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LETTERS

Isomerization of Simple Alkoxyl Radicals: New Temperature-Dependent Rate Data and Structure Activity Relationship

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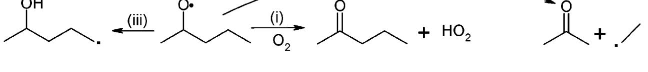
Relative-rate experiments have been carried out, at several different temperatures between 240 and 340 K, to determine the Arrhenius rate parameters for the isomerization of the 1-pentoxyl, 2-pentoxyl, and 5-methyl-2-hexoxyl radicals. Isomerization rates were measured relative to the bimolecular reaction of each alkoxyl radical ($RO^•$) with O_2. The order of reactivity, in terms of the rate of reaction for isomerization, was 5-methyl-2-hexoxyl > 1-pentoxyl > 2-pentoxyl, reflecting the relative-strengths of tertiary, secondary, and primary C−H bonds, i.e., the nature of the bond cleaved in the isomerization process. In addition to this, the measured Arrhenius activation barriers, and reported barriers for bimolecular reactions of the methoxyl radical with several simple hydrocarbons, are shown to correlate linearly with the bond strength of the cleaving C−H bond. The *A*-factors obtained for the three isomerization processes also scale linearly with the number of available abstractable H atoms, with a value of 3.0×10^{10} s^{-1} per H atom. This value combined with the activation barrier correlation constitutes a structure activity relationship for the estimation of the kinetics of the isomerization of simple alkoxyl radicals, at temperatures pertaining to the Earth's troposphere.

1. Introduction

Alkoxyl radicals ($RO^•$) are important radical intermediates in the gas-phase oxidation of volatile organic compounds (VOCs),[1,2] which are released into the Earth's atmosphere from both anthropogenic and biogenic sources. Under atmospheric conditions, there are three modes of reaction available to $RO^•$, namely, (i) bimolecular reaction with O_2 (giving a carbonyl product and the hydroperoxyl radical, HO_2), (ii) decomposition (giving alkyl radical and carbonyl fragments), and (iii) isomerization.[3,4] The three possible reaction pathways for the 2-pentoxyl radical are



As the fate of $RO^•$ determines the identity, and hence atmospheric impact, of the first-generation end products of the oxidation chemistry, it is important to understand the relative rates of processes i−iii for $RO^•$ species of different structures, and as a function of temperature. For example, the activation barriers for the isomerization of $RO^•$ (a H shift involving C−H bond cleavage) have been shown to be significantly higher than for the reactions of $RO^•$ with O_2,[3,4] and hence under the temperature conditions of the upper troposphere/lower stratosphere (UTLS) region of the atmosphere, reaction i will be of greater importance, compared to reaction iii, than in the warmer lower troposphere. The aim of the present study therefore was to investigate the temperature dependence of the kinetics of the isomerization of simple $RO^•$, process iii, to extend the current database of temperature-dependent rate data, and to rationalize reactivity trends in terms of the structure of the radical. This was achieved by using product analysis to determine relative-rate coefficients (relative to reaction with O_2) for the isomerization of the 2-pentoxyl (**1**), 1-pentoxyl (**2**), and 5-methyl-2-

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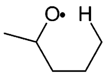
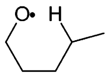
hexoxyl radicals (**3**). Yields of 2-pentanone, pentanal, and 5-methyl-2-hexanone were thus measured; these carbonyls result from the reaction of O_2 with **1**−**3**, respectively.



(1)



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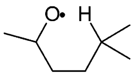

(3)

Isomerization reactions of $RO^{\bullet}$ are believed to be 1,5-sigmatropic H atom shifts, which occur through a six-membered transition state, yielding a δ-hydroxylated alkyl radical intermediate product.[3,4] Kinetic data do currently exist for a number of $RO^{\bullet}$ isomerization reactions, but in the vast majority of cases they comprise data obtained at room temperature, or from theoretical studies. No direct-kinetic data are currently available for these reactions.

2. Experimental Methodology

The experimental apparatus and methodology have been described in greater detail elsewhere.[5] Briefly, experiments were carried out using a meter-long, slow-flow photochemical reactor made of quartz. The alkoxyl radicals of interest were produced directly from the near-UV photodissociation of alkyl nitrite precursors using black-lamp radiation ($\lambda_{max} \approx 365$ nm). Pure samples of alkyl nitrite (RONO) were synthesized from the parent alcohol (ROH) by reaction with nitrous acid (HONO), at 0 °C, and stored under vacuum at 4 °C. A mixture of the RONO precursor, and sufficient cyclohexane to scavenge >95% of any OH formed during the experiments (from the reaction of HO_2 with NO), was prepared in N_2 (Air Products, grade 5.0) in a 300 L collapsable Tedlar bag. The temperature of the reactor was controlled, between ca. 250 and 340 K, by circulating an ethylene glycol/water mixture around the flow cell. Reactant gases, passing through the cell, comprised controlled flows of N_2 (Air products, grade 5.0) and O_2 (Air Products, grade 5.0) from cylinders, and a constant flow from the collapsable bag. The total flow through the cell, around 500 sccm, was regulated using a calibrated mass flow controller (Tylan), and the flow from the collapsible bag was achieved with a rotary pump connected after the mass flow controller. By varying the relative flows of N_2 and O_2, the mixing ratio of O_2 could be controlled in the range 0−80%. All experiments were carried out at atmospheric pressure (760 ± 10 Torr). Yields of carbonyl product from reaction i were determined using gas chromatography (Agilent 6890N) with flame ionization detection (GC-FID). Gas samples, of 150 cm^3 volume, were immobilized and hence concentrated using adsorbant tubes (containing Tenax TA) before being flash desorbed (Markers International Ltd. UNITY thermal desorber) and entering the capillary column (30 m, HP-5) of the GC. An example temperature program, for experiments involving 2-pentylnitrite, held the column at 35 °C for 2 min before being raised to 85 °C at a rate of 2 °C/min, before being raised to 250 °C at rate of 30 °C/min. This gave a good separation of the earlier eluting butane (added as an internal standard) and small carbonyls and accelerated the analysis of the slower eluting 2-pentylnitrite and 2-pentanone. A carrier gas pressure of 18 psi was used for these experiments. GC peak areas were converted to volume mixing ratios after calibration with pure standards. Standard mixtures were prepared by flushing a known pressure of pure vapor in a calibrated glass volume into an 80 L, collapsable Tedlar bag with a known volume of GC grade nitrogen. Five or six mixtures, of varying volume mixing ratios, were prepared and analyzed in the same way as described above for the experiment, to construct calibration curves. The linear regression statistics of these calibration curves gave an indication of the repeatability of analyses, 5% (2σ). The total uncertainty in measured mixing ratios, accounting for systematic uncertainties in the preparation of calibration mixtures, was of the order of 7%. All condensed-phase reagents were of analytical grade and underwent two freeze−pump−thaw cycles before being used.

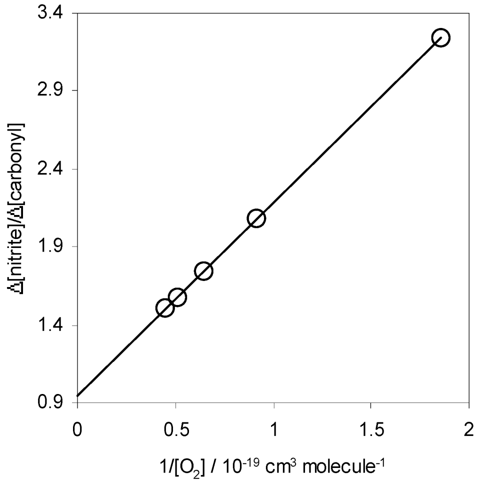

Figure 1. Analysis plot for the isomerization of 2-pentoxyl at 264 K. The slope of the line corresponds to k_{isom}/k_{O_2}. 2-Pentoxyl radicals were generated from the photolysis of 2-pentylnitrite, and yields of 2-pentanone were measured as a function of O_2 concentration.

For each experiment, the relative rates of reactions iii and i were assessed from the dependence of the yield of carbonyl resulting from reaction i upon the concentration of O_2. By assuming that any $RO^{\bullet}$ not reacting with O_2 isomerizes (decomposition of the alkoxyl radicals studied is expected to be slow compared to isomerization and reaction with O_2 under the conditions of the experiments; see the discussion section),[3,4] relative-rate coefficients were assessed using the following expression

$$\frac{\Delta[\mathrm{RONO}]}{\Delta[\mathrm{RC'(O)R''}]} = 1 + \frac{k_{\mathrm{isom}}}{k_{\mathrm{O_2}}}\frac{1}{[\mathrm{O_2}]}$$

where Δ[RONO] is the change in concentration of the alkyl nitrite precursor, Δ[R′C(O)R″] is the concentration of carbonyl formed following reaction i (pentanal for 1-pentoxyl, 2-pentanone for 2-pentoxyl, and 5-methyl-2-hexanone for 5-methyl-2-hexoxyl), and k_{isom} and k_{O_2} are rate coefficients for reactions iii and i, respectively. A typical relative-rate plot is shown in Figure 1.

3. Results

For each of the three $RO^{\bullet}$ studied, relative-rate coefficients were determined at five or six different temperatures (see Table 1 for details). The temperature-dependent relative-rate coefficients measured for the isomerization of 2-pentoxyl, 1-pentoxyl, and 5-methyl-2-hexoxyl were analyzed according to the Arrhenius expression, $k = A \exp(-E/T)$, to obtain the following expressions:

$$k_{\mathrm{isom}}/k_{\mathrm{O_2}}(\text{2-pentoxyl}) = 7.6 \times 10^{24} \exp(-3530/T)$$

$$k_{\mathrm{isom}}/k_{\mathrm{O_2}}(\text{1-pentoxyl}) = 2.2 \times 10^{24} \exp(-2600/T)$$

$$k_{\mathrm{isom}}/k_{\mathrm{O_2}}(\text{5-methyl-2-hexoxyl}) = 1.6 \times 10^{24} \exp(-2140/T)$$

TABLE 1: Relative- and Absolute-Rate Coefficients for the Isomerization of 2-Pentoxyl, 1-Pentoxyl, and 5-Methyl-2-hexoxyl Measured in the Present Investigation[a]

radical	T/K	k_{isom}/k_{O_2} [b]	k_{isom}/s^{-1}
2-pentoxyl	264	$(1.2 \pm 0.1) \times 10^{19}$	$(8.6 \pm 0.2) \times 10^{4}$ [c]
2-pentoxyl	273	$(1.8 \pm 0.5) \times 10^{19}$	$(1.3 \pm 0.3) \times 10^{5}$ [c]
2-pentoxyl	288	$(3.9 \pm 0.6) \times 10^{19}$	$(2.9 \pm 0.5) \times 10^{5}$ [c]
2-pentoxyl	298	$(5.2 \pm 2.1) \times 10^{19}$	$(4.0 \pm 1.6) \times 10^{5}$ [c]
2-pentoxyl	303	$(6.7 \pm 2.3) \times 10^{19}$	$(5.2 \pm 1.8) \times 10^{5}$ [c]
2-pentoxyl	319	$(1.2 \pm 0.2) \times 10^{20}$	$(9.3 \pm 1.4) \times 10^{5}$ [c]
1-pentoxyl	243	$(5.0 \pm 1.6) \times 10^{19}$	$(3.1 \pm 1.0) \times 10^{5}$ [d]
1-pentoxyl	253	$(7.5 \pm 1.6) \times 10^{19}$	$(5.1 \pm 1.1) \times 10^{5}$ [d]
1-pentoxyl	258	$(9.1 \pm 3.3) \times 10^{19}$	$(6.5 \pm 2.4) \times 10^{5}$ [d]
1-pentoxyl	263	$(1.4 \pm 0.3) \times 10^{20}$	$(1.1 \pm 0.3) \times 10^{6}$ [d]
1-pentoxyl	273	$(1.5 \pm 0.3) \times 10^{20}$	$(1.2 \pm 0.3) \times 10^{6}$ [d]
1-pentoxyl	283	$(2.3 \pm 0.6) \times 10^{20}$	$(2.0 \pm 0.5) \times 10^{6}$ [d]
5-methyl-2-hexoxyl	247	$(2.6 \pm 0.7) \times 10^{20}$	$(1.8 \pm 0.5) \times 10^{6}$ [c]
5-methyl-2-hexoxyl	257	$(4.0 \pm 0.7) \times 10^{20}$	$(2.7 \pm 0.5) \times 10^{6}$ [c]
5-methyl-2-hexoxyl	265	$(4.8 \pm 1.4) \times 10^{20}$	$(3.4 \pm 0.5) \times 10^{6}$ [c]
5-methyl-2-hexoxyl	273	$(7.1 \pm 0.6) \times 10^{20}$	$(5.1 \pm 1.0) \times 10^{6}$ [c]
5-methyl-2-hexoxyl	303	$(1.3 \pm 0.3) \times 10^{21}$	$(1.0 \pm 0.2) \times 10^{7}$ [c]

[a] All uncertainties are the 95% confidence limits from the analytical regression plots of the raw data. No account has been taken of the uncertainty in the reference rate coefficients. [b] Units of molecule cm^{-3}. [c] Relative-rate coefficient converted to absolute-rate coefficient using $k_{O_2} = 1.5 \times 10^{-14} \exp(-200/T)$, according to the recommendation of Atkinson.[3] [d] Relative-rate coefficient converted to absolute-rate coefficient using $k_{O_2} = 6.0 \times 10^{-14} \exp(-550/T)$, according to the recommendation of Atkinson.[3]

Relative-rate coefficients were converted to absolute-rate coefficients using values for k_{O_2} recommended by Atkinson.[3] Table 1 lists both relative- and absolute-rate coefficients obtained during the present investigation. The relative-rate coefficient measured for the isomerization of 2-pentoxyl agrees, within experimental uncertainty, with that obtained by Atkinson et al., as reported in ref 3 ($k_{isom}/k_{O_2} = 3.1 \times 10^{19}$ molecule cm^{-3}). The temperature-dependent absolute-rate data were analyzed using the Arrhenius expression, in the form $k = A \exp(-E_a/RT)$, to obtain the rate parameters listed in Table 2. Arrhenius plots are shown in Figure 2 for the isomerization of radicals **1**−**3**. Also included in Table 1 are activation barriers obtained from direct-kinetic studies of reactions of the methoxyl radical ($CH_3O^\bullet$) with several simple hydrocarbons. In addition to rate data, the table also lists calculated bond strengths (B3LYP-DFT/6-31G(d,p) quantum chemical calculations, at the 5d level of theory)[6,7] for the C−H bond cleavage in the various isomerization reactions, and the H atom abstraction reactions of $CH_3O^\bullet$.

4. Discussion and Structure Activity Relationship (SAR)

Before discussing the nature of the results with relation to our understanding of the reaction mechanism, it is necessary to quantitatively consider the effects of the decomposition of the alkoxyl radicals **1**−**3**, and the possible effects of the production of "hot" alkoxyl radicals (from the photolysis of alkyl nitrite precursors), on our derived isomerization rate data. For the 2-pentoxyl radical (for which isomerization is slowest) a decomposition rate coefficient of 9.1×10^{3} s^{-1} has been measured at 298 K, as reported by Atkinson.[3] At room temperature and atmospheric pressure of air, this is 20% as important as reaction of **1** with O_2. The analysis employed above to derive isomerization rate coefficients will incorporate this additional unimolecular transformation of **1** into the isomerization rate coefficient. However, as isomerization is almost a factor of 50 times faster, at this temperature, this leads to an "inflation" of the derived isomerization rate coefficient by only 2%, well within the uncertainty of each GC measurement. Even at the highest temperature studied, 319 K, the estimated "inflation" of the isomerization rate coefficient (based on the Arrenius parameters presented by Atkinson[3] for the decomposition of **1**) is still under 5%. Small amounts of acetaldehyde and propanal, the decomposition products of **1**, were observed in our chromatograms, but due to the scatter in these data and the fact that NO was not added to our reaction mixture (which would be necessary to quantitatively convert propyl radicals to propanal molecules) these data were not quantitatively analyzed. Thus decomposition was not taken into account in obtaining isomerization rate data. For the 1-pentoxyl and 5-methyl-2-hexoxyl radicals, isomerization is significantly faster and decomposition is expected to be about as slow (for **3**) or slower (for **2**), and so again decomposition will not significantly affect the rate data obtained in the present study. The possibility of producing excited alkoxyl radicals from the photolysis of alkyl nitrites

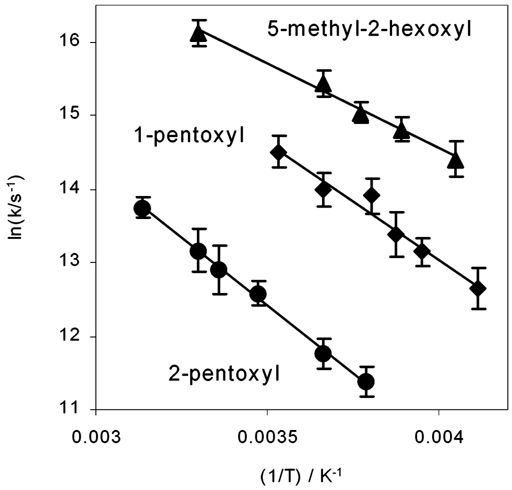

Figure 2. Arrhenius plot of measured rate data for the isomerization of 2-pentoxyl (circles), 1-pentoxyl (diamonds), and 5-methyl-2-hexoxyl (triangles).

TABLE 2: Arrhenius Parameters for RO$^\bullet$ Isomerization Reactions and Selected Bimolecular Reactions of $CH_3O^\bullet$, and Calculated C−H Bond Strengths[a]

reaction	A/s^{-1}	E_a/kJ mol^{-1}	C−H bond strength/kJ mol^{-1}
2-pentoxyl isomerization	9.2×10^{10}	30.5 ± 2.1	418.0[g]
1-pentoxyl isomerization	6.1×10^{10}	24.3 ± 6.3	400.0[h]
5-methyl-2-hexoxyl isomerization	2.5×10^{10}	19.5 ± 4.1	385.3[i]
1-butoxyl isomerization[b]	8.4×10^{10}	30.7 ± 1.8	418.0[g]
$CH_3O^\bullet + CH_4$ [c]		37.0 ± 4.2	437.2
$CH_3O^\bullet + C_2H_6$ [c]		29.7 ± 4.1[f]	416.6[h]
$CH_3O^\bullet +$ *cyclo*-C_6H_{12} [d]		24.5 ± 3.0[f]	403.1
$CH_3O^\bullet + HCHO$[e]		9.6 ± 1.0	363.0

[a] The uncertainties in the isomerization rate data are the 95% confidence limits of the Arrhenius plot. [b] Rate data taken from ref 5. [c] Rate data taken from ref 13. [d] Rate data taken from ref 14. [e] Rate data taken from ref 15. [f] Errors based on the quoted uncertainty and assumed to be entirely in the activation barrier. [g] Typical value for primary C−H. [h] Typical value for secondary C−H. [i] Typical value for tertiary C−H.

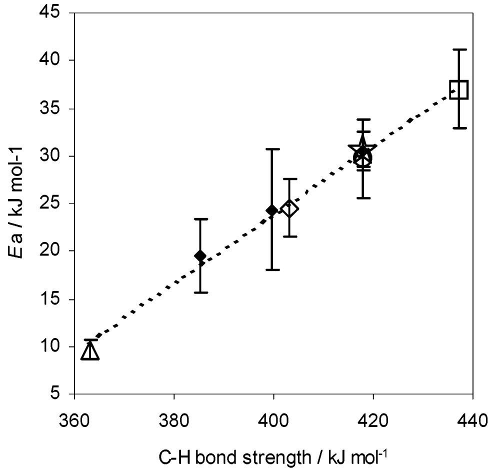

Figure 3. Correlation plot of experimentally determined activation barriers vs calculated C−H bond strengths for a series of RO$^\bullet$ isomerization reactions, and bimolecular reactions of $CH_3O^\bullet$. Filled diamonds correspond to isomerization data. The star corresponds to data for the isomerization of 1-butoxyl. The remaining open symbols correspond to data for the reaction of $CH_3O^\bullet$ with methane (square), ethane (circle), cyclohexane (diamond), and formaldehyde (triangle).

should also be addressed. Such “hot” radicals would be expected to isomerize promptly, on a time scale faster than molecular collisions, thus precluding the possibility of their being quenched and reacting with O_2. The presence of “hot” alkoxyl radicals would result in an intercept in the analytical plots, exemplified by Figure 1, of greater than 1. Given the uncertainty of our GC calibrations and analyses, and the resultant scatter in our analysis plots, no evidence was seen of the production of a significant proportion of “hot” alkoxyl radicals in the present study. This is in accord with a previous investigation in this laboratory[5] of the chemistry of the 1-butoxyl radical in which non-unity intercepts were also not observed. We estimate that the extent of “hot” RO$^\bullet$ production was less than 10%. This is consistent the conclusion of Heicklen[8] that around 5% of RO$^\bullet$ produced from the photolysis of alkyl nitrites at 360 nm are excited. Again, no account was taken of this small potential source of error.

Energy barriers for RO$^\bullet$ isomerizations are expected to comprise two main contributions: first, the strain-energy associated with the formation of a cyclic transition state and, second, the barrier for abstraction of a H atom. A six-membered transition state is not expected to be very strained, as pointed out by Baldwin et al.,[9] and hence the second contribution will dominate. Thus it may be reasonably expected that the measured Arrhenius barriers for the isomerization of alkoxyl radicals correlate with the strength of the cleaving C−H bond. This is indeed shown to be the case by the linear relationship in Figure 3. The correlation is strong ($R^2 = 0.99$, for all data shown) and indicates that the energetics of intermolecular H abstraction by the methoxyl radical is a good model for isomerization reactions (intramolecular H atom atom abstractions) of larger RO$^\bullet$. The data obtained in the present study, and a barrier for the isomerization of 1-butoxyl previously obtained in this laboratory,[5] fit excellently within the correlation plot and indicate that 5-methyl-2-hexoxyl isomerizes more rapidly than 1-pentoxyl, which isomerizes more rapidly than 2-pentoxyl (and 1-butoxyl). This reflects the fact that tertiary C−H bonds are weaker than secondary C−H bonds, which are weaker than primary C−H bonds. The relationship is usefully extended by the measured barrier for H abstraction, by $CH_3O^\bullet$, from CH_4 (with the strongest C−H bond), and from HCHO (with a significantly weaker, aldehydic C−H bond). Some discussion should be made of the Arrhenius *A* factors for the isomerization reactions. An assessment of *A* factors can be made from the observed linear dependence of *A* upon a number of abstractable H atoms from the data for the isomerization of 5-methyl-2-hexoxyl ($A = 2.5 \times 10^{10}$ s^{-1}, one abstractable H atom), 1-pentoxyl ($A = 6.1 \times 10^{10}$ s^{-1}, two abstractable H atoms), 1-butoxyl ($A = 8.4 \times 10^{10}$ s^{-1}, three abstractable H atoms),[5] and 2-pentoxyl ($A = 9.2 \times 10^{10}$ s^{-1}, three abstractable H atoms), thus yielding a value for *A* of 3.0×10^{10} s^{-1} per abstractable H atom. This latter value is significantly lower than the estimate of Baldwin et al.[9] (7.9×10^{10} s^{-1} per H atom), although in agreement within the mutual uncertainties, and constitutes a more reliable determination. The low *A* factors obtained here are also an order of magnitude smaller than the recent theoretical calculations of Somnitz and Zellner[10] (e.g., $A_{1\text{atm}} = 1.8 \times 10^{12}$ s^{-1} for 1-butoxyl), and Méreau et al.[11] (e.g., $A_\infty = 2.5 \times 10^{12}$ s^{-1} for 1-butoxyl), but in good agreement with the calculations of Vereecken and Peeters[12] ($A_{1\text{atm}} = 1.4 \times 10^{11}$ s^{-1} for 1-butoxyl). It is difficult to explain the discrepancies between the theoretically calculated *A* factors. The tightness of the transition state, and the concomitant negative entropy of activation can, for the most part, be associated with the loss of internal rotations in the cyclic transition state. The linear relationship presented in Figure 3 provides a means for the estimation of activation barriers for the isomerization of simple alkoxyl radicals at temperatures pertaining to the Earth’s troposphere, with the expression

$$E_a/\text{kJ mol}^{-1} = 0.363D_e(\text{C}-\text{H}) - 121.3$$

where D_e(C−H) is the calculated bond strength of cleaving C−H bond. To a good approximation, the calculated strength of primary, secondary and tertiary C−H bonds are 418.0, 400.0, and 385.3 kJ mol^{-1}, respectively. An estimation of rate coefficients can then be made by assuming an *A* factor of 3.0×10^{10} s^{-1} per abstractable H atom, as described above. It is finally worth mentioning here that the currently recommended method for the estimation of temperature-dependent rate data for the isomerization of simple alkoxyl radicals proposes significantly higher barriers than those that we have obtained.[5] According to the rate data obtained in the present study, the current recommendations translate to underestimations of isomerization rate coefficients by a factor of around 5−10 at 220 K, a temperature relevant to the chemistry of the UTLS.

5. Conclusions

Relative-rate data have been measured for the isomerization of the 1- and 2-pentoxyl radicals and 5-methyl-2-hexoxyl at several different temperatures relevant to the chemistry of the Earth’s troposphere. After conversion to absolute-rate coefficients, Arrhenius parameters have been calculated and the activation barriers shown to correlate strongly with the strength of the cleaving C−H bond, along with barriers reported in the literature for the bimolecular reactions of $CH_3O^\bullet$ with several simple hydrocarbons. The presented correlation constitutes the first quantitative structure activity relationship to be presented for rate data for the isomerization of alkoxyl radicals. Additionally, the three *A* factors measured scale linearly with the number of abstractable H atoms, indicating that $A = 3.0 \times 10^{10}$ s^{-1} per abstractable H atom. This latter value, and the activation barrier correlation provide a means for the estimation of rate coefficients over a range of temperatures pertaining to the Earth’s troposphere. From the experimental data obtained in the present study, the correlation plot in Figure 3, and the typical C−H bond strengths listed above, we propose the following rate coefficient expressions for isomerization processes involving primary, secondary and tertiary C−H bond cleavage: $k_{\mathrm{isom}}(\mathrm{primary}) = 9.0 \times 10^{10} \exp(-30.3\ \mathrm{kJ\ mol^{-1}}/RT)$, $k_{\mathrm{isom}}(\mathrm{secondary}) = 6.0 \times 10^{10} \exp(-23.8\ \mathrm{kJ\ mol^{-1}}/RT)$, and $k_{\mathrm{isom}}(\mathrm{tertiary}) = 3.0 \times 10^{10} \exp(-18.5\ \mathrm{kJ\ mol^{-1}}/RT)$.

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