The Electrochemistry of $C_{60}Ph_5Cl$: A Very Special Fullerene Derivative

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Abstract: $C_{60}Ph_5Cl$ has electrochemical properties strikingly different from pristine C_{60}: the cyclovoltammetric curves show that, in the first reduction peak, two electrons are sequentially and irreversibly injected at the same potential. Analysis of the corresponding kinetics suggests that the carbon−chlorine bond is concomitantly severed and that back-oxidation of the resulting fragments regenerates the pristine fullerene derivative. The different oxidation states of this derivative of C_{60} therefore repel and attract the chlorine atom, a property that further adds to the well-known special character of fullerene anions.

Introduction

$C_{60}Ph_5Cl$ seems naturally designed as a textbook molecule in which chemically “classic” moieties are brought together. The electron accepting C_{60} cage is partly saturated by five phenyl groups which are located at the end of hexagon−hexagon edges extending radially from one of the twelve pentagons of Buckminsterfullerene.[1a] Saturation of six trivalent carbon atoms with phenyl groups and a chlorine atom should decrease the molecule’s capacity to accept electrons. The five phenyls should, however, increase it via inductive effects. The presence of a chlorine atom has the additional effect of breaking the 5-fold symmetry of the $C_{60}Ph_5$ moiety. This atom sits on one of the carbons of the pentagon surrounded by the phenyls to effectively form a chlorocyclopentadiene fragment.[1a] Interactions between the ring and the rest of the cage occur through saturated bonds, although strong endohedral homoconjugation has been proposed to occur between the C_{50} and the cyclopentadiene moieties.[1b−d] The electrochemical reduction of the related species $C_{60}Ph_5H$ has been shown to cause the rapid expulsion of $H^\bullet$ from the one-electron reduced $C_{60}Ph_5H^{\bullet-}$ species, with the formation of the corresponding $C_{60}Ph_5^-$ anion.[1b] The latter species may act as an effective cyclopentadienilic ligand, also obtainable by reaction of $C_{60}Ph_5H$ with alkali metal alkoxides, by which a whole series of pentahaptofullerene metal complexes was prepared.[1c] Very recently,[1d] stable $C_{60}Ar_5^+$ (Ar = Ph or 4-FC_6H_4) carbocations, with the positive charge localized into the cyclopentadiene moiety, were also obtained, by reacting the corresponding $C_{60}ArCl$ derivatives with $AlCl_3$. In this scenario, it is reasonable that the strong interplay between conjugation and inductive and polarization effects may lead to novel, unexpected phenomena whose investigation appears to be of fundamental interest.

In this work, cyclic voltammetry, CV, and quantum chemical calculations are used to characterize the reduced form of $C_{60}Ph_5Cl$. Analysis of the curves of reduction and back-oxidation, together with the simulation of their kinetics, affords a simple mechanism which can be rationalized in terms of the reductive homolytic cleavage of the C−Cl bond that may be reversed in the oxidation scan, a finding that agrees well with the electrochemical properties of the parent $C_{60}Ph_5H$ and adds to the well-known special characteristics of reduced Buckminsterfullerene ions.[2]

Experimental Section

Materials. A $C_{60}Ph_5Cl$ sample was prepared using the procedure outlined previously.[1a] All materials were reagent grade chemicals. TBAH (puriss, Fluka) was used as supporting electrolyte as received.

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(1) (a) Avent, A. G.; Birkett, P. R.; Crane, J. D.; Darwish, A. D.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1463. (b) Iikura, H.; Mori, S.; Sawamura, M.; Nakamura, E. *J. Org. Chem.* **1997**, *62*, 7912. (c) Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc*. **1996**, *118*, 12850. (d) Avent, A. G.; Birkett, P. R.; Kroto, H. W.; Taylor, R.; Walton, R. M. *J. Chem. Soc., Chem. Commun.* **1998**, 2153.

(2) (a) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc*. **1992**, *114*, 3978. (b) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun*. **1992**, 781. (c) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186. (d) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc*. **1992**, *114*, 6446. (e) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem*. **1992**, *96*, 7137. (f) Krisnan, V.; Moninot, G.; Dubois, D.; Kutner, W.; Kadish, K. M. *J. Electroanal. Chem*. **1993**, *356*, 93. (g) Boulas, P.; Subramanian, R.; Kutner, W.; Jones, M. T.; Kadish , K. M. *J. Electrochem. Soc*. **1993**, *140*, L130. (h) Soucaze-Guillous, B.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Electrochem. Soc*. **1996**, *143*, 550. (i) Noviandri, I.; Bolskar, R. D.; Lay, P. A.; Reed, C. A. *J. Phys. Chem. B* **1997**, *101*, 6350. (j) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Isaacs, L.; Anderson, H. L.; Faust, R.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 1334. (k) Cardullo, F.; Seiler, P.; Isaacs, L.; Nierengarten, J.-F.; Haldimann, R. F.; Diederich, F.; Mordasini-Denti, T.; Thiel, W.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 343. (l) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Herrmann, A.; Rüttiman, M.; Crassous, J.; Cardullo, F.; Echegoyen, L.; Diederich, F. *J. Am. Chem. Soc*. **1998**, *120*, 7860. (m) Paolucci, F.; Marcaccio, M.; Roffia, S.; Orlandi, G.; Zerbetto, F.; Prato, M.; Maggini M.; Scorrano, G. *J. Am. Chem. Soc.* **1995**, *117*, 6572. (n) Maggini, M.; Guldi, D. M.; Mondini, S.; Scorrano, G.; Paolucci, F.; Ceroni P.; Roffia, S. *Chem. Eur. J.* **1998**, *4*, 1992. (o) Da Ros, T.; Prato, M.; Carano, M.; Ceroni, P.; Paolucci F.; Roffia, S. *J. Am. Chem. Soc*. **1998**, *120*, 11645. (p) Prato, M. *J. Mater. Chem*. **1997**, *7*, 1097. (q) Boulas P. L.; Echegoyen, L. *Electrochem. Soc. Interface* **1997**, *6*, 36. (r) Echegoyen L.; Echegoyen, L. E. *Acc. Chem. Res*. **1998**, *31*, 593. (s) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev*. **1998**, *98*, 2527. (t) *Fullerenes and related Structures*; Hirsch, A., Ed.; Springer-Verlag: Berlin, 1999.

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CH_2Cl_2 (Fluka) was transferred, under argon, from the original airtight container into a Schlenk flask containing activated 4 Å molecular sieves and kept under vacuum prior to use. Tetrahydrofuran (THF, LiChrosolv, Merck) was treated according to a procedure described elsewhere.[3] For the electrochemical experiments, the solvent was distilled into the electrochemical cell, prior to use, using a trap-to-trap procedure.

Electrochemical Instrumentation and Measurements. The one-compartment electrochemical cell was of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Kalrez (DuPont) O-rings to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck containing the solvent were obtained by spherical joints also fitted with Kalrez O-rings. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically 1.0×10^{-5} to 2.0×10^{-5} mbar. The working electrode consisted of either a 0.6-mm-diameter platinum wire (0.15 cm^2 approximately) sealed in glass or a Pt disk ultramicroelectrode ($r = 5$ μm) also sealed in glass. The counter electrode consisted of a platinum spiral, and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm. Potentials were measured with the ferrocene standard and are always referred to the saturated calomel electrode (SCE). $E_{1/2}$ values correspond to $(E_{pc} + E_{pa})/2$ from CV. For irreversible peaks, the peak potential, E_p, is given, measured at 0.5 V s^{-1}. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple. The temperature dependence of the ferrocinium/ferrocene couple standard potential was measured with respect to SCE by a nonisothermal arrangement according to the method outlined in ref 4.

Voltammograms were recorded with a AMEL Model 552 potentiostat or a custom made fast potentiostat controlled by either a AMEL Model 568 function generator or a ELCHEMA Model FG-206F. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda Klein-Kryomat thermostat. The DigiSim 2.1 software by Bioanalytical Systems Inc. or the Antigona software developed by Dr. L. Mottier (http://www.ciam.unibo.it/electrochem.html/) was used for the simulation of the CV curves. The latter program was also used for the acquisition of the CV curves and their convolutive analysis.

Results and Discussion

The initial and crucial cyclic voltammetric measurements on the electrochemical properties of $C_{60}Ph_5Cl$ were carried out in CH_2Cl_2 solution at −50 °C on a sample prepared using the procedure outlined previously.[1a] The two CV curves in Figure 1a,b were obtained in CH_2Cl_2 solution with a scan rate of 0.5 V s^{-1} and contain important information. In the first anodic potential scan, Figure 1a, two reversible one-electron oxidation peaks, labeled O1 and O2, are observed at $E_{1/2} = 1.52$ and 1.93 V. This is in itself an important finding because it makes $C_{60}Ph_5Cl$ the first C_{60} derivative undergo two reversible one-electron oxidations (it must be mentioned that multiple reversible oxidations have been reported for C_{70}, higher fullerenes, and their derivatives[2j−l,t]). In the cathodic scan, three reductions, labeled I, II, and III, were located at $E_p = -1.05$ V, $E_{1/2} = -1.30$ V, and $E_p = -1.80$ V. The evaluation, by convolutive analysis of the cathodic curve,[5] of the number of electrons, *n*, involved in the processes was performed and proved that twice as many electrons are used in peak I as in peak II. Peak I is irreversible and remains such even when the potential scan is reversed before reaching the potentials typical of peak II. In particular, its height always corresponds to a two-electron reduction for all the scan rates investigated by us (up to 200 V s^{-1}).

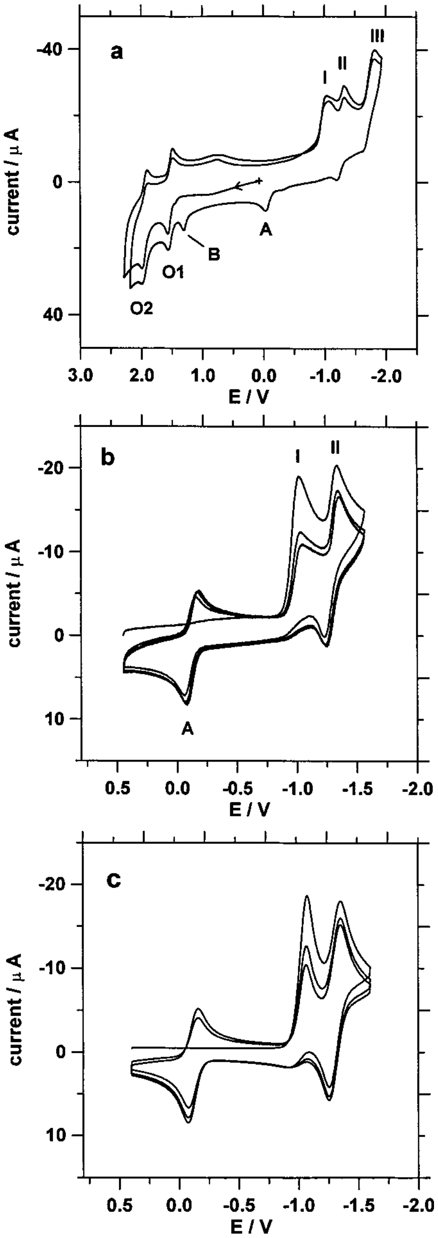

Figure 1. (a) Multiple-scan CV curve of a 0.5 mM $C_{60}Ph_5Cl$, 0.05 M Bu_4NPF_6•CH_2Cl_2 solution. Scan rate = 0.5 V s^{-1}; $T = -50$ °C; the working electrode is platinum. The initial scan starts anodically and the successive scans are performed without the renewal of the diffusion layer. (b) A limited region of scan a that excludes the B, O1, O2, and III processes. (c) Digitally simulated CV curve of scan b according to the mechanism outlined in the text. Similar simulations for the data of Figure 2 are available from the authors.

When a second anodic scan was run, two additional oxidation peaks, labeled A and B, were detected. These novel peaks were also observed if the cathodic scan was limited to peak I, and under the conditions of Figure 1a (wide anodic potential scan), both peaks were irreversible (i.e., they lacked a cathodic counterpart). *Remarkably, in subsequent scans, the CV curve consistently maintained the same features and both peaks A and B were present.* By contrast, narrowing of the anodic potential scan to exclude the B, O1, and O2 oxidations (Figure 1b) makes peak A reversible ($E_{1/2} = -0.10$ V) and, importantly, a large

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[3] Carano, M.; Ceroni, P.; Mottier, L.; Paolucci, F.; Roffia, S. *J. Electrochem. Soc.* **1999**, *146*, 3357.

[4] Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

[5] In the case of peaks I and II of the CV curve in Figure 1b, a two (unequal)-step sigmoidal curve is obtained after convolution, where each step is proportional to *n* of the corresponding CV peak; Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 236−242.

decrease of the height of peak I in the second and following scans is observed. This indicates that $C_{60}Ph_5Cl$ is not recovered during the oxidation.

A possible explanation for the two electrons consumed in peak I is the occurrence of an electrochemical−chemical−electrochemical (ECE) mechanism: The initial one-electron reduction of $C_{60}Ph_5Cl$, in peak I, is immediately followed by a quantitative, fast reaction whose product is subsequently reduced at the same potential. The product(s) is(are) then responsible for peaks II and III and, in the anodic scan, for the two additional oxidation processes, A and B. The digital simulation of the CV curve of Figure 1b, based on this working hypothesis, is shown in Figure 1c. The agreement with the experiment is very satisfactory. From the simulation of the CV curves obtained up to 200 V s^{-1}, a lower limiting value for the rate constant of the chemical process triggered in peak I can be set to 2000 s^{-1}. The species involved in the A and B oxidations are central to the understanding of the electrochemical dynamics of $C_{60}Ph_5Cl$. In short, one can summarize the results of the repeated cycling of the potential in the wider scans of Figure 1a as follows: (i) peak A is irreversible, (ii) the occurrence of the reaction coupled to peak I does not affect peaks O1 and O2, and (iii) the height of peak I remains almost unchanged in subsequent scans. The implication is that the species involved in peak A is a chemical modification of $C_{60}Ph_5Cl$ which is first produced in peak I and then, from peak B onward, is reconverted to the title molecule.

Insight into the ECE mechanism can be obtained by analogy with the electrochemical behavior of a similar species, namely the case of $C_{60}Ph_5H$,[1b] and by calculations. The electrochemical behavior of this species has been reported in THF solutions, where it undergoes a one-electron irreversible reduction which leads to the formation of $C_{60}Ph_5^-$ anion after expulsion of $H^\bullet$.[1b] The anion created by the homolytic C−H cleavage undergoes two further reversible reduction processes at more negative potentials, close to the II and III reductions observed here. In the reverse scan, $C_{60}Ph_5^-$ has a reversible oxidation that is located energetically close to the present oxidation A. In the cathodic region, the only difference between $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ seems to be the two-electron versus one-electron reduction I. De-chlorination of the title molecule, with the formation of $C_{60}Ph_5^-$ anion (eventually acquiring a proton from the (wet) solvent and giving therefore the $C_{60}Ph_5H$ species), has been shown to occur upon reaction with triphenylphosphine.[1a] The generation of $C_{60}Ph_5^-$ anion during cathodic reduction I of $C_{60}Ph_5Cl$ was confirmed by remeasuring the CV curves in THF solutions at −80 °C, i.e., conditions similar to those used in ref 1b. The results were in full agreement with those reported there (see Figure 2 analogous to Figure 1b), and only minor shifts of the peaks were observed: $E_{1/2}(A) = 0.05$ V, $E_p(I) = -0.80$ V; $E_{1/2}(II) = -1.27$ V.[6] Because of the wider cathodic window available in THF, reduction processes additional to those in CH_2Cl_2 can also be recorded (at −1.75, −2.40, and −2.85 V), while O1, O2, and B cannot be observed in this medium since they are located outside the THF anodic window which is narrower than that of CH_2Cl_2. It should be emphasized that, in contrast to the case of the measurements in CH_2Cl_2, the convolutive analysis of the CV curve in THF from −80 to 25 °C shows an ever decreasing n_I/n_{II} ratio that starts from values close to 2 and eventually reaches 1 at 25 °C. While at low temperatures the same CV pattern is observed in THF and CH_2Cl_2, in THF at room temperature, $C_{60}Ph_5Cl$ does not differ from $C_{60}Ph_5H$. A possible explanation is that the temperature increase promotes parallel homogeneous degradation pathways of the species generated in the reduction peak I. Traces of unidentified products of these reactions are in fact observed in the CV curves obtained at higher temperatures and low scan rates. However, $C_{60}Ph_5^-$ has been reported to be thermally stable in THF solutions at room temperature.[1c] From all of the above, it is inferred that, in analogy with the $H^\bullet$ radical release of $C_{60}Ph_5H$, $C_{60}Ph_5Cl$ may generate a $Cl^\bullet$ highly unstable radical (although generation of Cl^- cannot be discounted entirely).

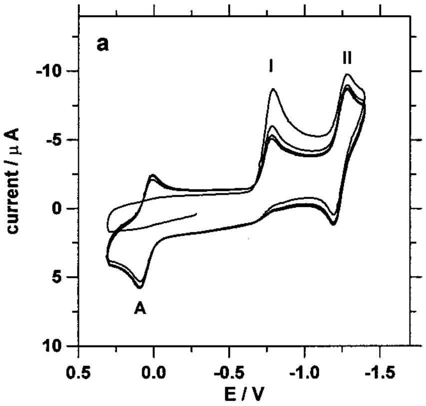

Figure 2. Multiple-scan CV curve of a 0.5 mM $C_{60}Ph_5Cl$, 0.05 M Bu_4NPF_6·THF solution. Scan rate = 0.5 V s^{-1}; *T* = −80 °C; the working electrode is platinum.

Quantum chemistry can be used to evaluate explicitly the amount of charge present in the dispatched atom when the C−Cl bond is elongated by 0.1−0.3 Å, a length beyond which other important effects, such as reaction/solvation of the exiting chlorine, are likely to take over. To appraise the chlorine charge, a three-step procedure was set up. The first two steps involved validation of a method to calculate the charge distribution on a system as large as $C_{60}Ph_5Cl$. The molecular geometries of both $C_{60}Ph_5Cl$ and 1-chloro-2,4-cyclopentadiene were optimized using the MM3 force field[7] and the calculations were run with the Tinker program[8] that has found wide application in our laboratory in a variety of cases.[9] C_5H_5Cl was taken as a reference molecule since it coincides with the conjugated ring moiety to which the chlorine atom is attached. The preference for a molecular mechanics model is due to the presence of the five phenyl groups whose relative orientation is governed by dispersion forces. In the case of two benzene molecules, such forces compete to form either a π-stack or a T-shaped complex. Molecular mechanics, in general, and MM3, in particular, is explicitly parametrized to account for the weak interactions that occur between the phenyls. Phenyl rotation can affect the through-space and through-bond interactions of the π electrons of the phenyls with those of the cyclopentadienyl moiety and

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(6) The reported [ref 1b] $E_{1/2}$ values for $C_{60}Ph_5/C_{60}Ph_5^-$ and $C_{60}Ph_5^-/C_{60}Ph_5^{2-}$ redox couples in THF at −78 °C, +0.07 and −1.32 V, respectively (based on an $E_{1/2}$ value for the ferrocinium/ferrocene internal standard of 0.50 V vs SCE), almost coincide with the values obtained here (peaks A and II).

(7) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *23*, 8551. Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *23*, 8566. Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *23*, 8576.

(8) Ponder, J.; Richards, F. *J. Comput. Chem.* **1987**, *8*, 1016. Kundrot, C.; Ponder, J.; Richards F. *J. Comput. Chem.* **1991**, *12*, 402; Dudek, M. J.; Ponder, J. *J. Comput. Chem.* **1995**, *16*, 791.

(9) Leigh, D. A.; Murphy, A.; Smart, J. P.; Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1998**, *120*, 6458−6467. Paci, B.; Deleuze, M. S.; Caciuffo, R.; Tomkinson, J.; Ugozzoli, F.; Zerbetto, F. *J. Phys. Chem. A* **1998**, *102*, 6910−6915. Caciuffo, R.; Degli Esposti, A.; Deleuze, M. S.; Leigh, D. A.; Murphy, A.; Paci, B.; Parker, S.; Zerbetto, F. *J. Chem. Phys.* **1998**, *109*, 11094−11100. Deleuze, M. S.; Leigh, D. A.; Zerbetto, F. *J. Am. Chem. Soc.* **1999**, *121*, 2364−2379. Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1999**, *121*, 5281−5286.

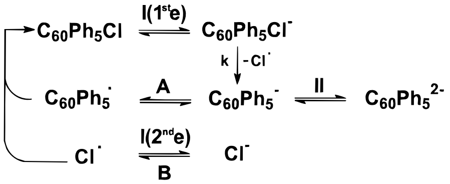
Table 1. B3LYP/6-31G*(AM1) Charge Variation as a Function of the C−Cl Elongation, δ_{C-Cl} in Å, in C_5H_5Cl and $C_{60}Ph_5Cl$

	C_5H_5Cl		$C_{60}Ph_5Cl$	
δ_{C-Cl}	neutral	radical anion	neutral	radical anion
0.1	−0.04(−0.04)	−0.08(−0.06)	(−0.04)	(−0.04)
0.2	−0.08(−0.07)	−0.17(−0.13)	(−0.07)	(−0.08)
0.3	−0.12(−0.11)	−0.24(−0.18)	(−0.10)	(−0.11)

stabilize or destabilize the reaction path that leads to the ejection of an atom. In the second step of the procedure, density functional theory at the B3LYP/6-31G* level[10] calculations were run with the Gaussian program[11] on the reference system to evaluate the suitability of the less computer intensive approach to calculate atomic charges. Table 1 shows the charges for the bond elongation in the neutral and the negatively charged C_5H_5Cl. The B3LYP results, by and large, parallel the AM1[12] ones. The agreement is particularly good for the neutral molecule while, in the anion, the simpler approach gives a lower value for the chlorine charge. Both quantum chemical models show that the negatively charged species localizes more charge on Cl. In neutral $C_{60}Ph_5Cl$, the chlorine charge parallels that of C_5H_5Cl. At odds with the model compound, addition of an electron does not affect the amount of charge on the exiting species. The indication one can draw from the present calculations is that the ejected chlorine atom has a higher chance of being a radical in $C_{60}Ph_5Cl$ than in C_5H_5Cl. This is not in contrast with the experiments; in fact, production of a $Cl^\bullet$ radical would result in immediate reduction to Cl^- so that the two electrons are inextricably linked in a single two-electron peak.[13]

The fundamental difference with the case of $C_{60}Ph_5H$ in THF solution is that reduction of $H^\bullet$ would occur at much more negative potentials, while reduction of $Cl^\bullet$ is a ready event. As the temperature increases, $Cl^\bullet$ can also react with THF (but not with CH_2Cl_2[14]) and is no longer available for reduction and consequently the n_I/n_{II} ratio tends to unity. Peak II is therefore the reduction of $C_{60}Ph_5^-$ anion to the dianion and peak III that of dianion to trianion. At peak A, the radical anion is back-oxidized to a radical. This species remains present when the potential scan is reversed before oxidation B is attained and disappears otherwise (compare scans a and b in Figure 1). The irreversible oxidation peak B, ∼1.3 V, corresponds to the oxidation of Cl^- to $Cl^\bullet$.[15] This was confirmed by adding tetrabuthylammonium chloride to the CH_2Cl_2 solution which brought about the increase of peak B height. The invariance of peaks O1 and O2 and the absence of the cathodic counterpart of peak A, under the conditions of Figure 1a (wider scan), are now reasonably explained by the rapid annihilation of $C_{60}Ph_5^\bullet$ by $Cl^\bullet$, also present (after peak B) in the diffusion layer.[15] For possible applications of the reversible C−Cl cleavage, it is important to notice that $C_{60}Ph_5^-$ is stable even at room temperature.[1b,c] The picture emerging from this work is presented in Scheme 1.

Scheme 1. Mechanistic Account for the CV Behavior of $C_{60}Ph_5Cl$



Conclusion

The electrochemical study of $C_{60}Ph_5Cl$ in CH_2Cl_2 solution has shown a very interesting CV behavior. The analysis of the measurements and their digital simulations suggest that cycling from reduction to oxidation, and back, initially generates a chloride anion and a $C_{60}Ph_5^-$ anion. The two fragments then undergo separate oxidation processes and ultimately re-assemble, although possibly from different initial species, to regenerate the original molecule. The cleavage and formation of the C−Cl bond is therefore driven by the electron flow. Pictorially, a rather playful analogy comes to mind: one could think that the coming and going electrons have the role of the string in a molecular yo-yo whose disk is the (disappearing) chlorine atom.

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[10] B3LYP: Becke, A. M. *J. Chem. Phys.* **1993**, *98*, 5648. 6-31G*: Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

[11] Gaussian 94, Revision B.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

[12] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[13] Since $Cl^\bullet$ is much easier to reduce than $C_{60}Ph_5Cl$ the homogeneous reaction between $Cl^\bullet$ and $C_{60}Ph_5Cl^{\bullet-}$ should, in principle, be taken into account (ECE-DISP competition: Andrieux, C. P.; Savéant, J.-M. In *Investigations of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, Chapter VII, pp 364−367). However, the bond cleavage is very fast ($k \geq 2000$ s^{-1}) and therefore $Cl^\bullet$ is generated very close to the electrode surface to which it can diffuse back to be reduced before reacting with $C_{60}Ph_5Cl^{\bullet-}$. Moreover, in view of its very large favorable driving force, the homogeneous electron-transfer reaction between the newly formed $C_{60}Ph_5^-$ and $Cl^\bullet$, leading to $C_{60}Ph_5^\bullet$ and Cl^-, respectively, is parallely expected to occur. In that case, the second electron consumed in peak I would involve $C_{60}Ph_5^\bullet$.

[14] The n_I/n_{II} ratio in CH_2Cl_2, although lower than at −50 °C, is still close to 2 at 25 °C. However, the CV pattern becomes more complex at high temperature, indicating the partial degradation, to a lesser extent than in THF, of the products of reduction I.

[15] Breikks, A. I.; Abruña, H. D. *J. Electroanal. Chem.* **1986**, *201*, 347. Chlorine is clearly among the possible products of the fast coupling of $Cl^\bullet$ radicals formed at the electrode. Therefore, pristine $C_{60}Ph_5Cl$ might also be regenerate, following peak B, by reaction between $C_{60}Ph_5^\bullet$ and Cl_2 to give $C_{60}Ph_5Cl$ and $Cl^\bullet$.