Chiral-Selective Chemistry Induced by Spin-Polarized Secondary Electrons from a Magnetic Substrate

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We demonstrate for the first time that low-energy spin-polarized secondary electrons, produced by irradiation of a magnetic substrate, can induce chiral-selective chemistry. Our approach was to perform detailed measurements of the reaction rate for x-ray induced, secondary electron photolysis of a model chiral compound, (*R*)- or (*S*)-2-butanol, adsorbed on a magnetized Permalloy substrate. The results showed that there is an enhancement of ~10% in the rate of CO bond cleavage that depends on the chirality of the molecule and the spin polarization of the substrate secondary electrons.

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Because of the fundamental nature that handedness (chirality) plays in biological processes, researchers have been striving for years to discover the possible mechanisms that could have led to this property [1,2]. External agents that are thought to induce chirality in organic molecules, such as circularly polarized UV photons and longitudinal spin-polarized electrons, have been extensively investigated with varying degrees of success [3–12]. It is widely recognized that delivery of exterrestrial organic compounds to Earth by comets or interstellar dust particles may be a potential source of prebiotic (leading to life) molecules. Furthermore, chiral amino acids have been detected in meteorites [13]. Thus, a significant effort has been directed towards understanding radiation-induced reactions occurring in the interstellar medium [5,7–9,14]. In the present Letter, we hypothesize that a previously unconsidered chiral agent can play a role in chiral-selective chemistry: namely, low-energy spin-polarized secondary electrons, produced by photon [15,16], electron [17,18], or ion [19] irradiation of a magnetic substrate. The direction of the spin is determined by the relative orientation of the magnetization vector with respect to the propagation direction of the particle beam. To test this premise we have performed detailed measurements of the reaction rate for x-ray induced, secondary electron photolysis of a model chiral compound, (*R*)- or (*S*)-2-butanol, adsorbed on a magnetized Permalloy ($Fe_{0.2}Ni_{0.8}$) substrate. We show that there is an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chirality of the molecule and the spin polarization of the substrate secondary electrons. This enhancement is well above that seen in most previous studies [1–12]. Furthermore, the present mechanism is more general in that it requires only a magnetic substrate and a source of ionizing radiation. Iron is one of the most common elements and is magnetic in many forms. Ionizing radiation and magnetic fields are ubiquitous throughout the Universe. Therefore, this proposed mechanism for inducing chirality should be viable in a wide variety of possible environments.

Our approach involves monitoring C-O bond cleavage of a model chiral molecule, (*R*) or (*S*)-2-butanol ($CH_3CHOHC_2H_5$, see models in Fig. 1), adsorbed on a magnetic Permalloy ($Fe_{0.2}Ni_{0.8}$) substrate, as a function of x-ray irradiation time. The chiral carbon on 2-butanol is bound to an -OH group. Experiments were carried out under UHV conditions using x-ray photoelectron spectros-

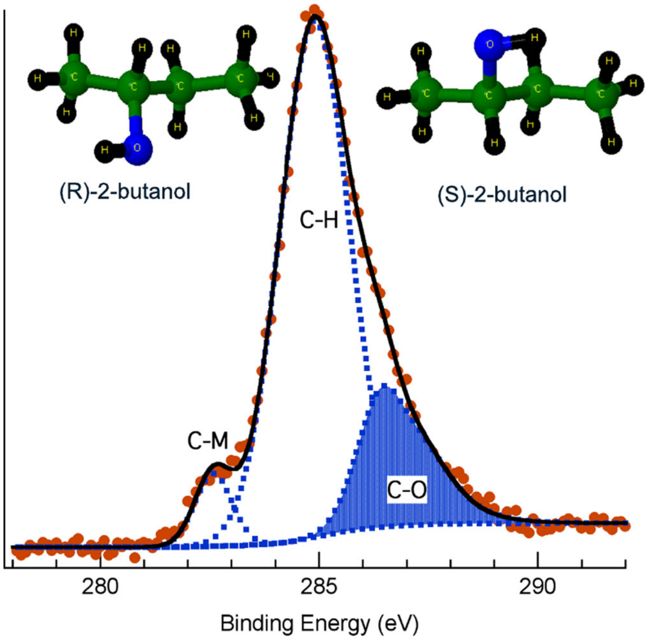

FIG. 1 (color online). C 1 s XPS spectrum of (*R*)-2-butanol adsorbed on Permalloy at 90 K obtained at the start of a photolysis series. The points are the raw data; the dashed lines are the individual fitted components, and the solid line is the synthesized curve. The filled-in region represents the C-O peak, which directly probes the chiral carbon. Also shown are models of (*S*)- and (*R*)-2-butanol.

copy (XPS) to monitor the intensity of the chemically shifted C-O peak. We found that the intensity of the C-O peak decreases exponentially as a function of irradiation time as a result of cleavage of the C-O bond. Using the kinetic relationship, $I = I_0 \exp(t/\tau)$, where $I =$ C-O peak area, $I_0 =$ initial CO peak area, $t =$ time, we are able to extract the time constant, τ, of the reaction as a function of the chirality of the adsorbed molecule and spin polarization of the substrate secondary electrons.

The x-ray source was synchrotron radiation generated at the Advanced Photon Source and transmitted by insertion device beam line 4IDC. Most of the measurements presented here were performed with left circularly polarized light. However, equivalent results were obtained when right circularly polarized light was used. Since changing the light polarization should not have a major effect on the secondary electron spin-polarization distribution [15], this is not surprising. A photon energy of 1190 eV was used for all XPS measurements. The substrate was a 1-μm-thick Permalloy ($Fe_{0.2}Ni_{0.8}$) film. All the sample preparation and measurements were performed with the sample cooled to 90 K. Before adsorption, the $\sim 1 \times 1$ cm^2 substrate was cleaned in UHV by 1-kV Ar^+ sputtering. (R)- and (S)-2-butanol (99% purity) were obtained from Sigma Aldrich, Milwaukee, WI. Prior to dosing, the butanol was purified by several freeze-pump-thaw cycles. Approximately 3 monolayers of (R)- or (S)-2-butanol were adsorbed on the substrate cooled to 90 K. All measurements were performed in a UHV chamber with a base pressure of 1.1×10^{-10} torr. X rays were incident at an angle of 60 deg with respect to the sample normal for all measurements. The substrate was magnetized in the surface plane either in the same direction as the propagation vector of the x-ray beam (+ magnetization) or in the opposite direction (− magnetization). The magnetization direction was verified by performing Ni L x-ray magnetic circular dichroism measurements [20].

A typical C 1s XPS spectrum obtained at the start of a photolysis series is shown in Fig. 1. The overall shape of the spectrum is the same as that obtained after adsorbing the same amount of butanol on the substrate cooled to 30 K and predosed with a multilayer Xe film. Since there should be no chemical interactions between butanol and Xe, this indicates that the adsorption state of butanol on the Permalloy surface is molecular (not dissociated). Molecular absorption is also indicated by results from previous studies [21,22]. Using curve-fitting techniques, the spectrum in Fig. 1 can be decomposed into three main peaks. The small one at ~282.5 eV is due to atomic carbon bound to a substrate metal atom (C-M). Some of this intensity is due to residual carbon that remained after sputter cleaning the surface (<0.03 monolayer) and some is due to carbon produced from butanol photolysis during the time it took to acquire the spectrum. The most intense peak at ~284.9 eV is due to alkyl carbons (C-H), while the peak at ~286.5 eV is due to the chiral C atom bound to the OH group [23].

A series of C 1 s XPS spectra obtained during irradiation with 1190 eV x rays is shown in Fig. 2. Photolysis results in a decrease in intensity of the C-O and C-H peaks and an increase in the C-M intensity. The C-H peak also shifts to lower binding energy. This shift is mainly due to C-O bond cleavage, which lowers the binding energy of the carbons in the resultant compound. This bond cleavage may also produce additional compounds that contribute to the C-H intensity. Photolysis may also cleave C-C bonds to produce gas phase and/or bound CH_x by-products. These factors make analysis of the C-H peak complex. Therefore, we focus our kinetic analysis on the C-O peak that directly probes the state of the chiral carbon atom. During the fitting of a photolysis series such as that shown in Fig. 2, the peak shape, width, and position were kept constant for the C-O and C-M structures, while the width and position of the C-H peak was allowed to vary for the reasons mentioned previously.

The inset in Fig. 2 shows the area of the C-O peak as a function of irradiation time. The points are the values of the peak areas and the solid line is a fit of a single exponential function, $A + B \exp(-t/\tau)$, that yields the reaction time constant τ. This procedure was done 6–8 times for each chirality and magnetization direction. The overall time

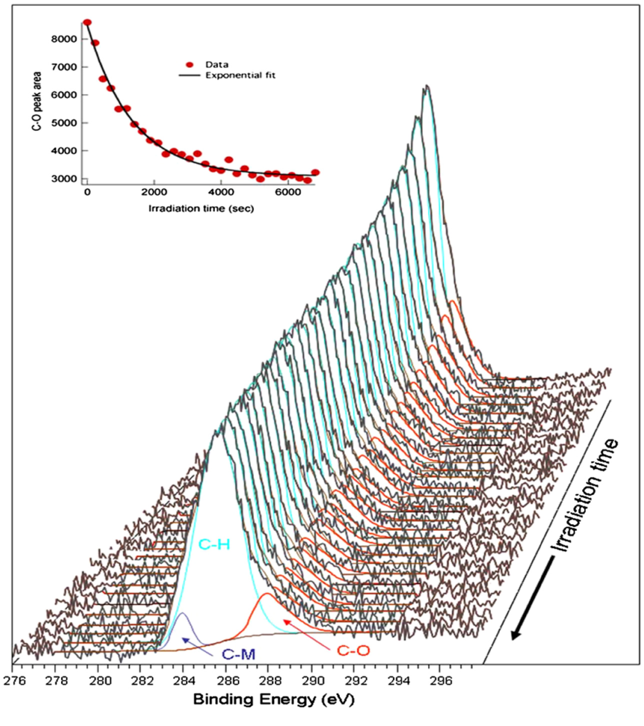

FIG. 2 (color online). Series of C 1 s XPS spectra of (R)-2-butanol adsorbed on Permalloy obtained sequentially while irradiating with 1190-eV x rays. The inset shows the area of the C-O peak as a function of irradiation time (data points), and the solid line is the curve resulting from least-squares fitting of a single exponential peak [$A + B \exp(-t/\tau)$] to the data.

constant results are summarized in Fig. 3. The individual time constants, with error bars, for the various photolysis series are shown by the data points, and the average value of τ, for each chirality and magnetization direction, is shown by the straight line and tabulated in the figure. This figure clearly indicates that a reversal of the secondary electron spin polarization results in a significant change in the reaction rate for a given chirality. For (*S*)-2-butanol this difference is $8.9 \pm 3.5\%$, while for (*R*)-2-butanol, it is $10.9 \pm 3.8\%$. The fact that the results for each enantiomer are mirror images of the other is compelling evidence of the validity of the proposed mechanism. It is also interesting to note that these differences in the time constants are approximately the same as the degree of secondary electron spin polarization observed for Permalloy (10%–15%) [17]. To further confirm these findings, a racemic 2-butanol mixture (equal amounts of both enantiomers) was employed. The obtained results indicated that changing the magnetization direction (spin polarization) does not change the reaction time constant of the racemic mixture.

The average difference between the time constants for the two enantiomers is ~10%. Using this value we have calculated the enantiomeric excess (*ee*) for an initial racemic mixture as a function of reaction time. After the time spent acquiring the data in Fig. 2, which equals 6900 sec and represents 4.3 time constants, the *ee* would be 25%. Based on an exponential decay, $e^{-4.3}$, 1.4% of the initial concentration would be left intact. After a time equivalent to 2 time constants the *ee* would be 12% with 14% of the initial population remaining. To our knowledge these are the largest values for enantiomeric excesses as the result of circularly polarized light or spin-polarized electron irradiation ever reported. There are several important reasons for the success of the present approach. First of all the measurements were performed under UHV condition with a well-characterized substrate and carefully controlled, reproducible adsorbate overlayers. Second, the reaction rate constants and thus the *ee* were all determined *in situ*. Prior approaches relied on removing the irradiated sample from the reaction vessel and analyzing the chirality using chromatography techniques, which also necessitated processing the sample for analysis. Finally, whereas previous work determined only the *ee* after a given period of irradiation, our approach yields the reaction time constant, which is a more fundamental value.

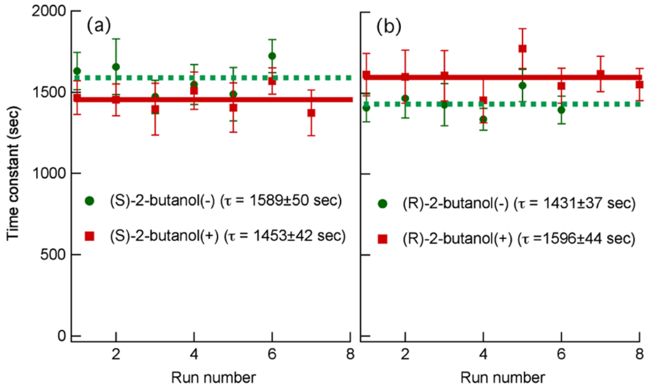

FIG. 3 (color online). Summary of the time constant results. The squares are the points for + magnetization, and the circles are the points for − magnetization. The lines represent the average values, which are also tabulated: (a) (*S*)-2-butanol and (b) (*R*)-2-butanol.

The extracted time constant τ equals $1/\chi f$, where f is the x-ray flux density and χ is the photolysis cross section. Using approximate values of the beam area (3×10^{-4} cm^2) and x-ray flux (3.5×10^{11} ph/sec), yields a flux density of 1.7×10^{15} ph/sec cm^2 and a χ of $\sim 6 \times 10^{-19}$ cm^2. Our results show that it is the secondary electrons that are inducing the chemical changes. Therefore, it is more applicable to use the secondary electron flux to compute the cross section. An upper bound to this is given by the total electron yield flux density. This is determined from the measured sample current of 3.8 nA or 2.4×10^{10} e/sec, which results in a cross section of 9×10^{-18} cm^2 (9 Mb). This value compares fairly well with reported dissociative electron impact cross sections for CO production from condensed films of acetone (9.6 Mb) [24] or methanol (4.2 Mb) [25] via a dissociative electron attachment (DEA) mechanism. In the present case a DEA mechanism, in which a temporary negative ion state is formed, is likely involved since the secondary electron energy distribution and their polarization is highest at low kinetic energies, ~2 eV [26]. If the orbital occupied during DEA is sufficiently diffuse so as to "sample" the regions of the molecule responsible for the chiral structure [27] then enantiomeric specific dissociation will result. On the other hand, it has been theorized that two enantiomers will be ionized at different rates by longitudinally spin-polarized electrons [28]. If there are sufficient numbers of higher energy spin-polarized secondary electrons and the final state reached following ionization is dissociative, then this could lead to chiral enhancement.

Experimental [11] and theoretical [10] studies have shown that relatively large asymmetries exist in the scattering of longitudinally polarized electrons by organized, adsorbed chiral molecules relative to isotropic species. Prior studies of low temperature 2-butanol adsorption on single metal crystal surfaces have shown that the adsorbate overlayer is ordered and the molecule is bound to the surface through the oxygen atom [21,22]. It is reasonable to assume a similar adsorption behavior of 2-butanol on the polycrystalline metallic Permalloy surface used in the present study. Therefore, it is likely that some degree of ordering exists in the first layer, as well as the overlayers (due to hydrogen bonding). Such ordering would enhance the reactive scattering of the polarized electrons by the 2-butanol molecules adsorbed on the Permalloy surface.

Previously, nuclear β decay was the only source considered for spin-polarized electrons [12]. However, the β

particles are high-energy electrons, unlikely to produce chiral-specific chemistry [12]. In the present Letter we propose that there is a much more probable source of spin-polarized electrons—low-energy secondary electrons produced by ionizing (photon, electron, ion) radiation impact with a magnetic substrate. Our measurements have shown that such electrons can produce chiral-specific chemistry. Iron is one of the most common elements and many iron compounds are magnetic where the degree of spin polarization of the secondary electrons has been shown to reach as high as 70% [15,16,18,19,29]. It is easy to imagine numerous scenarios where a magnetized iron substrate in an interstellar dust grain, a comet, a meteor, or on primitive Earth or another planet, would have produced spin-polarized secondary electrons as the result of irradiation. Furthermore, low-energy, primary spin-polarized electrons can also be produced directly by the interaction of circularly polarized UV light with a nonmagnetic substrate [11]. Based on the present results, low-energy, spin-polarized electrons interacting with adsorbed chiral molecules could produce a significant enantiomeric excess of a prebiotic molecule.

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