogen *i.e.* iodine we should favour ionic reactions over radical processes ($\Delta\chi = 1,15$ in SF₅I versus 0,85 in SF₅Br and 0,65 in SF₅Cl).^[16] Unfortunately, a literature survey revealed that the synthesis of SF₅I has not been reported.^[19, 17] It was said in the literature that “one can imagine that SF₅I might be very difficult to isolate and characterize”.^[18] If available SF₅I would be a potential source of SF₅ anion; however, rapid dissociation into the weak Lewis acid SF₄ does not argue in favor of the development of the SF₅ anion chemistry and taming this anion represents a great challenge (Figure 1A). Instead, halogen exchange,^[19] deoxyfluorination^[3d, 20] and oxidative fluorination^[21] are the reactions reported with the aid of SF₅ anion-containing species (Figure 1B). Salts containing the SF₅ anion could also afford SF₅Cl under oxidative chlorination by trichloroisocyanuric acid^[3d, 22] or chlorine^[23] (Figure 1B). Admittedly, fluoride transfer by means of SF₅ anion-containing salts prevents direct manipulation of hazardous gaseous reagents, but on the other hand SF₄ or molecular sulfur are generated as side-products. Pr Günter Haufe wrote in 2020 “the SF₅⁻ anion could not be used for the introduction of SF₅ into organic substrates yet” and that is still true today.^[5] Our aims are to

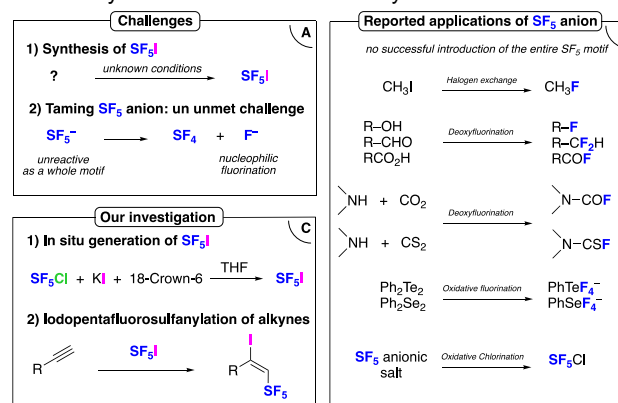
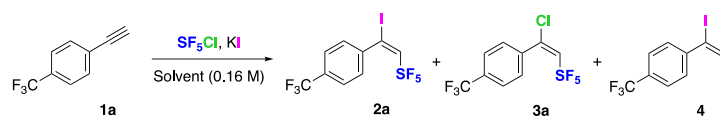


Figure 1. Pentapentafluorosulfanyl iodide: from curiosity to reality. A) challenging problems in fluorine chemistry. B) current uses of SF₅ salts. C) our contribution to a better understanding of SF₅ chemistry.

Table 1. Selected optimization reactions.



| Entry | SF ₅ Cl (eq) | Iodide source (eq) | Cryptand (eq) | Solvent | Time, temp. | Conversion | Yields ^[a] | | |
|-------|-------------------------|---------------------------------|------------------------|---------|-------------|--------------------|------------------------|----|----|
| | | | | | | | 2a | 3a | 4 |
| 1 | 2 | KI (4) | | Hexane | 2 h, -40 °C | 51 | 3 | 0 | 48 |
| 2 | 2 | KI (4) | | THF | 2 h, -40 °C | 90 | 62 | 0 | 28 |
| 3 | 3 | KI (4) | | THF | 2 h, -78 °C | 44 | 44 | 0 | 0 |
| 4 | 3 | KI (4) | 18-crown-6 ether (2) | THF | 2 h, -78 °C | 100 | 95 | 2 | 3 |
| 5 | 3 | KI (4) | 18-crown-6 ether (1) | THF | 2 h, -78 °C | 100 | 99 (85) ^[b] | 1 | 0 |
| 6 | 1.5 | KI (2) | 18-crown-6 ether (1) | THF | 2 h, -78 °C | 53 | 43 | 0 | 10 |
| 7 | 3 | KI (4) | 18-crown-6 ether (0.5) | THF | 5 h, -78 °C | 61 ^[c] | 45 | 0 | 3 |
| 8 | 3 | <i>n</i> Bu ₄ NI (4) | | THF | 2 h, -78 °C | 100 ^[c] | 3 | 94 | 0 |
| 9 | 3 | CsI (4) | 18-crown-6 ether (1) | THF | 2 h, -78 °C | 36 ^[c] | 29 | 0 | 0 |
| 10 | 3 | NaI (4) | 15-crown-5 ether (1) | THF | 2 h, -78 °C | 60 | 32 | 0 | 28 |
| 11 | 3 | KI (4) | Triglyme (10) | THF | 5 h, -78 °C | 57 | 57 | 0 | 0 |
| 12 | 3 | KI (4) | Kryptofix 2.2.2 (1) | THF | 2 h, -78 °C | 10 | 5 | 5 | 0 |

[a] Yields determined by ¹⁹F NMR of crude mixtures with PhSCF₃ as internal standard and by GC-MS. [b] Isolated yield. [c] The gap between conversion and yield of **2a+3+4** is due to the presence of α -SF₅ carbonyl side-products (3-13%).

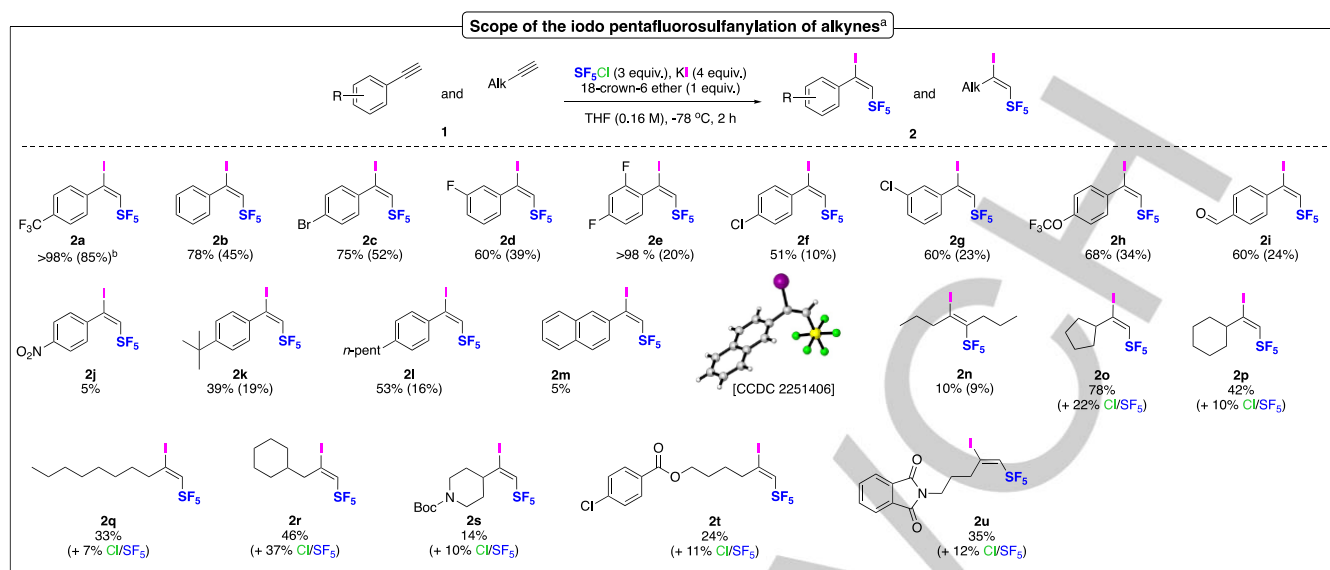
prepare the hitherto unknown SF₅I reagent, to study its reactivity in the novel reaction of iodopentafluorosulfanylation of alkynes and to get insights in the reaction mechanism (Figure 1C).

Results and discussion

At the onset, we speculated that halogen metathesis in SF₅Cl with an iodide source such as potassium iodide would provide SF₅I, pretty much the same as for *in-situ* generation of Me₃SiI from Me₃SiCl to multiply its reactivity in preparation of silyl enol ethers.^[24] We chose 4-(trifluoromethyl)phenylacetylene **1a** as model alkyne for addition of *in-situ* generated SF₅I and for easy tracing of the reaction progress by ¹⁹F NMR. Since hexane is most frequently used as solvent for reactions involving SF₅Cl, we prepared and titrated a solution of SF₅Cl in hexane that was added to **1a** in hexane and KI at -40 °C to maintain SF₅Cl (bp -21 °C) in solution. These conditions afforded a poor yield of the desired (*E*)-1-iodo-2-SF₅ alkene **2a** (3%) along with undesired diiodo alkene **4** as main product (Table 1, entry 1). Remarkably, the iodopentafluorosulfanylation product **2a** could be obtained predominantly by carrying out the reaction in the more polar THF solvent (Table 1, entry 2). A limited stability of SF₅Cl in THF was noticed during storage at -20 °C with the polymerization of THF forming a gel within 12 h at -20 °C. This pseudo-halogen catalyzed polymerization ceased at -78 °C allowing storage and use of SF₅Cl solutions for weeks. Hence, we selected the -78 °C temperature to carry out the generation of SF₅I and its subsequent addition onto alkyne **1a**. The use of 3 equivalents of SF₅Cl (Table 1, entry 3) gave a moderate conversion of **1a** but pleasingly only

the desired product **2a** was observed; nor the chloro SF₅ addition product **3a** nor the diiodo alkene **4** were detected. Then, we assumed that adding 18-crown-6 ether as a cryptand of the potassium cation would further enhance the halogen metathesis by increasing the nucleophilicity of iodide ions. We were delighted to get full conversion within 2 h with quasi exclusive formation of the desired (*E*)-1-iodo-2-SF₅ alkene **2a** in the presence of one equivalent of crown ether (Table 1, entries 4,5). Analytically pure **2a** was obtained after chromatography in 85% yield as a single *E* stereoisomer (as confirmed by X-ray diffraction, see Scheme 1). Deviation of the optimized conditions in attempts to reduce either the quantity of SF₅Cl or of 18-crown-6 ether gave only moderate conversions (Table 1, entries 6,7). We tested other iodide sources, *n*Bu₄NI, CsI, NaI but none of them gave satisfactory results; for example, *n*Bu₄NI did not allow the iodopentafluorosulfanylation and the (*E*)-1-chloro-2-SF₅ alkene **3a** was obtained almost exclusively highlighting the crucial role of potassium iodide (Table 1, entries 8-10). Other cryptands, triglyme and Kryptofix 2.2.2, also substantially underperformed in the iodopentafluorosulfanylation reaction (Table 1, entries 11, 12). Overall, we have succeeded in the concomitant addition of I and SF₅ onto alkynes as we would expect from manipulating SF₅I reagent with suppression of competitive chloropentafluorosulfanylation and other side-reactions. Moreover, the structure assignment of (*E*)-1-iodo-2-SF₅ alkenes **2** confirmed a full regio- and stereoselective reaction.

Building on this preliminary exciting result, we explored the scope of alkynes as matched reaction partners (Scheme 1). All products **2** are new compounds that feature the novel 1-iodo-2-SF₅ alkene



Scheme 1. Iodo pentafluorosulfanylation of aryl- and alkyl alkynes by means of the combination $\text{SF}_5\text{Cl}/\text{KI}/18\text{-crown-6}$ ether. Notes: [a] Yield determined by ^{19}F NMR of the crude mixture with PhSCF_3 as internal standard and by GC-MS. [b] Isolated yield.

motif. Aromatic alkynes featuring inductively withdrawing (–I) groups (CF_3 , OCF_3 , and halogens) as well as phenyl acetylene (**1a–h**) gave yields of **2a–h** in the range 51 to $>98\%$. Particular attention must be paid to the isolation of pure products because of the high volatility or easy sublimation of the products at all stages of the purification; discrepancy between calculated yields by ^{19}F NMR or GC and yields of isolated pure products can be noted. Importantly, **2b** was obtained as a single reaction product whereas using the Dolbier radical conditions with SF_5Cl ended up with a mixture of chlorinated analogue **3b** and a 2:1 adduct (phenylacetylene / SF_5Cl , 64:36)^[6, 12c] highlighting the greater selectivity of the iodopentafluorosulfanylation. Aldehyde **2i** was also obtained in a moderate yield, whereas strong (–M) NO_2 substituent in **1j** inhibits the reaction probably by decreasing the electron density of the alkyne. Inductively donating (+I) alkyl groups afforded moderate yields of **2k, l** whereas fused aryl system in **1m** gave a poor 5% yield of the desired products. The *E* configuration of **2m** was ascertained by X-ray diffraction (CCDC 2251406)^[25] and we assumed that all other products have the same *E* configuration as they share the same NMR spectral characteristics. One internal alkyne featuring two alkyl groups gave product **2n** in 10% yield. Better yields were reached with terminal alkyl alkynes that afforded alkyl 1-iodo-2- SF_5 alkenes **2o–u** featuring simple (cyclo)alkyl groups or functional groups. However, alkyl alkynes are more prone than aryl alkynes to react directly with SF_5Cl ,^[5, 6] causing competitive chloro/iodo pentafluorosulfanylation reactions. Indeed, mixtures of the desired 1-iodo-2- SF_5 alkenes and undesired 1-chloro-2- SF_5 addition products are often obtained; besides, chloro and iodo compounds cannot be separated by column chromatography due to similar polarities.

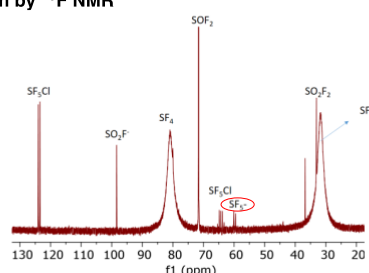
At this stage of our investigation, we can state that we have formally tamed SF_5I reagent in the iodopentafluorosulfanylation of alkynes. Yet, going into mechanistic details would provide us with a clearer overview of the reaction pathway. Our initial hypothesis was that SF_5I could be a donor of electrophilic iodine and the SF_5 anion due to the sufficiently different electronegativity of iodine

and the SF_5 motif. A possible iodonium intermediate was envisaged similarly to the proposed bromonium intermediate by Gard.^[12] Obtaining insights on the nature of intermediates, whether ionic or radical processes, is precisely the mechanistic point of elucidation on which we will now focus. Experimental observations and design experiments were carried out along with computational DFT studies.

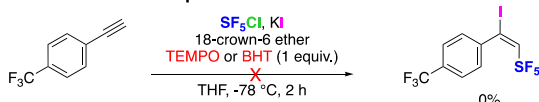
A first visual information of the reaction is the reddish colour that we attributed to iodine and/or iodine monochlorine as the color faded by quench with sodium thiosulfate. The ^{19}F NMR spectrum of the reaction mixture, in the absence of alkyne, was recorded and revealed a doublet at 60 ppm for the four equatorial fluorine atoms of SF_5 (Figure 2A) indicating the formation of the SF_5 anion. The expected quintet at ca 89 ppm was masked by a broad signal of SF_4 , which is dissociated product of SF_5^- anion.^[26] On the other hand, radical inhibition experiments were performed with TEMPO and BHT that efficiently inhibited the reaction, supporting radical process might be involved (Figure 2B). The reaction run in complete darkness still produced the (*E*)-1-iodo-2- SF_5 alkene **2a** (67%) without chloro alkene **3a** but with significant amount of diiodo alkene **4** (Figure 2C) supporting once again the formation of molecular iodine *in-situ*. By treatment of diiodo alkene **4** under the optimal reaction conditions, we demonstrated that this side-product is not an intermediate toward **2a** as it was postulated in some sulfenylation reactions (Figure 2C).^[27] Cyclopropylacetylene as a radical clock was reacted under our conditions and under Dolbier conditions with BEt_3 ; only the latter experiment gave the SF_5 -substituted allene through radical clock rearrangement (monitoring by ^{13}C NMR) (Figure 2D). Our conditions resulted in the formation of both iodo- and chloropentafluorosulfanylated products as already observed with other alkyl alkynes (see Scheme 1). These experiments are not conclusive of an ionic mechanism under our reaction conditions nor of a fast trapping of vinylic radical with halogen (I and Cl). Based on this information, it is not possible to conclude with a high degree of certainty that the mechanism is ionic or radical, as we have divergent data. Computational DFT studies were conducted to shed light on the species involved in the

A) Looking for SF_5^- anion by ^{19}F NMR

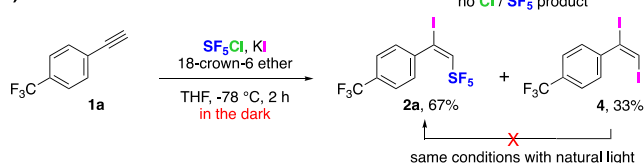
SF_5Cl in THF-D8
+ KI + 18-crown-6
-78 °C, 30 min
 ^{19}F NMR recorded at rt



B) Radical inhibition experiments



C) Reaction in the dark



D) Radical clock experiments

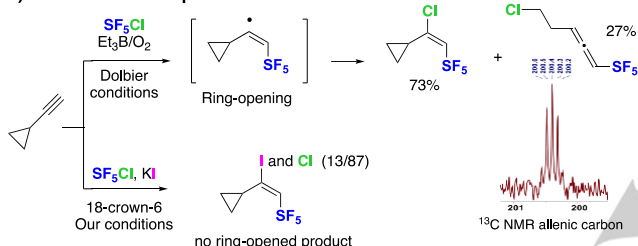


Figure 2. Experiments conducted for mechanistic study.

iodopentafluorosulfanylation reaction. Model substrate **1a** was used for the study. The geometries were optimized at the M062X/Def2TZVP(Def2TZVPD(ECP) for iodine) level, using SMD implicit solvation model for tetrahydrofuran (See Supporting Information for complete details). The free energies are computed for a state of 193.15 K (-78 °C) and 1 mol/L and are reported in kJ/mol. The first aspect we explored was the reactivity of SF_5Cl with the iodide anion, a key component of the newly developed reaction conditions. The overall reaction was described as six specific states, illustrated in Figure 3.

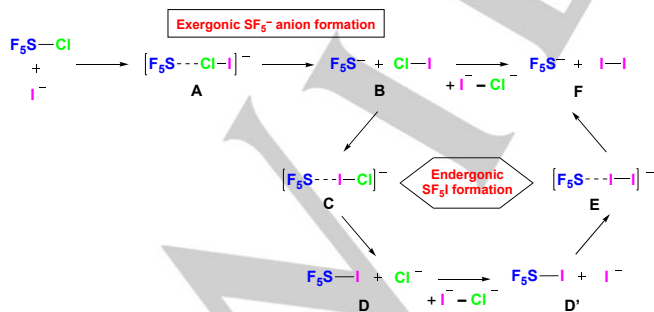


Figure 3. Steps of reaction of SF_5Cl with iodide anion. The counterion is omitted for simplicity.

These halogen atom exchanges were expected to be facile (i.e. fast) steps; consequently, we focused solely on the thermodynamics of these processes. Despite this simplification,

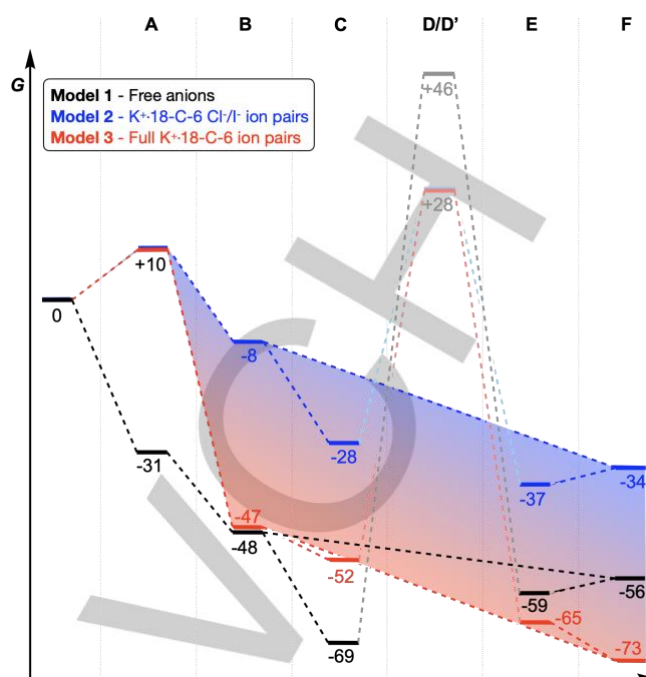


Figure 4. Energy diagrams of reaction of SF_5Cl with iodide anion (free energies in kJ/mol).

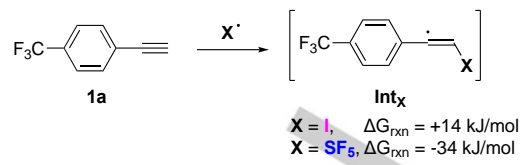
modelling these species is challenging due to the potential effect of the iodide anion counterion. Consequently, we modelled the key steps of the processes using three different models: 1) full counterion dissociation; 2) exclusive counterion pairing with halide anions (Cl^- and I^-); 3) full ion pairing for all anionic species. For the sake of providing realistic cationic species, the potassium cation (K^+) was modelled as a complex with crown ether (18-C-6). The superimposed energy diagrams of the three models are illustrated in Figure 4. The optimal experimental conditions, involving crown ether and KI would logically fall within models 2 and 3. Indeed, the partial (model 2) and full (model 3) ion pairing diagrams (blue and red lines, respectively) support a similar behavior, in which the initial association of the iodide anion is slightly endergonic (state A), followed by exergonic release of ICl and SF_5^- anion (state B). From this point, ICl can reassociate to SF_5^- anion leading to the more stable state C. Conversely, free ICl could react with the excess iodide anion to directly generate I_2 , which would essentially result in state F. Dissociation of chloride anion would lead to the generation of SF_5I (state D and state D') by anion exchange. The process is endergonic and its overall free energy profile ($\Delta G_{C-D} = +(56-80)$ kJ/mol, $\Delta G_{E-D} = +(65-93)$ kJ/mol) does not strongly support its existence in any relevant amount at -78 °C. States E and F are either slightly endergonic (model 2) or exergonic (model 3) for both ion pairing models, suggesting a facile release of molecular iodine (I_2) in solution, in line with experimental observations.

In contrast, the free anion model (1), which could represent the conditions involving a counterion such as a tetrabutylammonium cation (TBA^+), provides a different energetic profile. Indeed, access to SF_5I in solution would be clearly impossible due to the large thermodynamic preference for state C, as well as the larger endergonicity to move toward state D. Furthermore, while models 2 and 3 thermodynamically favor states E and F, leading to a preferential formation of molecular iodine, model 1 would favor preferential presence of ICl (state C) in solution. At this point, the

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main conclusions are as follow: Formation of SF_5^- anion is probable, with concomitant presence of I_2 in the mixture. With a non-complexing cation (e.g. TBA^+), ICl would instead be present. Consequently, we next investigated the potential activation of

Table 2. Computed energetics of dihalogen activation and nucleophilic addition on alkyne **1a** (free energies in kJ/mol).



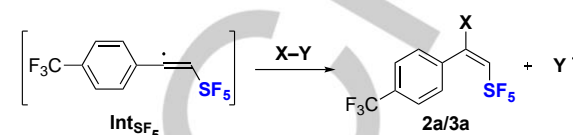
| IX | Nu | ΔG (1a:IX) | ΔG^\ddagger ($\text{TS}^\ddagger_{\text{Ar}}$) | ΔG^\ddagger ($\text{TS}^\ddagger_{\text{H}}$) |
|--------------|--|--------------------|--|---|
| ICl | SF_5^- | -4 | 59 | 65(+6) |
| I_2 | SF_5^- | +5 | 85 | 87(+2) |
| I_2 | $\text{SF}_5^- \cdot \text{K} \cdot 18\text{-C-6}$ | +5 | 91 | 93(+2) |

alkyne **1a** with I_2 and ICl , with subsequent nucleophilic attack of SF_5^- anion. The results are summarized in Table 2. In both cases, the predicted regioselectivity, as expected for an aryl-conjugated alkyne, is not in line with the observed exclusive formation of product **2a**. Indeed, calculations suggest a very slight preference for adding SF_5^- anion on the carbon bearing the aromatic group. Furthermore, the computed activation barriers are too high, at least for I_2 , for a process completed over 2 hours at -78°C ($\Delta G^\ddagger = 85 \text{ kJ/mol}$ ($t_{1/2}[1\text{M}] = 4.0 \times 10^6 \text{ h}$)). We envisioned that tight ion pairing could occur, and that $\text{K} \cdot 18\text{-C-6}$ complex could be involved in the transition structures, having both an activating and regioselectivity-inducing effect. These tight ion pairs transition structures were thus also computed (Table 2, last line). The activation barriers were higher (i.e. no activation effect) and regioselectivity remained almost identical for molecular iodine, the energetics for ICl were thus not computed. Direct addition (i.e. without activation) of the SF_5^- anion on the alkyne could lead to the right regioisomer but was found to be impossible as no stable addition adduct could be optimized. Finally, we look at the activation of alkyne with SF_5Cl and SF_5I . The Lewis acidity of SF_5Cl is too low to find an actual activation complex. In the case of SF_5I , the association is possible, but lead to the same, inverse, regioselectivity profile found for I_2 and ICl . The computational results thus suggest that an anionic mechanism is not operative under the given experimental conditions.

At this point, we thus turned to potential radical pathways that could lead to the observed product (**2a**). The energy diagrams in Figure 4 point toward the formation of molecular iodine in solution, which could potentially lead to the formation of iodine radical ($\text{I}\cdot$) in the presence of light. Furthermore, the fact that the SF_5 group is bound to the terminal carbon of the alkyne substrate **1a** suggests that the process involves the addition of the $\text{SF}_5\cdot$ radical on the former. We thus computed the thermodynamics of adding $\text{I}\cdot$ and $\text{SF}_5\cdot$ radicals to **1a**. The addition of $\text{SF}_5\cdot$ was found to be exergonic, while the addition of $\text{I}\cdot$ was found to be slightly endergonic (Scheme 2). These results suggest that indeed an efficient radical chain is foreseeable with $\text{SF}_5\cdot$, even in the presence of iodine radical ($\text{I}\cdot$).

Scheme 2. Energetics of addition of radicals to alkyne **1a**.

Table 3. Computed energetics of halogen abstraction (free energies in kJ/mol).



| Entry | X-Y | Product | X | Y | ΔG_{rxn} |
|-------|------------------------|-----------|----|---------------|-------------------------|
| 1 | SF_5Cl | 3a | Cl | SF_5 | -83 |
| 2 | SF_5I | 2a | I | SF_5 | -73 |
| 3 | I_2 | 2a | I | I | -51 |
| 4 | ICl | 2a | I | Cl | +10 |
| 5 | ICl | 3a | Cl | I | -114 |

An efficient radical process would also require an exergonic final step. We computed the thermodynamics of Cl/I abstraction from different species potentially in solution, they are illustrated in Table 3. The common species could all provide an efficient turnover of the radical chain (Table 3, entries 1-3). The fact that chlorine abstraction on SF_5Cl is highly exergonic (Table 3, entry 1) suggests that either: a) SF_5Cl is consumed extremely rapidly in the initial halogen metathesis process (Figure 3); b) iodine abstraction on I_2 is kinetically favored, since product **2a** is exclusively formed under the optimal conditions. Furthermore, the thermodynamics computed for ICl could also rationalize the interesting result obtained when TBAI is used instead of KI (Table 1, entry 8). Indeed, the abstraction of the chloride atom of ICl with radical intermediate Int_{SF_5} would be greatly favored based on thermodynamics (Table 3, entry 5 vs 4).

One question remains: How is the SF_5 radical formed? The fact that the diiodo compound **4** is observed in 33% yield when the reaction is performed in the dark (Figure 2C) suggests that light is at least partially responsible to initiate the chain reaction; under darkness, the ionic process involving activation of **1a** with I_2 , followed by nucleophilic addition of an iodide anion, could be kinetically competitive with the radical chain. With that in mind, the most probable initiator is thus photochemically-generated iodine radical ($\text{I}\cdot$). One could envision direct halogen abstraction on SF_5Cl ; chlorine abstraction on SF_5Cl is found to be endergonic but energetically accessible (+32 kJ/mol). Alternatively, SF_5^- anion is expected to be found in larger quantities in solution (Figure 4). Single electron transfer from this species could result in the generation of the putative radical chain initiator, the thermodynamics of SET were computed and summarized in Table 4. The oxidation of SF_5^- anion is difficult, the SET being endergonic in all cases. Only the $\text{I}_3\cdot$ radical, which can realistically be formed in solution from $\text{I}\cdot$ and I_2 ($\Delta G = -5 \text{ kJ/mol}$) could provide a small enough free energy cost to operate under the reaction conditions. This cost could be compensated by the exergonicity of addition of $\text{SF}_5\cdot$ radical on alkyne substrates (Scheme 2).

Table 4. Computed energetics of single electron transfer.

| Entry | X ⁿ | ΔG _{rxn} (kJ/mol) |
|-------|-----------------------------|----------------------------|
| 1 | I ₂ | +151 |
| 2 | ICl | +144 |
| 3 | SF ₅ Cl | +151 |
| 4 | SF ₅ I | +94 |
| 5 | I [·] | +80 |
| 6 | I ₃ [·] | +29 |

At this time, we can thus propose that the most probable reaction mechanism involves the following steps: 1) generation of SF₅⁻ anion and I₂ through the reaction of SF₅Cl with iodide anion; 2) generation of iodine radical (I[·]), possibly by photodissociation; 3) generation of the SF₅ radical through either SET oxidation of SF₅⁻ anion by I₃[·] radical, or halogen abstraction on SF₅Cl by I[·], respectively; 4) radical chain by addition of SF₅ radical on alkyne substrates, followed by regeneration of the iodine radical.

Conclusion and perspectives

This work was motivated by the quest of the hitherto unknown reagent SF₅I. From a methodological point of view, we formally succeeded in the iodopentafluorosulfanylation of alkynes. It is a novel chemical reaction operating under mild reaction conditions, free of activation such as Et₃B/O₂ or specific light irradiation. By experiments and DFT calculations, we gathered a body of corroborating evidence that SF₅⁻ anion is probably formed in solution while access to SF₅I would be thermodynamically impossible. Although SF₅⁻ anion is formed, an anionic iodopentafluorosulfanylation is not operative as it would lead to the opposite regioisomer. Arguably, the reaction most probably proceeds through a radical mechanism by *in-situ* generation of SF₅ and iodine radicals. Taken together, our survey provides important information for future investigation in this vibrant field. Further developments of direct iodopentafluorosulfanylation to other π-systems as well as post-functionalizations are under investigation in our laboratories.^[28]

Experimental Section

General procedure for the synthesis of I / SF₅ products:

Caution: SF₅Cl is highly toxic. It should only be manipulated in a well-ventilated fume hood. Under N₂ atmosphere, into a dried microwave vial equipped with a stirring bar, were added potassium iodide (4 equiv.), 18-crown-6 ether (1 equiv.) and the alkyne in distilled THF (0.16 M). The glass tube was sealed, followed by cooling to -78 °C. Then, into the mixture was added a freshly prepared solution of SF₅Cl in THF 1.5 M (3 equiv.). The reaction mixture was stirred at -78 °C in the natural light for 2 hours. The mixture was further quenched at -78 °C with saturated aq. Na₂S₂O₃ and was extracted with Et₂O twice. The organic phase was dried with Na₂SO₄ and was concentrated in vacuo. ¹⁹F NMR and GC-MS analyses were performed to calculate the conversion and products ratio. The crude product was purified by column chromatography using 100% pentane as eluent to afford the desired product. Products are volatile and solids easily sublimate. A special care is required during solvent evaporation on a rotavapor.

Supporting Information

The authors have cited additional references within the Supporting Information.^[29-38]

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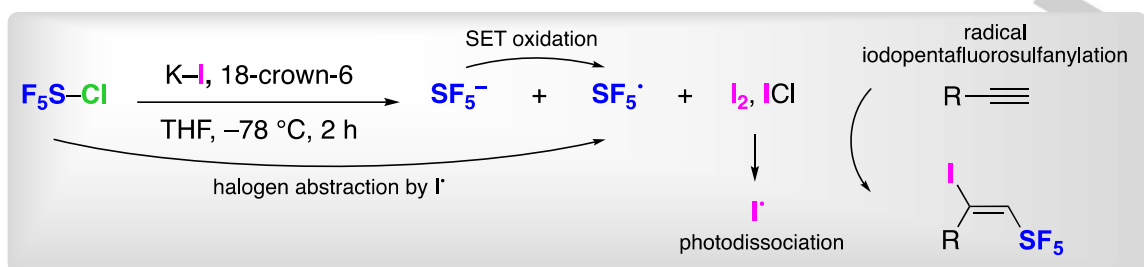
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Keywords: pseudo-halogen • pentafluorosulfanylation • iodination • alkyne • radical reaction

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Tracking SF₅I in the Iodopentafluorosulfanylation of Alkynes

The iodopentafluorosulfanylation of alkynes was made possible through formal manipulation of SF₅I. This method requests the combination SF₅Cl / KI / 18-crown-6 in THF at low temperature. Mechanistic investigations by DFT revealed ionic pathway is not viable and radical mechanism is preponderant.