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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.

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.

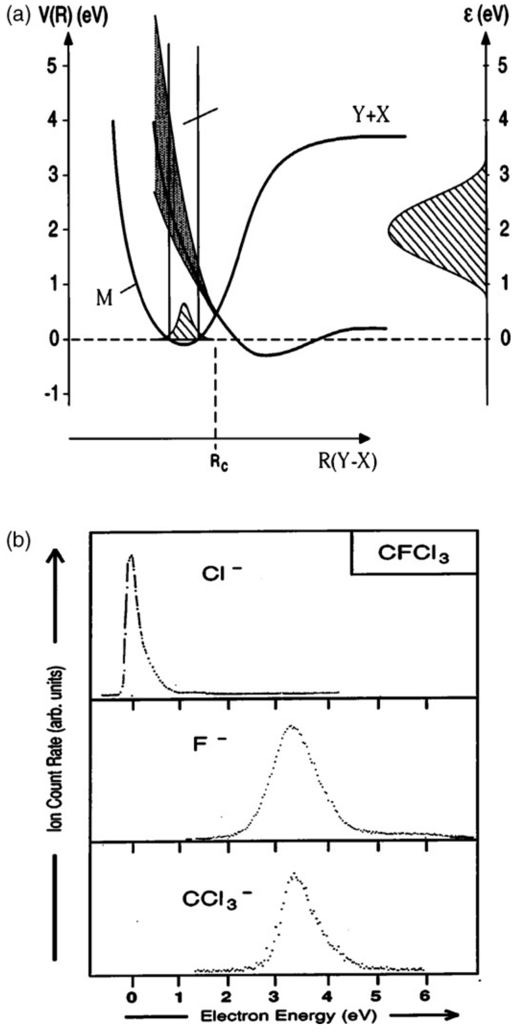

Fig. 1. (a) Schematic potential energy curves for an anionic state (XY^-) and the corresponding ground state of the neutral XY. (b) Selective bond cleavage induced by dissociative electron attachment to $CFCl_3$ [9].

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

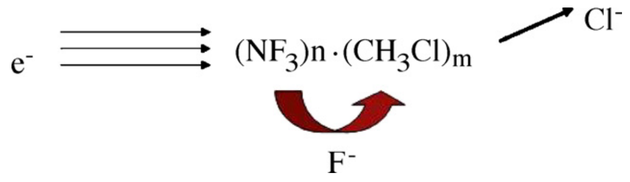

Fig. 2. Schematic of electron induced S_N2 reaction in a mixed film of NF_3 and CH_3Cl molecules.

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