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Electron-induced chemistry: A forward look

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This special issue is dedicated to Professor Eugen Illenberger.

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ABSTRACT

The ability to understand, manipulate and control physico-chemical processes at the molecular level is one of the great challenges of modern research and underpins the development of vibrant new technologies of the 21st century, for example the development of nanolithography. Such 'single molecule engineering' requires selective bond cleavage in target molecules to allow subsequent management of the local site chemistry. Recent research has revealed that it is possible to influence the excitation and dissociation of molecules through the manipulation of electron interactions at the individual molecular level. Since electrons are ubiquitous in nature and electron-induced reactions initiate and drive the basic physical–chemical processes in many areas of science and technology from industrial plasmas to living tissues, our ability to control electron interactions provides exciting new opportunities that can be exploited in both the research and technological communities.

1. Introduction; electron-induced chemistry—a new technology

The ability to control chemical reactions and select chemical pathways has been long term goal of modern chemistry. Several methods for chemical control have been proposed with photonic control through the use of synchrotron radiation [1–4], femtosecond laser pulses [5] and manipulation of molecular wavepackets [6,7] being the latest to be demonstrated. However such methods, while extremely elegant, are far from being able to be adopted in commercial processing since they are:

- Expensive—a typical laser system costing in excess of £0.5M.
- Limited to specific systems (e.g., each laser system being tuned to one specified reaction process).
- Poorly suited to mass manufacture and
- Require a high degree of training in specialised equipment that is unlikely to be available in an industrial plant.

Accordingly the industrial community requires techniques that are:

- Inexpensive.
- Composed of apparatus that is able to be easily adapted to different chemical systems and
- Requires modest technical skills of the operator.

A good example of such an industry led ethos is the development of plasma technology for preparation of semiconductors and other surface fabrication/treatments. The plasma is self-contained with pre-programmed parameters known (by experience) to give reproducible and efficient results each and every time it is run. The operator has a very limited number of diagnostics with which to check the processing and very limited ability to alter any experimental parameters. Therefore in chemical processing a technique is required that offers the user a 'clean' methodology for initiating reactions by the formation of well characterised reaction products from a set of stable parent species. One such process is that of *electron-induced chemistry*.

2. Electron controlled cleavage of chemical bonds

The opportunity of using electron-induced dissociation of molecules as a tool for chemical control has been recognised for several years and is widely adopted by the low temperature RF plasma community to prepare reactive species for surface processing. For example in the semiconductor industry the electron temperature (energy) in a fluorocarbon plasma is optimized to produce CF_x ($x = 1–3$) radicals which subsequently etch SiO_2 substrates. However, one of the most exciting advances of recent molecular

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physics has been the discovery of the ability *of low energy electrons*[1] to initiate and effectively drive *selective bond cleavage* processes in molecular systems efficiently [8]. At these low energies the dissociation process is driven by *Dissociative Electron Attachment* (*DEA*). DEA of a molecule M as summarized is follows:

$$e^- + XY \rightarrow XY^{\#-} \rightarrow X^- + Y$$

Here $XY^{\#-}$ is a transient negative ion (TNI), that leads to the production of a negative charged fragment X^- accompanied by one or more associated neutral counterpart(s) Y. In the condensed phase or on a surface these neutral and generally highly reactive products may initiate further chemistry through reactions with neighbouring molecules i.e.,

$$Y + AB \rightarrow AY + B$$

The formation of a TNI is usually a '*resonant*' process, i.e., one that occurs only over a narrow incident energy range. It is the formation of such TNI resonances that provides DEA with its chemical selectivity and ability to initiate low energy chemistry. Furthermore, in contrast to *direct* electron impact where an excess energy of several eV (e.g., 4–5 eV) is required to fragment a molecule, DEA can dissociate a molecule with a zero electron energy threshold. Fig. 1(a) shows how the potential energy surface of the anionic TNI state crosses that of the neutral and lies *below* that of the neutral. This provides a route to $X^- + Y$ formation though 0 eV electrons, as the dissociation process is driven by the electron affinity (EA) of the product X relative to the bond energy $D(X-Y)$; $\Delta H_0 = D(X-Y) - EA(X)$.

In numerous cases DEA effectively occurs at electron impact energies of meV, that is at thermal energies (kT). Generally, these low energy processes have very large cross-sections of 100s to 1000s of Å^2. *DEA can therefore lead to a new form of very low energy but extremely efficient chemical reaction dynamics*. Furthermore DEA is bond selective, each TNI often having a preferred dissociation channel. Consider DEA to $CFCl_3$ (Fig. 1b), electrons with meV incident energies cleave the C–Cl bond producing Cl^- and CCl_2F with very high cross-sections, whereas at 3.2 eV the electrons only cleave the C–F bond resulting in F^- and $CCl_3{}^-$ [9]. Hence the process of DEA may provide remarkable 100% selectivity with respect to the cleavage of a particular bond. This opens interesting prospects for developing selective chemistry induced by electrons since chemical control of any reaction (through varying the production/yield of chemical reactants) may be achieved by 'tuning' the electron energy.

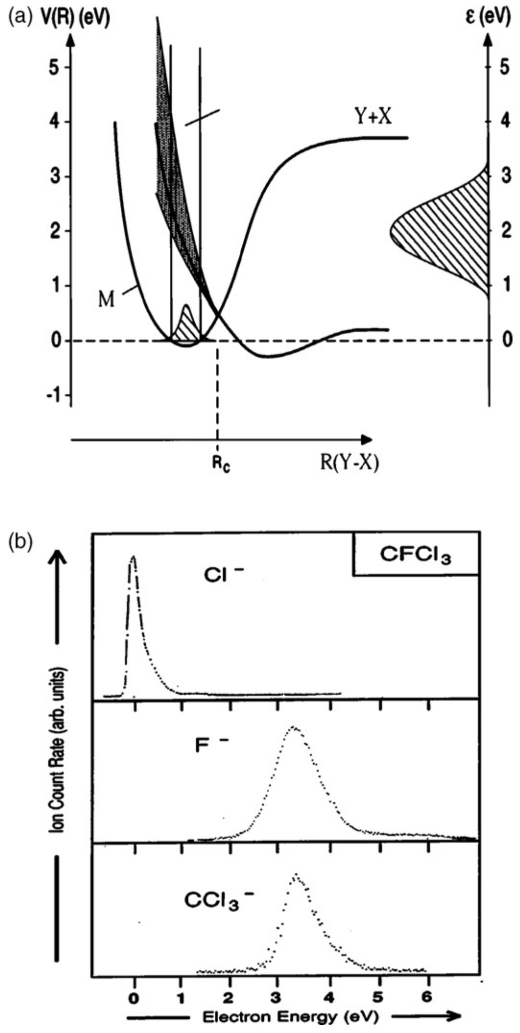

Fig. 1. (a) Schematic potential energy curves for an anionic state (XY^-) and the corresponding ground state of the neutral XY. (b) Selective bond cleavage induced by dissociative electron attachment to $CFCl_3$ [9].

3. Electron controlled chemical synthesis

Recently such DEA-induced chemistry has been extended to organic molecules due to their applications in surface lithography. At sub-excitation energies (<3 eV) many organic molecules are subjected to the loss of a *neutral* H atom via the DEA reaction $e^- + M \rightarrow M^{-\#} \rightarrow R^- + H$. Such reactions are energetically driven by the appreciable electron affinity of the radical R which is close to the corresponding binding energy of H–R and thus can take place close to, or even at zero energy (see above). DEA is also important in electron impact upon biomolecules. Recent studies on biologically relevant molecules (alcohols, organic acids, amino acids, DNA bases, etc.) have indicated a remarkable selectivity in such hydrogen abstraction reactions. This selectivity concerns not only the specific bond (C–H, O–H, N–H) but also the particular site within the molecule, e.g., a particular N–H position in an isolated DNA base [10–12]. The complementary reaction, namely loss of a hydrogen *anion* via $e^- + M \rightarrow M^{-\#} \rightarrow R + H^-$ is energetically less favourable due to the small electron affinity of H (0.75 eV). However, though such reactions are observed in higher energy resonances at 5–10 eV, i.e., in the vicinity of electronic excited states of the targets, they still maintain bond and site selectivity. By exchanging these hydrogen atoms with suitable high electron affinity exit-groups we may activate specific bond ruptures.

While DEA is an important process in electron interactions with gas phase molecular species and may be used to control the chemistry of plasmas [13–16] it is in the condensed phase that DEA may be used most effectively. When the molecules are adsorbed upon the surface, $M_{ad,}$ additional processes must be considered compared to the gas phase. In the condensed phase the products formed

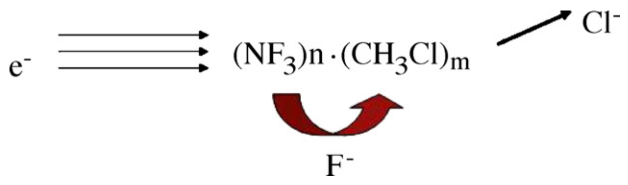

Fig. 2. Schematic of electron induced S_N2 reaction in a mixed film of NF_3 and CH_3Cl molecules.

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[1] Where low energy (or 'subexcitation') electrons means electrons with insufficient energy to form electronically excited targets.

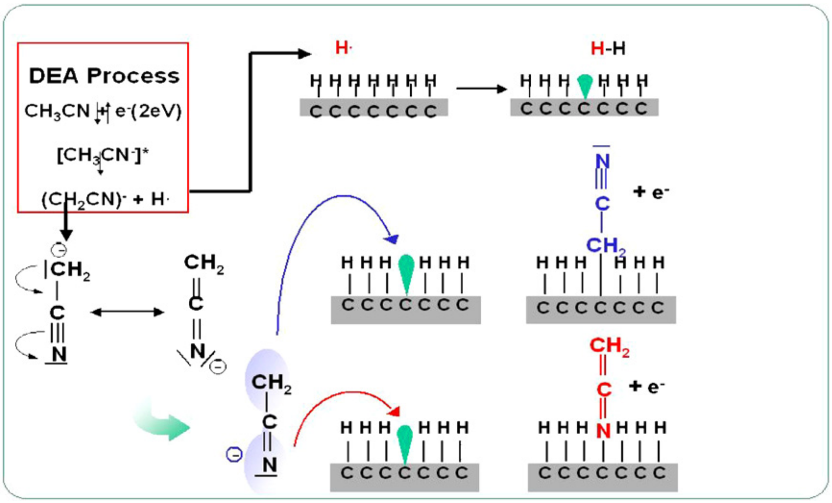

Fig. 3. Electron-induced functionalization of a diamond surface using CH_3CN (from [18]).

at/on the surface must have sufficient energy to escape from the surface hence there are four routes:

$$\begin{aligned} e^- + M_{ad} \rightarrow M_{ad}^{-\#} &\rightarrow R_{ad} + X \ \text{(a) } R \text{ remains on surface/in the film } X^-\text{desorbs} \\ &\rightarrow R + X_{ad} \text{(b) } R \text{ desorbs } X^- \text{ remains on surface/in the film} \\ &\rightarrow R_{ad} + X_{ad} \text{(c) } R \text{ and } X^- \text{ remain on the surface/in the film} \\ &\rightarrow M_{ad}^- \qquad \text{(d) The is stabilized within the film.} \end{aligned}$$

Hence in order to determine the products of electron irradiation simple monitoring of the desorbed anionic fragments is not sufficient. Instead in order to monitor R_{ad} it is necessary to probe the film itself. Typical techniques are: electron energy loss spectroscopy (EELS); infrared/ultraviolet spectroscopy (IRS/UV) and temperature programmed desorption (TPD)—though the latter may itself lead to additional thermally driven chemical changes in the film.

Once DEA has released fragments they are free to initiate further chemical reaction. Consider a mixed film of NF_3 and CH_3Cl (Fig. 2). The cross-section for Cl^- production from CH_3Cl by direct electron impact is negligible (the cross-section being $<10^{-23}$ cm^2) however in the mixed film of CH_3Cl and NF_3 F^- ions may be liberated from NF_3 and then react with CH_3Cl by the well known nucleophilic displacement (S_N2) reaction $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$ [17]. These Cl^- ions could then be liberated from the film and the molecular species CH_3F formed left on the surface/in the film (Fig. 3).

Such specific chemical reactions can also be used to bind *specific functional groups* to the surface of a solid material in a controlled way. Indeed recently it has been shown that DEA of acetonitrile ($CH_3CN + e^-(2\,eV) \rightarrow CH_2CN^- + H$) may be used in the functionalization of hydrogenated diamond to attach organic groups to surfaces [18] the released H reacting with surface hydrogen to create a dangling bond to which the larger fragment attaches under electron detachment.

Low-energy electron-induced reactions have also opened new perspectives for the formation of chemical nanostructures on surfaces with relevance to biochips relying on the immobilization of proteins or nucleotides or of nanoparticle patterned surfaces [19]. A selective transformation according to $R–NO_2 \rightarrow R–NH_2$ has been established as a basis for these applications and entitled *chemical lithography* [20]. Nanostructures are transferred to the surface either by irradiation through a mask or by using electron beam techniques.

4. Electron controlled chemistry using scanning tunnel microscopy

One of the most exciting recent developments in the area of surface modification is the use of the scanning tunnelling microscope (STM) to cleave specific bonds on surfaces and adsorbates. Many of these single molecule reactions are mediated by non-adiabatic coupling of electronic energy into vibrational motion, placing energy into *specific reaction coordinates*.

Electronic excitation of the adsorbed molecule by using inelastic tunnelling of electrons from the STM tip appears to be the most appropriate method for controlling, with precision, molecular reactions. Using inelastic tunnelling effects, individual bonds in molecules or bonds between a molecule and the substrate can be broken in order to induce selective dissociation or desorption of the molecules. In recent years, there have been several examples of chemical control at the level of a single atom or molecule by electronic excitation using tunnel electrons from the STM tip. For example individual bond breaking of hydrogen on a Si(1 0 0) surface [21] has been used to pattern atomic lines on a surface while the mechanisms for desorption and dissociation of chlorobenzene on Si(1 1 1) have been studied in great detail [22]. Recently it has also been shown that inelastic tunnelling may be applied to form bonds

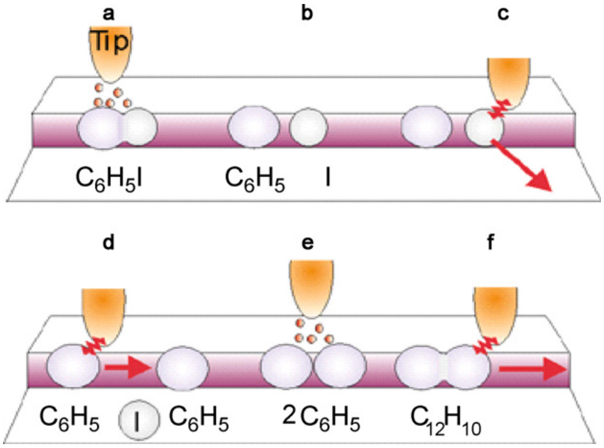

Fig. 4. Schematic of molecular synthesis of $C_{12}H_{10}$ using STM manipulation of iodobenzene [23].

between molecules, opening up the way for the tailored synthesis of molecules on surfaces, an important step towards molecular engineering with the STM tip. Such “molecular surgery” introduces the prospect of *designer synthesis on the nanoscale* and has already been demonstrated for the iodobenzene molecule [23] (Fig. 4) where DEA liberates a C_6H_5 fragment which can subsequently be transported to a specific surface site, there to combine with a second C_6H_5 fragment to form $C_{12}H_{10}$.

The future of these atomic-scale STM manipulations lie (i) in a better understanding of the inelastic tunnelling electronic processes and (ii) in the use of these manipulations for activating more complex molecular reactions (molecular recognition, molecular nano-machines) at the atomic-scale. Hence it is vital to understand the coupling of electrons with molecules on surfaces and the mechanism of energy transfer by tunnelling electrons in STMs.

5. Conclusions

Electron-induced chemistry as a methodology for chemical control is a new but promising technique that may give us the ability to control chemical reactions and select chemical pathways in a manner (and at a cost) never before possible.

The ideal of being able to control chemical reactions by the simple alteration of a single parameter (i.e., the electron energy) has long been the goal of modern chemistry (and its predecessor ‘alchemy’). The first evidence that such control may be possible through the development of dissociative electron attachment in both the gas phase and within condensed phase has been demonstrated, while DEA-based STM provides the ultimate ability to control reactions at the single molecule level and at any specific site. The age of ‘single molecular engineering’ and ‘chemical control’ may, therefore, be nearer than we ever hoped.

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‘Finally’ I wish to take this opportunity to acknowledge Professor Eugen Illenberger. Eugen is one of the pioneers of the study of electron interactions with molecular systems and in particular the study of dissociative electron attachment upon which much of this article is based and on which so many innovative technologies and exciting scientific discoveries are based. So many of the papers in this volume reflect his influence on the field and if the current younger researchers and the next generation of researchers in the field ‘Stand on the shoulders of giants’ it is upon Eugen’s broad shoulders! He is an example to us all not only for his superb skills as an innovative and creative scientist but as a true leader of the field and, to so many of us, a loyal and dedicated friend.

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