Electron-induced chemistry of alcohols

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Electron-induced chemistry of alcohols

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Abstract. We studied dissociative electron attachment (DEA) to a series of compounds with one or two hydroxyl groups. For the monoalcohols we found, apart from the known fragmentations in the 6 – 12 eV range proceeding via Feshbach resonances, also new weaker bands at lower energies, around 3 eV. They have a steep onset at the dissociation threshold and we assigned them as proceeding via shape resonances with temporary occupation of $\sigma^*$ orbitals. These low energy fragmentations become much stronger in the larger molecules and even the strongest DEA process in the compounds with two hydroxyl groups. Above 6 eV, in the Feshbach resonance regime, the dominant process is a fast loss of a hydrogen atom from the hydroxyl group. In some cases the resulting ($M - 1$)$^-$ anion (loss of hydrogen atom) is sufficiently energy-rich to further dissociate by loss of stable, closed shell molecules like H$_2$ or ethene.

1. Introduction
The interest in electron-induced chemical processes has been renewed by the discovery that electrons at subionization [1] and even subexcitation energies [2] damage DNA and by the emerging applications in materials science [3]. These applications inspired studies of the corresponding elementary step, the DEA to isolated polyatomic molecules in the gas phase and in particular to molecules of biological interest, with many interesting findings [4–7]. In our earlier work we studied several saturated compounds containing the amino and the hydroxy groups which could be considered as model compounds for biomolecules [8, 9]. Saturated compounds do not have $\pi^*$ shape resonances and fragmentations are generally mediated by Feshbach resonances in the 6 – 12 eV region. Feshbach resonances with occupation of Rydberg-like orbitals are well known from scattering experiments other than DEA, in particular ETS of rare gases, diatomic and polyatomic molecules [10, 11] or in the vibrational excitation cross sections [12]. The energies of these Feshbach resonances were found to have a simple relation to the energies of the parent Rydberg states and the grandparent state of the cation[13]. The relation depends only weakly on the molecule in question and can be used to identify and assign the Feshbach resonances. This paper presents dissociative electron attachment spectra of a series of alcohols and assigns the observed bands to various types of resonances, guided by comparison with HeI photoelectron spectra and vibrational excitation cross sections.

2. Methods
The dissociative electron attachment spectrometer used to measure the yield of mass-selected stable anions as a function of electron energy has been described previously [14, 15]. The
vibrational excitation (VE) cross sections were recorded with a spectrometer using hemispherical electron-energy selectors [16]. The photoelectron (PE) spectra were recorded with a modified Perkin Elmer PS18 HeI photoelectron spectrometer.

Threshold energies for various fragmentations were calculated as the differences of the total energies of the products and the targets at 0 K, corrected for the zero point vibrational energy, using the density functional theory (DFT) B3LYP/6−311+G(2df,2p) model [17].

3. Results and Discussion

The spectra of the alcohols studied in this work – the two simplest alcohols (methanol and ethanol), one cyclic alcohol (cyclopentanol) and a pair of cyclic diols (cis-1,2-cyclopentadiol and trans-1,2-cyclopentanediol) – are shown in figures 1 and 2. The cyclic diols were chosen because of their relation to ribose, relevant for the study of DNA [18, 19].

The spectra can be divided in two domains: low energy (0 - 5 eV) and high energy (5 - 10 eV). In the latter domain the chemistry, already well-known from smaller alcohols [20, 21], proceeds via Feshbach resonances, with a grandparent positive ion core and two electrons in diffuse Rydberg-like orbitals.

Additionally to the dissociations mediated by the Feshbach resonances, we report bands at lower energies, 2−3 eV. In all molecules the left sides of low energy bands are steep and consistent with vertical onsets at energetic thresholds (Table 1). Comparison of the threshold energies determined from experimental thermochemical data and calculated using quantum chemical methods for methanol and ethanol indicates that the latter are reliable within about ±0.2 eV, sufficient for the present purposes.
Table 1. Threshold energies for the reactions $e^{-} + ROH \rightarrow RO^{-} + H$, in eV. The DFT values were calculated as described in section 2. The “therm.” values were derived from experimental thermochemical data [22]. The onsets of the DEA bands are from the present spectra.

<table>
<thead>
<tr>
<th>Target</th>
<th>$E_{thr}^{DFT}$</th>
<th>$E_{thr}^{therm.}$</th>
<th>Onset of DEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>2.82</td>
<td>2.94</td>
<td>2.86</td>
</tr>
<tr>
<td>ethanol</td>
<td>2.69</td>
<td>2.81</td>
<td>2.75</td>
</tr>
<tr>
<td>cyclopentanol</td>
<td>2.53</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>cis-cyclopentane-1,2-diol</td>
<td>1.89</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>trans-cyclopentane-1,2-diol</td>
<td>2.43</td>
<td>2.43</td>
<td></td>
</tr>
</tbody>
</table>

The low energy bands can not be assigned to core-excited resonances due to lack of suitable electronically excited parent state (either Rydberg or valence). At the same time the energy is too high for an assignment to a dipole-bound resonance or a virtual state. The dissociation must thus proceed via a $2(\sigma^*)$ shape resonance.

![Figure 2](image_url)

Figure 2. DEA spectra and PE spectra (shifted by $-4.5$ eV) of cis-cyclopentane-1,2-diol (left) and trans-cyclopentane-1,2-diol (right).

Additional evidence for the identity of resonance processes is provided, in the case of ethanol, by the cross sections for vibrational excitation (VE)(figure 1). The spectrum for the excitation of the C−H stretch vibration is similar to the C−H stretch excitation in hydrocarbons [23] – it consists of a very broad band peaking around 7.5 eV which could be assigned to a temporary occupation of $\sigma_{CH}^*$ orbitals. The cross section for the excitation of the O−H stretch vibration is similar to the cross section observed in formic acid [24] – it peaks at threshold and then decreases slowly over an energy range of several eV. The electron cloud associated with this
resonant process must be located on the O–H bond. The band in the O–H stretch vibrational excitation cross section is much broader than the band in the \((M - 1)^-\) DEA band in Fig. 1, but we propose that both processes are due to the same \(\sigma^*\) shape resonance, possibly enhanced by dipole binding at low energies. The DEA bands at higher energies do not have any obvious analogs in VE, providing a further evidence that they are due to core excited Feshbach resonances and not to \(\sigma^*\) shape resonances.

The \(\text{H}^-\) yield is very similar in shape to the \(\text{CH}_3\text{O}^-\) yield above 6 eV, indicating that the same Feshbach resonances dissociate into both fragments – the charge distribution is not selective. The low energy band is missing in the \(\text{H}^-\) yield – probably because of the higher threshold for \(\text{H}^-\) formation.

Figure 2 shows the PES and DEA spectra of two representative diols. The oxygen lone pair orbitals give rise to two bands in the photoelectron spectrum. They are affected by a hydrogen bridge in the case of the cis compound while in the case of the trans compound they are subject to a destabilizing through-bond interaction, leading to the ‘reverse order’ of the cationic states [25].

The most striking feature of the DEA spectra of the diols is the decreasing energy and increasing relative intensity of the low energy band in comparison to the monoalcohols – they are more intense than the Feshbach resonance bands, in sharp contrast to the simple alcohols. The decreasing thresholds are the results of the increased electron affinity of the fragments, particularly for the cis compound where the negative charge is stabilized by a hydrogen bridge. The increase in intensity could be a consequence of decreasing autodetachment width of the lowest \(\sigma^*\) resonance as a result of its decreased energy.

References
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