



## Editor's choice

Anion photoelectron spectroscopy of the linear  $C_nH_{2n+1}O^-$  ( $n = 1-9$ ) alkoxides

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## HIGHLIGHTS

- Photoelectron spectra (PES) were taken of the linear  $C_nH_{2n+1}O^-$  ( $n = 1-9$ ) alkoxides.
- Electron affinities (EAs) and vertical detachment energies (VDEs) were determined.
- EA and VDE values increased monotonically with carbon chain length.
- O–H bond dissociation energies (BDEs) of the corresponding alcohols can be found.
- O–H BDEs were found using our EAs, gas phase acidities, and a thermochemical cycle.

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## ABSTRACT

The photoelectron spectra of the linear  $C_nH_{2n+1}O^-$  ( $n = 1-9$ ) alkoxide anions are presented, building on previous reports pertaining to  $n = 1-3$ . The vertical detachment energies (VDE) and electron affinities (EA) show a monotonic increase with carbon chain length and are used in thermochemical cycles in conjunction with previously reported gas phase acidities of their corresponding alcohols to determine the O–H bond dissociation energies for these alcohols.

## 1. Introduction

Alkoxy radicals have enjoyed much study as a result of their importance in atmospheric chemistry and also because of their fundamental significance in organic chemistry. This has been especially true for the methoxy and ethoxy radicals; indeed the photoelectron spectra of their corresponding alkoxide anions alone have been measured on four and three occasions respectively [1–6]. Numerous, hundreds, of other spectroscopic and theoretical studies have been focused on these smaller alkoxy radicals. Comparatively fewer studies have been done on their larger counterparts, especially the 1-alkoxy radicals. Photoelectron and photodetachment studies of higher alkoxide anions have focused on other isomers, 2-propoxide [2,4], t-butoxide [2,4,7], n-pentoxide [7], as well as some cyclic analogues, c-propoxide, c-butoxide, and c-pentoxide [8,9]. Recently, however, laser induced fluorescence (LIF) and dispersed fluorescence spectra of the 1-alkoxy radicals through  $n = 10$  have been collected [10–19] and a few theoretical

studies have calculated electron affinities and simulated photoelectron spectra of the linear, anionic alkoxides [20–23].

Of no less import, the measurement of the electron affinities of the alkoxides allows for the calculation of O–H bond dissociation energies (BDE's) of the corresponding alcohol; this is done via a thermochemical cycle presented in the discussion below using the gas phase acidities of the alcohol of interest. The measurement of gas phase acidities of the linear alcohols has also occupied some space in the scientific literature especially after the discovery that the gas phase acidities of these alcohols runs exactly opposite to their solution phase acidities [24–33]. Bond dissociation energies for the smaller alcohols have also been measured directly or calculated via this thermochemical cycle [1,4,31,34]. Accurate bond dissociation energies are required to model combustion processes of alcohols which brings us full circle back to the importance of the alkoxy radicals in atmospheric chemistry.

Here we present our photoelectron spectra of the linear, 1-alkoxides,  $C_nH_{2n+1}O^-$ , where  $n = 1-9$ . We extract VDE's and EA's from

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our spectra and where applicable peak positions and splittings are provided. Comparisons to the earlier work of Lineberger and Neumark [1–6] on the smaller alkoxides in this series,  $n = 1–3$  are made to anchor our work. We focus our discussion on three main points: (1) the overall monotonic increase in electron affinities over the entire series of spectra, (2) a closer look at the  $n = 3$  and  $n = 4$  alkoxides as for 1-propoxide we are able to see a new peak relative to the earlier work of Lineberger [2] and the new PES of 1-butoxide is the largest in the series to retain some vibrational structure in its spectrum, and (3) the calculation of the O–H BDE's using the anion thermochemical cycle.

## 2. Experimental

Negative ion photoelectron spectroscopy was used to measure the electron affinities and vertical detachment energies of several alkoxy radicals and their alkoxide anions. Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the relationship,

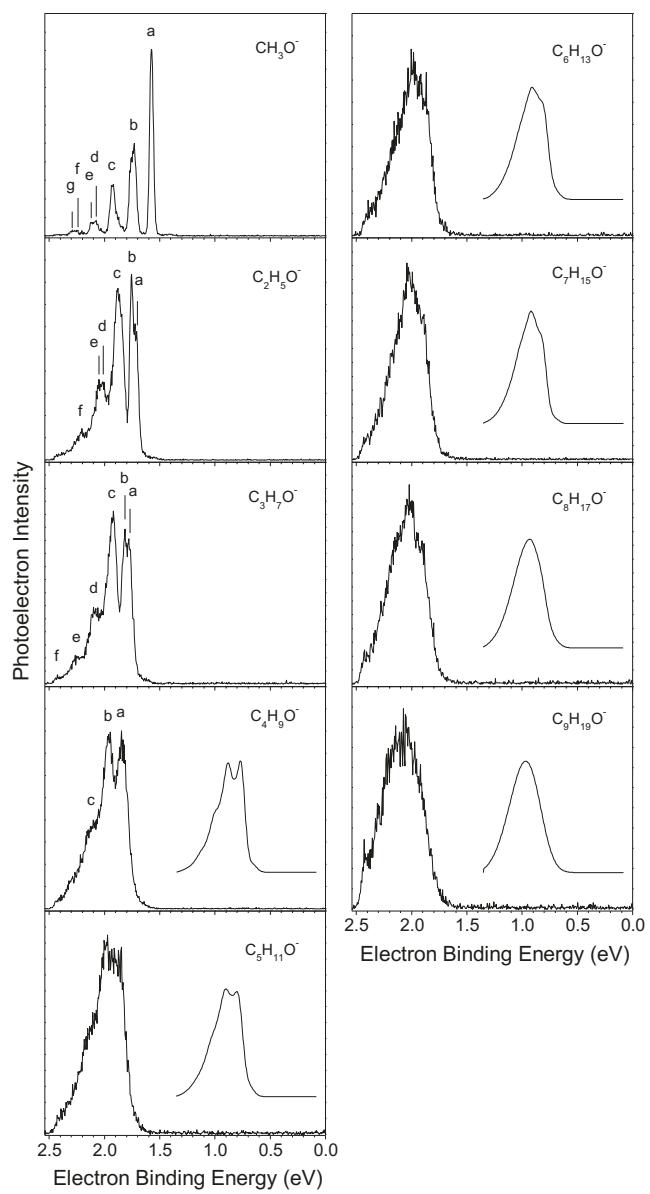
$$h\nu = \text{EBE} + \text{EKE} \quad (1)$$

where  $h\nu$  is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Essentially, the photon energy is subdivided into the transition energy needed to take the anion to a particular vibronic state of its neutral counterpart, i.e., EBE, and the kinetic energy of the electron, i.e., EKE. [Supplementary Fig. 1](#) illustrates the energetics of photodetachment transitions. Since photodetachment is a fast process, the essentially instantaneous Franck-Condon overlap of anion and neutral wavefunctions is reflected in the vertical detachment energy, VDE. When the structures of the anion,  $X^-$ , and its corresponding neutral,  $X$  are different (as in [Supp. Fig. 1](#)), the VDE is the EBE of the maxima in the broadened photoelectron spectral profile, and as such, it is a well-defined quantity.

When there is Franck-Condon overlap between the lowest vibrational level of the anion ( $v''$ ) and the lowest vibrational level of its corresponding neutral ( $v'$ ), the photoelectron spectrum carries information about the adiabatic (thermodynamic) electron affinity of the neutral species. When the spectral profile is vibrationally resolved, an assignment of the spectrum can identify the  $v'' = 0 \rightarrow v' = 0$  transition. For this transition, its EBE value is equal to the adiabatic electron affinity,  $\text{EA}_a$ . When the profile is unresolved, however, the determination of  $\text{EA}_a$  is more approximate. If the anion were to be cold, i.e., if only  $v'' = 0$  were occupied, then the low EBE threshold value of the spectrum would equal the  $\text{EA}_a$  value. But since anions are generated with finite internal temperatures, the first few vibrational levels of anions may also be occupied, leading to some degree of photoelectron intensity at EBE values less than that corresponding to the  $\text{EA}_a$ , i.e., hot bands. Thus, in order to extract reasonable estimates of  $\text{EA}_a$  values from unresolved photoelectron spectral profiles (bands), we have performed Franck-Condon fittings of our spectra.

The apparatus consists of a source for generating anions, a magnetic sector for mass analysis and mass selection, and argon ion laser operated intra-cavity as the photon source, and a hemispherical electron energy analyzer. The mass analyzer/selector has a mass resolution of  $\sim 400$ , and the electron energy analyzer has a resolution of 33 meV. All photoelectron spectra reported here were recorded with 2.540 eV photons and calibrated against the photoelectron spectrum of  $\text{O}^-$  [35]. Our apparatus has been described previously [36].

Selected alkoxide anions were generated in a supersonic expansion, nozzle-ion source which was biased at  $-500$  V. Samples of the alcohols of interest were placed inside the stagnation chamber of the source and heated to temperatures ranging between 30 and 120 °C in order to partially vaporize them. The resulting vapor was then co-expanded with argon (2–3 psig) through a  $50\text{ }\mu\text{m}$  orifice into vacuum. Negative ions were formed by injecting electrons from a biased filament into the



**Fig. 1.** Photoelectron spectra of the linear  $\text{C}_n\text{H}_{2n+1}\text{O}^-$  alkoxides where  $n = 1–9$  taken with 2.54 eV photons. Franck-Condon fittings are shown for  $n = 4–9$  in the insets.

expanding jet, where a microplasma was formed with the help of an external magnetic field. Negative ions were then extracted into the beam-line of the apparatus and subsequently mass-selected so that the anions of interest could be photodetached.

## 3. Results

The photoelectron spectra of the linear  $\text{C}_n\text{H}_{2n+1}\text{O}^-$  alkoxides where  $n = 1–9$  are presented below in [Fig. 1](#). The first three spectra have been reported in the literature before [1–6] but are presented here to show the progression of the series of alkoxides in its entirety. The first of the new photoelectron spectra, that of  $\text{C}_4\text{H}_9\text{O}^-$ , shows two definitive peaks in the photoelectron spectrum while spectra of subsequent alkoxides show a single, broad band that moves to progressively higher binding energies as carbon chain length increases. Note that there is a monotonic increase in electron binding energies as one progressively lengthens the alkane tail via the addition of  $-\text{CH}_2-$  groups. This observation can be quantified primarily using the EA's and VDE's given in [Table 1](#). The extraction of these values from the photoelectron spectra

**Table 1**

<sup>1</sup>EA's were assigned using Franck Condon fittings as a guide. <sup>2</sup>ΔEA's are the change in EA between adjacent (in terms of n) alkoxides. <sup>3</sup>EA's in kJ/mol will be used in thermochemical calculations presented in **Table 3**. <sup>4</sup>VDE's were found by fitting a Gaussian function to the photoelectron spectra after they were cropped below the FWHM line. <sup>5</sup>ΔVDE's are tabulated similarly to ΔEA's.

Species	EA (eV) <sup>1</sup>	ΔEA (eV) <sup>2</sup>	EA (kJ/mol) <sup>3</sup>	VDE (eV) <sup>4</sup>	ΔVDE (eV) <sup>5</sup>
CH <sub>3</sub> O <sup>-</sup>	1.578 ± 0.02	–	152 ± 2	1.578	–
C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>	1.710 ± 0.02	0.133	165 ± 2	1.755	0.178
C <sub>3</sub> H <sub>7</sub> O <sup>-</sup>	1.781 ± 0.02	0.071	172 ± 2	1.921	0.166
C <sub>4</sub> H <sub>9</sub> O <sup>-</sup>	1.849 ± 0.02	0.068	178 ± 2	1.920	– 0.001
C <sub>5</sub> H <sub>11</sub> O <sup>-</sup>	1.88 ± 0.05	0.03	181 ± 5	1.944	0.024
C <sub>6</sub> H <sub>13</sub> O <sup>-</sup>	1.90 ± 0.05	0.02	183 ± 5	1.976	0.032
C <sub>7</sub> H <sub>15</sub> O <sup>-</sup>	1.92 ± 0.05	0.02	185 ± 5	2.004	0.028
C <sub>8</sub> H <sub>17</sub> O <sup>-</sup>	1.95 ± 0.05	0.03	188 ± 5	2.031	0.027
C <sub>9</sub> H <sub>19</sub> O <sup>-</sup>	1.98 ± 0.05	0.03	191 ± 5	2.095	0.064

required some care particularly for the larger alkoxides as their spectra are unresolved, thus, Franck-Condon fittings were done using the PESCAL 2010 program from Ervin and Lineberger [37]. These fittings are included in **Fig. 1** in the insets next to their respective PES. Franck-Condon fittings were done only for the n = 4–9 alkoxides for two reasons, first the n = 1–3 PES and EA's have been recorded previously, and secondly these first three alkoxides exhibit non-adiabatic effects making Franck-Condon fittings suspect. Great care was taken in the assignment of electron affinities; for the first three alkoxides we were able to compare our spectra with multiple points of reference to the literature. We see that our n = 1–3 photoelectron spectra share the same profile as previously recorded spectra provided differences in resolution are taken into account. Secondly, the electron affinities we find for these three alkoxides are in excellent agreement with those reported by Lineberger and Neumark [1–6]. These three provide the ground work for assignments of electron affinities for the larger alkoxides. We use the same methodology and extend it to the new systems. While there are no literature PES for these specific isomers of the n = 4–9 alkoxides we are able to make comparisons to other isomers (see below). The electron affinities for the n = 5–9 alkoxides should be expected to have larger error bars associated with them as a result of the spectra being unresolved. **Supplementary Figure 3** (and the graphical abstract) shows a plot VDE and EA vs. carbon chain length which shows graphically what can be seen on inspection of the PES which again is the largely monotonic increase in electron binding energy as chain length increases.

## 4. Discussion

### 4.1. Comparison to earlier photoelectron studies

#### 4.1.1. Methoxide and ethoxide

The photoelectron spectra of the methoxide and ethoxide anions have each been taken on several previous occasions, each time with higher resolution [1–6]. Our photoelectron spectra have comparatively lower resolution than these latest studies and thus are presented to show the progression of the entire series of n-alkoxides and as a point of comparison to the literature. That being said our photoelectron spectra of these ions broadly match the spectra of Lineberger and Neumark; because of the higher resolution of their spectra they are able to resolve two peaks where often we see only one broader peak, however, the EA and overall peak spacings are in agreement. Peak positions and splittings in the photoelectron spectra of the n = 1–4 alkoxides are summarized in **Table 2**; the EA's of the larger alkoxides are also given again for comparison.

#### 4.1.2. 1-Propoxide

As carbon chain length increases one needs to be cognizant that there are not only two isomers of the propoxide anion (and propoxy

**Table 2**

Summary of peak positions and splitting for labeled spectra (n = 1–4); EA's for the larger (n = 5–9) alkoxides are again included for comparison.

Species	Peak Label	Position (eV)	Shift from origin (eV)	Shift from origin (cm <sup>-1</sup> )
CH <sub>3</sub> O <sup>-</sup>	a, origin	1.578		
	B	1.733	0.155	1250
	C	1.923	0.345	2780
	D	2.077	0.499	4020
	E	2.117	0.539	4350
	F	2.243	0.665	5360
	G	2.293	0.715	5770
C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>	a, origin	1.710		
	B	1.755	0.045	360
	C	1.880	0.170	1440
	D	2.020	0.310	2500
	E	2.050	0.340	2740
	F	2.205	0.495	3990
C <sub>3</sub> H <sub>7</sub> O <sup>-</sup>	a, origin	1.781		
	B	1.816	0.035	280
	C	1.921	0.140	1130
	D	2.101	0.320	2580
	E	2.256	0.475	3830
	F	2.426	0.645	5200
C <sub>4</sub> H <sub>9</sub> O <sup>-</sup>	a, origin	1.849		
	B	1.964	0.115	930
	C	2.104	0.155	1250
C <sub>5</sub> H <sub>11</sub> O <sup>-</sup>		1.88		
C <sub>6</sub> H <sub>13</sub> O <sup>-</sup>		1.90		
C <sub>7</sub> H <sub>15</sub> O <sup>-</sup>		1.92		
C <sub>8</sub> H <sub>17</sub> O <sup>-</sup>		1.95		
C <sub>9</sub> H <sub>19</sub> O <sup>-</sup>		1.98		

radical), 1-propoxide and 2-propoxide (isopropoxide) separable of course, but also 2 conformers of the 1-propoxy radical, identified as the trans, T conformer (C<sub>1</sub>-symmetry) and the gauche, G conformer (C<sub>s</sub>-symmetry) by Miller and coworkers [16]. Hereafter we will use 'anti' and A instead of 'trans' and T in accordance with conventional organic nomenclature. These conformers are both present in the fluorescence studies of Miller; they are separated in energy by only 20 cm<sup>-1</sup>. Here we assume both will be present and that our photoelectron spectrum of 1-propoxide will have contributions from both conformers. Multiple conformers will also necessarily be the case for the larger alkoxy radicals as discussed below.

Of the two isomers 2-propoxide is certainly the better studied; to our knowledge the photoelectron spectrum of the 1-propoxide anion has been collected on only one previous occasion by Lineberger and coworkers [2]. Here our PES of this anion has somewhat improved resolution and thus we are able to just resolve two additional peaks, six in total relative to that of the previous study with four features. We see what had been the origin transition at 1.789 eV in the earlier spectrum split into two peaks, 280 cm<sup>-1</sup> apart labeled a and b at 1.781 eV and 1.816 eV respectively; thus our assigned EA is, as expected, a bit smaller than that reported by Lineberger and coworkers. Peak positions and spacings are comparable within experimental error to those reported by Lineberger with the exception noted above.

Recent dispersed fluorescence measurements from Miller [16], allows for two possible assignments for peak b (observed in our spectra 280 cm<sup>-1</sup> above the origin). The first possible assignment is to the 0<sub>0</sub><sup>+</sup> A → X transition, between the ground electronic state of the anion and the first low-lying excited electronic state of the radical. Miller reports the A-X energy separation in the radical to be 321 cm<sup>-1</sup> and 214 cm<sup>-1</sup> for the 1-propoxy A conformer and G conformer respectively. The second possible assignment of this peak is to the X → X 3<sub>0</sub><sup>1</sup> vibrational mode, an in-plane CCO bend with a CCC bend contribution to this normal mode. Miller finds this transition at 274 cm<sup>-1</sup> (A) and 302 cm<sup>-1</sup> (G) above the vibrational ground state. We will make the case that we do see the first low-lying electronic state of the neutral for

reasons that follow.

Lineberger [4], in the case of ethoxide, was able to differentiate between anion electronic ground state to neutral electronic ground state transitions ( $X \leftarrow X$ ) and anion electronic ground state to the first electronically excited state of the neutral ( $A \leftarrow X$ ) using photoelectron angular distribution data. Ethoxide's first electronically excited state lies  $360 \text{ cm}^{-1}$  above the ground electronic state as seen in the angular distribution data has been collected by Lineberger. In the case of 1-propoxide we are unable to conclusively differentiate between the two above possibilities but we think it is likely that we do observe the first electronically excited state of the radical in analogy to the ethoxy radical. One may wonder that we do not make the comparison to 2-propoxide. Lineberger identifies the transition to the first electronically excited state of the radical  $1225 \text{ cm}^{-1}$  above the origin. This finding is at odds with Miller's later finding of  $68 \text{ cm}^{-1}$  for the  $A-X$  energy separation which the calculations of Yarkony confirms [16,22]. Miller finds low-lying electronic excited states of the radicals of 1-propoxy, 2-propoxy, 1-butoxy, and 2-butoxy, thus we are reassured that this transition is seen in our 1-propoxide spectrum and likely our 1-butoxide spectrum though unresolved.

Without photoelectron angular distribution data specifically for 1-propoxide we are unable to decide which peaks can be ascribed to transitions to the ground electronic state of the radical versus the first low lying excited electronic state of the 1-propoxy radical; making definitive assignments is further impeded by the assumed presence of both  $A$  and  $G$  conformers.

#### 4.1.3. 1-Butoxide and the higher alkoxides ( $n = 4-9$ )

This is the first time the PES of the 1-butoxide anion has been taken; this is also the last alkoxide PES in the series to show any structure in its spectrum and as such its electron affinity,  $1.849 \text{ eV}$  is still readily assigned (confirmed also via the FC fitting). The EA we have measured for 1-butoxide is comparable to an experimentally reported EA of Williams and Hamill [38] of  $1.90 \pm 0.1 \text{ eV}$  and to a theoretical value from Li and coworkers of  $1.83 \text{ eV}$  [23]. The EA of 1-butoxide sits in between that of 1-propoxide,  $1.789 \pm 0.033 \text{ eV}$  and t-butoxide,  $1.909 \pm 0.004 \text{ eV}$  [2,4]. There are 4 isomers of butoxide, 1-butoxide, 2-butoxide (chiral R,S), s-butoxide, and t-butoxide; to our knowledge only the PES of the t-butoxide anion has been taken thus far by Lineberger; the photodetachment spectrum of this ion was taken by Brauman [4,7].

As mentioned above in the discussion of 1-propoxide multiple conformers may contribute to our photoelectron spectrum of 1-butoxide. Miller [16,17] identifies five unique conformers of the 1-butoxy radical we label as  $A_1A_2$  (Miller uses  $T_1T_2$  and trans nomenclature), an all anti conformer,  $G_1G_2$ , and  $G_1^{'G_2^{'}}$ , two all gauche conformers and  $G_1A_2$  and  $A_1G_2$ . In his fluorescence spectra not every conformer is observed only the  $A_1A_2$ ,  $G_1A_2$  and  $A_1G_2$  conformers are seen; he speculates that this is due to energy considerations and conversion of the all gauche conformations to the hydroxy butyl radical ( $\bullet\text{CH} - (\text{CH}_2)_2 - \text{CH}_2\text{OH}$ ) [17]. Thus we anticipate that our spectrum will include contributions from at least the three conformers Miller observes. We also note that because our source conditions are hotter than those reported by Miller we would expect to have higher energy conformations populated and so we expect our spectra to have contributions from at minimum the number of conformers seen in the fluorescence experiments if not more. As carbon chain length increases the number of possible conformers increases dramatically to 14 for 1-pentyloxy, 41 for 1-hexaoxy, 122 for 1-heptoxy, 365 for 1-octoxy, and 1094 for 1-nonoxy, however, at least in Miller's fluorescence spectra of the  $n = 3-7$  alkoxy radicals the number of conformers that he observes is still a reasonably small number, 1-hexaoxy and 1-heptoxy are dominated by two conformers, the all anti ( $A_1A_2...A_{n-2}$ ) and the ( $G_1A_2...A_{n-2}$ ) conformers only [16-18].

In the spectrum of  $\text{C}_4\text{H}_9\text{O}^-$ , peak *b* appears at  $1.964 \text{ eV}$  giving a splitting of  $0.115 \text{ eV}$  or  $930 \text{ cm}^{-1}$ . As was the case in 1-propoxide assigning this transition is precarious owing to the possibility of a low-lying excited electronic state in the neutral as well as contributions from

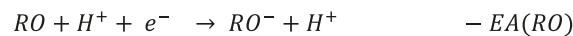
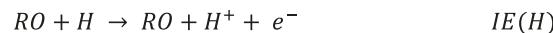
at minimum three conformers.

Photoelectron spectra of 1-pentoxide through 1-nonoide are also presented for the first time; please see Table 1 for EA and VDE assignments for these alkoxides. Comparatively few studies have been done on these larger alkoxides; Brauman and coworkers have taken the photodetachment spectrum of neo-pentoxide [7] another of the many isomers of  $\text{C}_5\text{H}_{11}\text{O}$ . Brauman reports the EA of neo-pentoxide as  $1.93 \pm 0.06 \text{ eV}$  which, not surprisingly, is similar to our reported EA of n-pentoxide of  $1.88 \text{ eV}$ . The photodetachment spectra of the linear  $\text{C}_n\text{H}_{2n+1}\text{S}^-$  ( $n = 1-5$ ) have been taken and their EA's assigned by Brauman and coworkers [39]. Theoretical calculations have also tabulated EA's for these alkylthio anions [40] each of which has a higher EA as compared to the alkoxide anions but follow the same overall trend with a monotonic increase to higher binding energy as the carbon chain length increases.

Thus far it seems to be the overall case that the electron affinities for the 1-alkoxides are lower than those of their respective structural isomers. Additionally, it also seems to be the case that these 1-alkoxides share more in common with one another than with their respective isomers; we have generally found it more helpful to make comparisons between 1-propoxide and ethoxide or between 1-butoxide and 1-propoxide than to compare 1-propoxide to 2-propoxide or to compare 1-butoxide to 2-butoxide or t-butoxide.

#### 4.2. Thermochemistry

The electron affinities extracted from our photoelectron spectra when combined with gas-phase acidities available in the NIST database [41-43] afford the O–H bond dissociation energies (BDE's) of each alcohol via the following cycle:



Which yields:

$$\Delta_{\text{acid}}\text{H}^\circ = \text{DH}^\circ(\text{RO} - \text{H}) + \text{IE}(\text{H}) - \text{EA}(\text{RO}) \quad \text{or} \quad (2)$$

$$\text{DH}^\circ(\text{RO} - \text{H}) = \Delta_{\text{acid}}\text{H}^\circ - \text{IE}(\text{H}) + \text{EA}(\text{RO}) \quad (3)$$

The ionization energy for hydrogen is  $1312.05 \text{ kJ}$  ( $13.58944 \text{ eV}$ ). Enthalpies of formation of alkoxy radicals and their alkoxide anions can also be found via Eqs. (4) and (5) below given  $\Delta_f\text{H}^\circ(\text{H}) = 217.998 \text{ kJ/mol}$  and using enthalpies of formation of the alcohols,  $\Delta_f\text{H}^\circ(\text{ROH})$ , that are again readily available in the NIST database.

$$\Delta_f\text{H}^\circ(\text{RO}) = \text{DH}^\circ(\text{RO} - \text{H}) + \Delta_f\text{H}^\circ(\text{ROH}) - \Delta_f\text{H}^\circ(\text{H}) \quad (4)$$

$$\Delta_f\text{H}^\circ(\text{RO}^-) = \Delta_f\text{H}^\circ(\text{RO}) - \text{EA}(\text{RO}) \quad (5)$$

Supplementary Table 1 presents four sets of acidities for these alcohols all of which can be found in the NIST database. We then use each of these four sets to calculate four sets of BDE's presented in Table 3. Finally, Supplementary Table 2 presents the sets of enthalpies of formation of the neutral radical,  $\Delta_f\text{H}^\circ(\text{RO})$  and the anion,  $\Delta_f\text{H}^\circ(\text{RO}^-)$ . The enthalpies of formation of the alcohols,  $\Delta_f\text{H}^\circ(\text{ROH})$ , used to calculate the enthalpies in Supplementary Table 2 are those found in the NIST database. The errors associated with the ionization energy and enthalpy of formation of hydrogen, are negligibly small relative to errors associated with the acidities and electron affinities of the alcohols and alkoxides respectively.

Some commentary on the values in supplementary Tables 1 and 3;

**Table 3**

BDE's calculated using our EA's and the acidities presented in Supp. Table 1 via the thermochemical cycle presented in the discussion.

Species	DH <sup>o</sup> (RO-H) <sup>1</sup>	DH <sup>o</sup> (RO-H) <sup>2,3</sup>	DH <sup>o</sup> (RO-H) <sup>4</sup>	DH <sup>o</sup> (RO-H) <sup>5</sup>
CH <sub>3</sub> OH	439 ± 4	432 ± 9	435 ± 8	
CH <sub>3</sub> CH <sub>2</sub> OH	439 ± 2	432 ± 9	435 ± 8	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH		433 ± 9	434 ± 8	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH		437 ± 9	436 ± 8	435 ± 12
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH		434 ± 10	437 ± 9	433 ± 13
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OH		436 ± 10	436 ± 10	432 ± 13
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> OH		440 ± 10	437 ± 14	432 ± 13
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> OH		442 ± 10	439 ± 14	432 ± 13
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> OH		446 ± 10	440 ± 14	432 ± 13

All values are in units of kJ/mol.

<sup>1</sup> Acidities from DeTuri and Ervin.

<sup>2,3</sup> from Bartmess, Scott, and McIver, reference [25] and Higgins and Bartmess, Ref. [30].

<sup>4</sup> Haas and Harrison, Ref. [29].

<sup>5</sup> Board, Houriet, and Gaumann, Ref. [27].

errors in BDE's and the enthalpies of formation of the alkoxy radicals and alkoxide anions arise primarily through the uncertainty in the gas phase acidities of their corresponding alcohols. Measurements by Ervin and coworkers [31] using threshold collision induced dissociation (TCID) of the acidities of methanol and ethanol have reduced the errors associated with these acidities. Other acidities are those of Haas and Harrison [29], Board and coworkers [27], and Bartmess and coworkers [25,26,30] as designated in **supplementary Table 1**. Using the acidities from each of these groups produces the BDE's presented in **Table 3**. The greatest disparity is found in the BDE of 1-nonanol using the acidity from Board's work which produces a BDE of 432 kJ/mol, 12 kJ/mol smaller than that using Harrison's acidity value, yet still within experimental error. The BDE for 1-propanol, despite being somewhat smaller than the others in the series is in good agreement with the BDE from Zhang's photodissociation experiments of 433 ± 2 kJ/mol [34].

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2019.136638>.

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