Ion-Molecule Surface Reactions Induced by Slow (5–20 eV) Electrons

L. Sanche and L. Parenteau

Groupe du Conseil de Recherche Médicale du Canada en Sciences des Radiations,
*Faculté de Médecine, Université de Sherbrooke, Sherbrooke, Québec, Canada J1H 5N4*

Electron-stimulated desorption of H^-, O^-, and OH^- ions from a metal-deposited multilayer O_2 film covered with C_nH_{2n+2} molecules is reported for the incident-energy range 5–20 eV. By producing selectively with the electron beam $O^-(^2P)$ ions on the film, via the dissociative attachment reaction $O_2(^3\Sigma_g^-)+e^- \to O_2^-(^2\Pi_u,{}^2\Sigma_g^+) \to O^-(^2P)+O(^3P)$, the surface reaction $O^-+C_nH_{2n+2} \to OH^- +C_nH_{2n+1}$ can be induced and controlled.

Ion-molecule reactions are processes of fundamental and practical importance in many areas[1,2] of physics and chemistry. Experimental methods to investigate *specific reactions* have been developed in the gas phase,[1] essentially in response to the need for data relating to atmospheric chemistry[3] and plasma confinement.[4] Details of ion-molecule interactions occurring over a wide energy range have recently been investigated by beam techniques[5] which often led to the identification[5,6] of the product channels and the potential energy curves involved in reactive scattering.

We show in this Letter that *anion-molecule reactive processes can be investigated in the condensed phase* by electron-stimulated desorption (ESD) from molecular films condensed (i.e., physisorbed) on a metal substrate. In other terms, we show that *a low-energy (5–20 eV) electron beam can trigger and control a specific ion-molecule surface reaction.* This finding indicates the possibility of inducing with a low-energy electron beam specific chemical modifications at well-defined positions on a solid surface, and of investigating in more detail the mechanisms of ion-molecule reactions which occur on surfaces (e.g., at the walls of controlled-fusion devices[7]) and within irradiated solids.[2,8]

The method consists of generating with an electron beam impinging on molecules condensed on a surface a specific negative ion via a dissociative attachment reaction. The anions thus created can react with surrounding molecules at the surface *with energies defined by the dissociative attachment process.* The uniqueness and pathways of the reaction can be deduced by monitoring the magnitude of a reaction-product signal as a function of incident electron energy and surface coverage of one of the reactants. As examples, we report the observation of reactions

$$O^- + C_nH_{2n+2} \to OH^- + C_nH_{2n+1} \qquad (1)$$
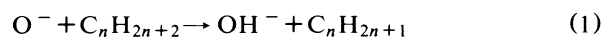
($n=1$, 2, 4, 5, and 6) for C_nH_{2n+2} molecules condensed on the surface of a multilayer O_2 film deposited on a platinum substrate. The energetic O^- ions are generated

by the reaction

$$e^- + O_2(^3\Sigma_g^-) \to O_2^-(^2\Pi_u,{}^2\Sigma_g^+)$$
$$\to O^-(^2P)+O(^3P). \qquad (2)$$
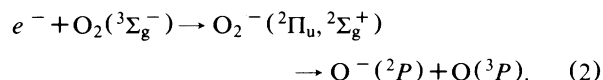
The features in the curve representing the electron energy dependence of the O^- yield are reflected into the electron energy dependence of the OH^- yield and thus serve as a "signature" to detect and identify reaction (1). Previous investigations of abstraction reaction (1) have been performed in gaseous hydrocarbons, at thermal energies[9] and up to 2 eV relative energy[10] of the anion O^-. We also report in this Letter H^- formation from dissociative attachment reactions produced by electron impact on pure saturated-hydrocarbon films.

The apparatus, described previously,[11] consists essentially of an electron gun, a closed-cycle refrigerated cryostat, and a mass spectrometer. These components are housed in an UHV chamber reaching pressures below 5×10^{-11} Torr. Sample gases or vapors are introduced into the UHV chamber via an UHV manifold which allows precise amounts of target molecules to be leaked in front of the cold tip of the cryostat.[12] These molecules condense on a clean electrically isolated polycrystalline platinum (Pt) ribbon press fitted on the cold tip of the cryostat. Electrons are incident on the target at an angle of 20° from the plane of the Pt surface. Ions produced near the surface of the condensed film, either directly by electron impact or via secondary reactions, are measured by a quadrupole mass spectrometer. This latter is positioned at 70° from the target surface and is equipped with ion lenses.

In the present experiment, condensed layers of O_2 and C_nH_{2n+2} ($n=1$, 2, 4, 5, and 6) hydrocarbons were grown on the cold substrate with thicknesses estimated within 50% accuracy by the dosing procedure previously described.[12,13] These compounds were available with a stated purity of 99.98%, 99.99%, 99%, 99.5%, 99%, and 99%, respectively. The absolute energy of the electron beam was calibrated within 0.4 eV with respect to the vacuum level by measuring the onset of electron
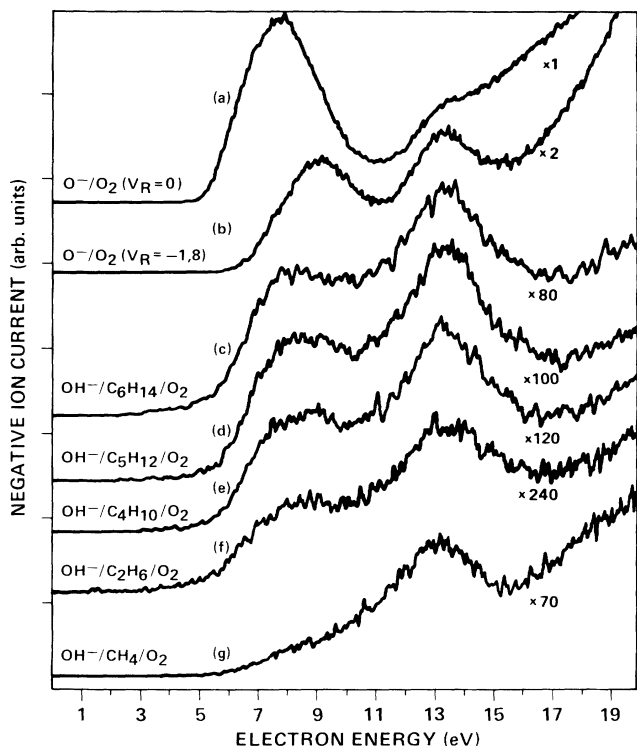
FIG. 1. Energy dependence of electron-stimulated desorption of negative ions in the range 1–20 eV. Curves a and b, O^- desorption form a three-layer O_2 film. V_R is a potential retarding the negative ions at the entrance of the mass spectrometer. Curves c–g, OH^- desorption from a three-layer O_2 film covered with a single layer of C_nH_{2n+2} ($n=1$, 2, 4, 5, and 6) molecules. All these curves were recorded with $V_R=0$.

transmission through the films.[13] The data were recorded with incident electron currents of 10^{-8} A, an energy resolution of 0.3 eV, and a target temperature of 17 K.

O^- *production by electron impact on O_2 films.*— The two curves in Fig. 1 represent the energy dependence of the O^- current produced by electron impact on a three-layer-thick film of O_2. Curve b was recorded with a retarding potential $V_R = -1.8$ eV applied to the rods of the mass spectrometer. All other curves reported in this Letter were recorded with $V_R = 0$. The broad peaks located around 8 and 13 eV in curves a and b have recently been ascribed to the dissociative attachment reaction (2).[11,14] The 8-eV peak arises from the decay of the $^2\Pi_u$ transitory state[11,14] of O_2^-, whereas the 13-eV peak contains contributions from the $^2\Pi_u$ anion and the higher-energy $^2\Sigma_g^+$ O_2^- states.[14] Since both of these states lead to the same dissociation limit, O^- ions produced by 13-eV electrons are, on the average, more energetic and their intensity is therefore less affected by the retarding potential V_R. Accordingly, the 8-eV feature is shifted to higher energy with $V_R = -1.8$ eV as a result of discrimination of lower-energy ions, whereas
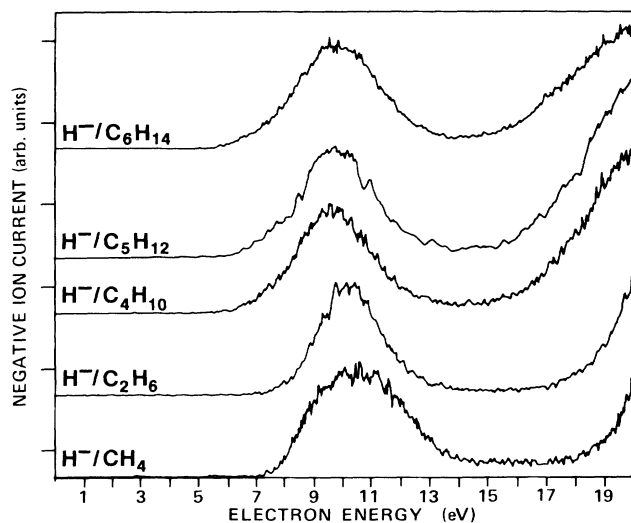

FIG. 2. Energy dependence of H^- signal desorbed by electrons impinging on a six-layer-thick film of C_nH_{2n+2} molecules deposited on a Pt substrate.

the energy of the 13-eV feature is practically unaffected by this potential. The line shapes of these curves remain the same when the O_2 film is covered with a monolayer or less of C_nH_{2n+2} molecules.

Anion production by electron impact on C_nH_{2n+2} films.— The H^- currents appearing on the vertical scale in Fig. 2 were measured as a function of the energy of electrons impinging on six-layer films composed of saturated hydrocarbons. All curves exhibit a single peak whose maxima is located around 10 eV and a rise which onsets at higher energy (16–18 eV). Similar data have been previously obtained[15] in gaseous CH_4 and C_4H_{10} where the 10-eV maxima is caused by the dissociative attachment reaction

$$e^- + C_nH_{2n+2} \rightarrow (C_nH_{2n+2})^-$$
$$\rightarrow H^- + C_nH_{2n+1}. \quad (3)$$
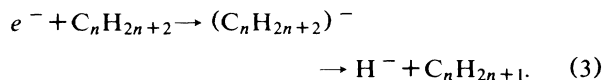
We therefore attribute the peaks in Fig. 2 to reaction (3) occurring at or near the surface of each hydrocarbon film. Similar yield functions are observed for CH_3^-, CH_2^-, and CH^- ions, in order of decreasing intensity. These anions are also believed to arise from the decay of transitory $(C_nH_{2n+2})^-$ states. All yield functions have their line shapes practically unchanged when the hydrocarbons are condensed, at monolayer or submonolayer coverages, on multilayer O_2 films.

Reaction of O^- with hydrocarbons deposited on O_2 films.— Curves c to g in Fig. 1 represent the energy dependence of the OH^- yields produced by electron impact on a three-layer oxygen film covered by a "monolayer" of C_nH_{2n+2} molecules. At submonolayer coverages, these OH^- yield functions exhibit the same
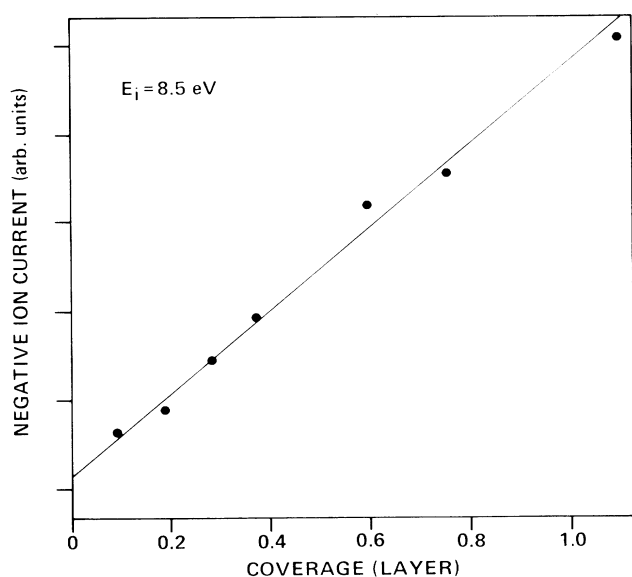
137

FIG. 3. Current of OH$^-$ ions desorbed by 8.5-eV electrons as a function of the pentane (C_5H_{12}) coverage of a three-layer O_2 film deposited on Pt. A similar behavior is observed for the other C_nH_{2n+2} molecules investigated (i.e., $n = 1, 2, 4$, and 6).

characteristics but the signal is lower. In fact, in the submonolayer regime the magnitude of the OH$^-$ signal is found to be directly proportional to the number of condensed hydrocarbon molecules. We illustrate this behavior in Fig. 3 with the results for submonolayer pentane/three-layer–O_2/Pt targets bombarded with 8.5-eV electrons. The remaining "background" intensity at zero coverage in this figure can be attributed to isotopic oxygen-17 current. Results similar to those in Figs. 1 and 3 were obtained for submonolayer coverages of O_2 on three-layer hydrocarbon films. In this case, however, the OH$^-$ signal was found to be linear with O_2 coverage up to half of an O_2 layer.

Since no compound at the film surface contains both hydrogen and oxygen, OH$^-$ ions cannot be produced by direct electron impact. However, they can result from surface reactions between ground-state molecules (i.e., O_2 and C_nH_{2n+2}) and anions produced directly by the electron beam (i.e., O$^-$, H$^-$, and CH$_n$$^-$, $n = 1-3$). *A priori*, OH$^-$ can be formed via reaction (1) or the reactions

$$H^- + O_2 \rightarrow OH^- + O, \tag{4}$$

$$CH_n^- + O_2 \rightarrow OH^- + CH_{n-1}O. \tag{5}$$

The possibility of higher-order reactions among the film constituents and bombardment products can be eliminated from the observed linearity of the OH$^-$ signal as a function of hydrocarbon coverage on multilayer O_2 films (e.g., Fig. 3) and as a function of O_2 coverage on hydrocarbon multilayer films.

Any OH$^-$ formed by reactions (4) and (5) would bear the "signature" of the yield functions for H$^-$ production shown in Fig. 2. In other words, the energy dependence of the OH$^-$ yield would exhibit a single peak around 10 eV since reactions (4) and (5) depend on the primary formation of H$^-$ or CH$_n$$^-$ via reaction (3). As seen in Fig. 1, the OH$^-$ yield functions are similar to the O$^-$/O$_2$ yield curves *a* and *b* indicating that *OH$^-$ formation at the surface is governed by reaction (1)*. This conclusion is reinforced from measurements of the relative magnitudes of the OH$^-$, H$^-$, and CH$_n$$^-$ signals in the 8–15-eV range which indicate that the energy-integrated intensity is larger for OH$^-$ ions than that for H$^-$ and CH$_n$$^-$ ions. Hence, any reaction involving H$^-$ or CH$_n$$^-$ should necessarily result in OH$^-$ magnitudes lower than those observed experimentally. Finally, we point out that the relative magnitude between the two structures in each curve *c* to *g* in Fig. 1 indicates that higher energy O$^-$ ions have increased probability to be involved in reaction (1). Since only ions having enough kinetic energy to overcome the film polarization energy (~ 1 eV)[16] can escape the film, we expect most ions produced by reaction (1) to have energies in excess of 1 eV.

Even though we could not establish experimentally the existence of an intermediate $C_nH_{2n+2}O^-$ state leading to the products of reaction (1), this possibility is suggested by gas-phase results. By measuring the energy of electrons emitted from the collision O$^-$ with CH$_4$ molecules, Comer and Schulz[17] demonstrated that existence of the associative detachment reaction O$^-$ + CH$_4$ $\rightarrow$ CH$_4$O$^-$ $\rightarrow$ CH$_4$O + e$^-$ and thereby that of an intermediate stage involving the anion CH$_4$O$^-$.

Conclusion.—The ability of energetic (i.e., kiloelectronvolt) electron bombardment to *enhance* the chemical reactivity of surfaces has been previously established for such diverse processes as semiconductor etching,[18] silicon oxidation,[19] and hydrocarbon formation from graphite.[20] We have shown in this Letter that, via the formation of transient anions and their decay by dissociative attachment, much lower energy (5–20 eV) electrons can *induce* and *control* a *specific* abstraction reaction near a platinum surface covered with oxygen and hydrocarbon layers.

[1]M. T. Bowers, *Gas-Phase Ion Chemistry* (Academic, New York, 1979).

[2]S. G. Lias and P. Ausloos, *Ion-Molecule Reactions* (American Chemical Society, Washington, D.C., 1975).

[3]See Ref. 1, Vol. 1, Chap. 1.

[4]M. F. A. Harrison, in *Physics of Plasma-Wall Interactions in Controlled Fusion,* edited by D. E. Post and R. Behrisch (Plenum, New York, 1985).

[5]See Ref. 1, Vol. 2, Chap. 15.

[6]See also J. T. Cheung and S. Datz, J. Chem. Phys. **73**, 3159 (1980); D. L. Champion and L. D. Doverspike, Phys. Rev. A **13**, 609 (1976); M. Barat, J. C. Benot, J. A. Fayeton, J. C. Houver, J. B. Ozenne, R. S. Berry, and M. Durup-Ferguson, Chem. Phys. **97**, 165 (1985).

[7]J. Bohdansky and J. Roth, Radiat. Eff. **89**, 49 (1985).

[8]G. Foldiak, *Studies in Physical and Theoretical Chemistry 14: Radiation Chemistry of Hydrocarbons* (Elsevier, New York, 1981).

[9]D. K. Bohme and F. C. Fehsenfeld, Can. J. Chem. **47**, 2717 (1969); D. A. Parkes, J. Chem. Soc. Faraday Trans. 1 **68**, 613 (1972).

[10]W. Lindinger, D. L. Abbritton, F. C. Feshenfeld, and E. E. Fergusson, J. Chem. Phys. **63**, 3238 (1975).

[11]L. Sanche, Phys. Rev. Lett. **53**, 1638 (1984).

[12]L. Sanche and M. Michaud, Phys. Rev. B **30**, 6078 (1984).

[13]L. Sanche, J. Chem. Phys. **71**, 4680 (1979).

[14]R. Azria, L. Parenteau, and L. Sanche, unpublished.

[15]L. V. Trepka, Z. Naturforsch. A: Astrophys. Phys. Phys. Chem. **18**, 1122 (1963).

[16]L. Sanche, G. Perluzzo, and M. Michaud, J. Chem. Phys. **83**, 3837 (1985).

[17]J. Comer and G. J. Schulz, Phys. Rev. A **10**, 2100 (1974).

[18]J. W. Coburn and H. F. Winters, J. Appl. Phys. **50**, 3189 (1979).

[19]M. C. Munoz and J. L. Sacedon, J. Chem. Phys. **74**, 4693 (1981).

[20]C. I. H. Ashby, J. Nucl. Mater. **111 & 112**, 750 (1982).