

Predicting the reactivity of fluorinated compounds with copper using semi-empirical calculations

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Abstract

Both electron affinities and LUMO energies have been shown to be useful predictors of the reactivity of a series of fluorinated halides with copper. They were calculated using the semi-empirical PM3 method. © 2001 Elsevier Science B.V. All rights reserved.

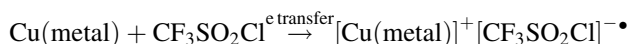
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1. Introduction

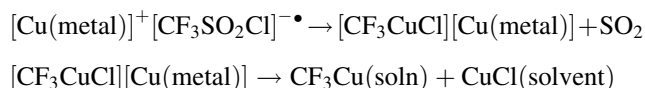
The generation of organometallic perfluoroalkyl reagents by the reaction of perfluoroalkyl halides with metals is well known and has been used to introduce perfluoroalkyl groups into organic substrates via coupling reactions [1]. Pioneering work was carried out by McLoughlin et al., who studied the reaction of metallic copper with iodotrifluoromethane and other perfluoroalkyl iodides in dipolar, aprotic solvents [2]. Although they reported that perfluoroalkyl bromides reacted under more forcing conditions they gave no details. Subsequent work has shown that the latter will react readily with more electropositive metals such as Zn and Cd. Burton et al. showed that CF₂XY (X, Y = Cl, Br) reacts with Cd and Zn to produce CF₃MX while Clark et al. demonstrated that CF₂Br₂ would react with Cu in dimethylacetamide (DMAC) to generate 'CF₃Cu' [3]. Although there appear to be no literature reports of perfluoroalkyl chlorides reacting with copper we surmised that CF₃SO₂Cl might be a sufficiently powerful electron acceptor to react with the metal since the CF₃SO₂ group is even more strongly electron withdrawing than CF₃. This indeed proved to be the case and our preliminary results have been reported earlier [4].

The electron withdrawing effects of the CF₃ or CF₃SO₂ groups render the Cl, Br and I atoms positively charged and capable of accepting electrons. Following the ideas of Chen et al. [5] we presume that all fluorinated halides react with

metallic copper via a single electron transfer (SET) reaction (see scheme below).



In the presence of dipolar aprotic solvents



During a programme to further explore the CF₃SO₂Cl/Cu system we have used semi-empirical molecular orbital calculations to rank various fluorinated halides in order of estimated reactivity for comparison with experimental data, assuming that a substrate's reactivity is determined by its ability to accept an electron from the copper metal. We report the results in this note.

For the purposes of this study electron affinity (EA) has been taken as an index directly related to the electron accepting ability of a substrate. It was defined as the difference between the calculated heats of formation of the substrate and of the corresponding radical anion having the same geometry as the neutral molecule. In other words it was assumed that in accordance with the Franck–Condon principle the electronic reorganisation following SET is much faster than nuclear rearrangement. This is slightly different from the normally accepted definition of EA as the energy difference between the lowest energy states of the substrate and the SET product. Within the limited precision of the calculations it makes little difference which is adopted.

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Tabel 1

Substrate	Electron affinity (eV)	LUMO energy (eV)	Reported reaction conditions with Cu			
			References	Solvent	Temperature (°C)	Time (h)
CF ₄	-0.40	0.49	None			
CF ₃ Cl	1.26	-0.96	None			
CF ₃ CH ₂ I ^a	1.87	-1.34	[2]	?	?	?
CF ₃ Br ^b	2.32	-2.06	[7]	HMPA ^c	130	20
CF ₂ Br ₂	2.50	-2.12	[3]	DMAC	100	0.5
CF ₃ I	2.83	-2.34	[8]	HMPA	120	2.5
C ₃ F ₇ I	3.04	-2.40	[2]	DMSO ^c , DMF ^c	120	1
FSO ₂ CF ₂ I	3.08	-2.41	[9]	DMF	60	6
CF ₃ N(NO)SO ₂ CF ₃	3.16	-2.72	[10]	CH ₃ CN/NMP ^c	Room temperature	3
CF ₃ SO ₂ Cl	3.24	-2.94	[4]	DMF	Room temperature	Fast

^a Reported yield ~10%. Reaction conditions not reported; presumably comparable with those for C₃F₇I given in the same paper.

^b Maximum reported yield ~22%.

^c HMPA, hexamethylphosphoramide; DMSO, dimethylsulfoxide; DMF, dimethylformamide; NMP, 1-methyl-2-pyrrolidinone.

For simplicity solvent effects were ignored and the molecular energy calculations were performed on the gas phase species. This may appear a rather sweeping assumption, but the experimental data used for comparison were all drawn from reactions in dipolar, aprotic solvents so this approach was considered justified, at least for the intended simple reactivity ranking.

The calculations used the semi-empirical PM3 method developed by Stewart et al. in the version provided by the commercial 'HyperchemTM' package [6]. The geometries of the structures were optimised to an energy gradient of less than 0.01 kcal, annealed via molecular dynamics, and then re-optimised to ensure that a geometry with an energy close to the global energy minimum had been found at 0 K. Table 1 summarises the results of the calculations and indicates which compounds have been reported in the literature to react with copper. Although the experiments were designed for synthetic, not kinetic, purposes, the wide range of conditions required allows a clear reactivity ranking. The examples in Table 1 have been chosen because either they can be identified as relating just to the copper reaction, or they represent the most facile reactions reported. In most cases yields are in excess of 70%, except where indicated.

The LUMO energy is the theoretical energy change in transferring an electron with zero kinetic energy to the LUMO orbital assuming that there is neither nuclear nor electronic rearrangement of the molecule in the process. Clearly this is also a measure of a molecule's ability to accept an electron and is readily calculated using PM3 so LUMO energies are also included in Table 1. The relationship between EAs and LUMO energies is discussed towards the end of the paper.

Based on the reactions reported in the literature the reactivity cut-off appears to lie between a calculated EA of 1.26 eV (CF₃Cl) and of 1.87 eV (CF₃CH₂I). Qualitatively those substrates predicted to be least reactive from their calculated EA values appear to require the more forcing conditions. The most reactive substrates are predicted to be CF₃SO₂Cl and CF₃N(NO)SO₂CF₃, which is consistent with

experiment. The only significant anomaly is the apparent higher reactivity of CF₂Br₂ than is indicated by its calculated EA and LUMO energy.

Possible rationalisations include the effects of differing reaction conditions, but the presence of two Br atoms providing two reactive sites could be likely explanation.

In anticipation of further experimental work the LUMO energies and electron affinities of various other substrates were calculated to predict those which might be most reactive with copper. Table 2 summarises the results.

Although the electron affinities in Table 2 provide useful predictors of reactivity, possibly LUMO energies of the substrates would be adequate? They would certainly be simpler to obtain since they result directly from the semi-empirical calculations on the substrates although they do allow for any changes in electron reorganisation in forming the anions. Fig. 1 shows an essentially linear relationship between LUMO energies and calculated EAs thus confirming that LUMO energies can equally well be used for ranking substrate reactivities.

In summary, we consider that semi-empirical calculation of EAs and LUMO energies, even with the sweeping assumptions we have made, provide a useful method for rationalising the reactivity of various fluorinated halides with copper metal.

Table 2
Calculated electron affinities and LUMO energies for various carbonyl and sulfonyl compounds

Compound	EA (eV)	LUMO (eV)
CF ₃ COCl	1.44	-0.93
CF ₃ COBr	2.28	-1.86
CH ₂ FSO ₂ Cl	2.29	-2.00
CH ₂ FSO ₂ Br	2.90	-2.59
CHF ₂ SO ₂ Cl	2.68	-2.38
CHF ₂ SO ₂ Br	3.37	-3.08
CF ₃ SO ₂ Br	3.77	-3.47
CF ₃ SO ₂ CN	2.64	-2.10
(CF ₃ SO ₂) ₂ O	3.04	-2.57

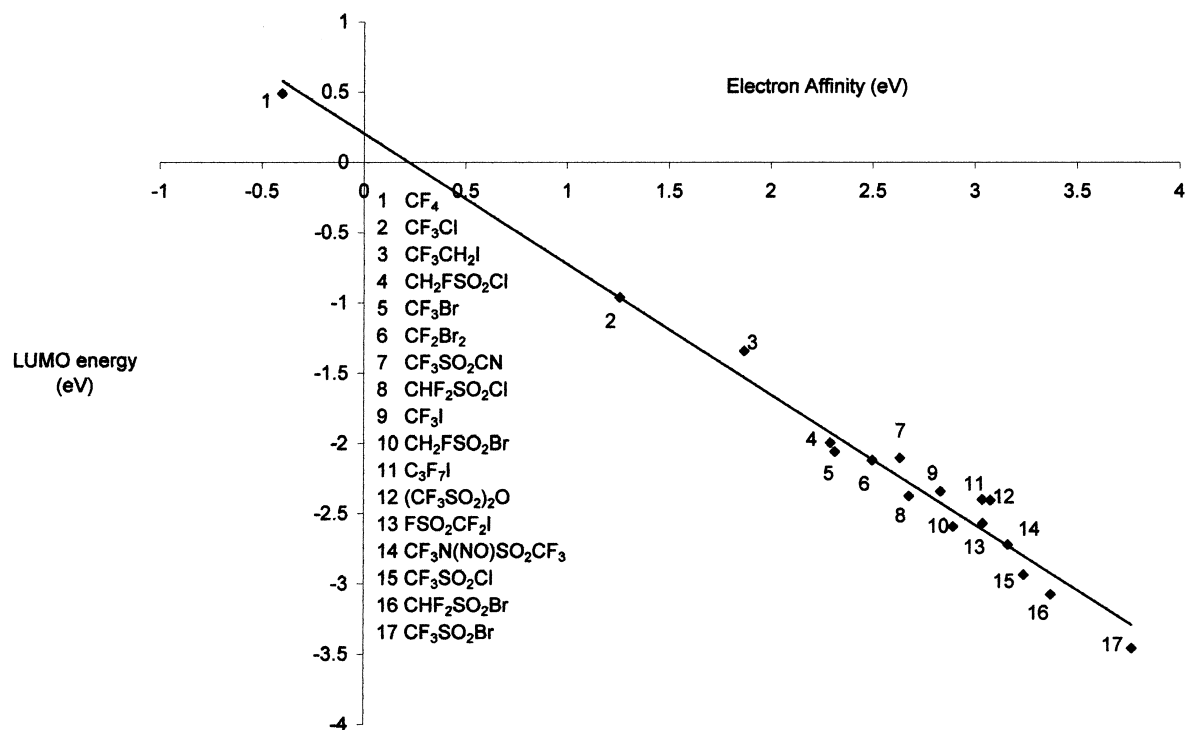


Fig. 1. Relationship between calculated electron affinities and LUMO energies.

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