reaction energy was converted to internal energy of the ion. This would tend to shorten the lifetime of any persistent complex that might be formed in the $C_2H_3^+ + C_2H_2$ reaction and may be a contributing factor our failure to see a long-lived complex in this reaction under binary collision conditions.

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Thermal Decomposition of Ions. 1. Pyrolysis of Protonated Ethers. Activation **Energies and A Factors**

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Unimolecular rate constants (k_d) have been measured at the high-pressure limit for the thermal decomposition of protonated dimethoxyethane (glyme) and bis(2-methoxyethyl) ether (diglyme). In both cases the decomposition involves loss of CH₃OH and formation of an oxycarbonium ion. The variation of k_d with temperature gives log A = 11.1 and $E_a = 21.1$ kcal·mol⁻¹ for the pyrolysis of (glyme)H⁺ and log A = 13.7 and $E_a = 30.7$ for (diglyme)H⁺. To the best of our knowledge these are the first Arrhenius parameters ever determined for the decomposition of cations in the vapor phase under equilibrium conditions at the high-pressure limit. The data and thermochemistry are consistent with a transition state in which electron shifts result in the disruption of an internal hydrogen bond.

Introduction

The thermally activated unimolecular decomposition and rearrangement of neutral molecules is one of the most thoroughly documented areas of chemical kinetics, both experimentally and theoretically. Much attention has also been given to the fragmentation of energetic ions, such as those formed by electron impact.¹ However, with the exception of two studies involving carbonium ions in the lower pressure "falloff" region of unimolecular kinetics,² no quantitative information concerning the thermally induced decomposition of gaseous ions is available.

Pulsed high-pressure mass spectrometry provides a unique tool for investigating the temporal behavior of reactive ionic systems. Although the main application has been in the area of equilibrium measurements,³ the combined capabilities of high pressure, wide temperature range, and time resolution also offer a powerful method for quantifying the unimolecular decomposition kinetics of thermalized ions.

In this study we have examined two protonated methoxy ethers. Protonated ethers were chosen as models because the pyrolysis results solely in the elimination of CH₃OH⁴ at moderate temperatures (<650 K), which simplifies the kinetic analysis. Furthermore, the analogous vapor-phase acid-catalyzed chain decompositions of acetals and ethers have been extensively studied⁵ under static conditions, and polar transition states have been invoked to explain the magnitude of the frequency (A) factors and activation energies (E_a) for CH₃OH elimination, which again is the only mode of decomposition. Our goal, then, was to attempt to evaluate A and E_a for these systems at the high-pressure limit using pulsed mass spectrometry, interpret the values in terms of the overall thermochemistry, and generate a consistent description

of the transition state (mechanism) for the decomposition.

Experimental Section

All measurements were carried out with the NBS pulsed high-pressure mass spectrometer.⁶ The ion source (reaction chamber) is fabricated from a single block of stainless steel 12 cm in length and 5 cm in diameter. Uniform temperature regulation is provided by three 100-W cartridge heaters implanted in the walls of the chamber along its long axis. Temperatures are monitored at various interior points with thermocouples, and to ensure efficient heating, the gaseous sample passes through a 3-mm-diameter bored-out section of the chamber walls for a distance of 8 cm before introduction into the reaction volume. Mixtures of the compounds of interest were prepared in an external vacuum manifold prior to introduction into the reaction chamber via micrometering valves. Cyclohexane vapor was used as the bath gas, and dilution factors varied from 10^2 to 10^5 , depending upon the particular measurement. Total source pressures normally fell within the range 0.1-1.5 torr at temperatures between 400 and 640 K.

The experimental-kinetic sequence may be summarized as follows: (i) the desired total pressure of the ether-cyclohexane mixture was first established at the chosen temperature; (ii) the electron beam circuitry was adjusted to provide an ionizing pulse of 0.6-1-keV electrons having a typical duration of 0.1-0.5 ms repeated every 10-20 ms; (iii) since the bulk component was cyclohexane, the energy initially deposited during the electron pulse lead to the instantaneous formation of species such as $C_6H_{12}^+$, $C_6H_{11}^+$, $C_6H_{10}^+$, $C_5H_9^+$, $C_4H_8^+$, etc.; (iv) these moieties, in turn, reacted with the ether via proton transfer and/or charge exchange to generate protonated parent molecules and/or fragment ions characteristic of the ether (mainly ROCH₃·H⁺). Since fragment cations derived from the ether are unreactive toward cyclohexane, essentially all of these reacted further with the ether via proton

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^{(7) 1} kcal·mol⁻¹ = 4.184 kJ·mol⁻¹. Unless otherwise stated, all ΔH_{f}° values have an absolute uncertainty of ± 1.0 kcal-mol⁻¹ and all ΔS° values have an absolute uncertainty of ±1.5 cal·deg⁻¹·mol⁻¹.



Figure 1. Normalized ion intensities as a function of time for the reaction $MH^+ \rightarrow FH^+ + CH_3OH$: case I, irreversible kinetics; case II, reversible kinetics.

transfer to also yield $ROCH_3$ ·H⁺. This chemical induction period occurred very rapidly and was complete shortly after the termination of the ionizing pulse. Any unreactive fragment ions present in the system were not considered in the subsequent kinetic analysis, and the temperatures were sufficiently high to prevent clustering of the ions which are monitored.

Under the conditions of the present measurements the protonated ethers decomposed by a single channel, elimination of CH_3OH :

$$ROCH_{3} \cdot H^{+} \rightarrow R^{+} + CH_{3}OH$$
(1)

The rate of fragmentation or, more specifically, the rate constant for unimolecular dissociation of ROCH₃·H⁺ was determined by first recording the ion signals from ROCH, H⁺ and R⁺ as a function of time after the chemical induction period was over. The resultant signals were usually monitored for 3-10 ms, in channels of 10- or 20-µs width, and accumulated in a multichannel scaler serving as a signal averager. The collected data were fed into a minicomputer, which normalized the intensities at each reaction time. Two types of temporal behavior were observed, which are illustrated in Figure 1 (reproduced from actual data). Case I represents the situation in which the fragment (FH⁺) generated in the thermal decomposition was unreactive and simply grew in irreversibly at the expense of the protonated ether (MH^+) . The unimolecular rate constant, k_d , was then computer calculated by using the normalized rate of decay of MH⁺. Case II illustrates the more complex behavior associated with reversible kinetics, where the fragment ion reprotonated the parent ether and initiated an ion-catalyzed chain reaction

$$MH^{+} \xrightarrow{k_{d}} FH^{+} + CH_{3}OH$$
 (2)

followed by

$$FH^+ + M \xrightarrow{\kappa_2} MH^+ + F$$
 (2a)

At higher concentrations of M, a steady state was achieved at longer reaction times (3 ms in Figure 1). In concentrated samples the chain length was limited only by the value of k_2 and the rate of ionic diffusion to the walls of the reaction chamber. k_d was evaluated either at short reaction times during the approach to the steady state or after the steady state had been reached. The latter treatment required that k_2 was independently known; k_d is then given by

$$k_{\rm d} = k_2 [{\rm M}] / [{\rm M}{\rm H}^+ / {\rm F}{\rm H}^+]_{\rm ss}$$
 (3)

A standard reversible kinetics program was used to evaluate the appropriate rate parameters.



Figure 2. Unimolecular rate constant, k_d for the decomposition of protonated glyme (upper) and diglyme (lower) at several temperatures as a function of cyclohexane pressure. Ether pressures were held constant at 6.0×10^{-4} torr.

Results and Discussion

The present study focuses on the thermally induced dissociation of two protonated ethers: dimethoxyethane, $CH_3OCH_2CH_2OCH_3$ (glyme), and bis(2-methoxyethyl) ether, $CH_3O(CH_2)_2O(C-H_2)_2OCH_3$ (diglyme). As indicated earlier, these were chosen as model systems because of the simplicity of the fragmentation pattern and the fact that the enthalpies and entropies of protonation have recently been established.⁴ Unfortunately, the simplest dimethoxy ether, dimethoxymethane ($CH_3OCH_2OCH_3$), could not be studied quantitatively because protonation results in immediate elimination of H₂, even at moderate temperatures ($k_d > 10^5 \text{ s}^{-1}$ at 400 K).

Dimethoxyethane. This system exhibits class II (reversible) kinetics. The fragment ion, represented empirically as $(CH_2CHOCH_3)H^+$, initiates a slow chain reaction by reprotonating the parent ether:

$$(CH_{3}OCH_{2}CH_{2}OCH_{3})H^{+} \xrightarrow{k_{4}} (CH_{2}CHOCH_{3})H^{+} + CH_{3}OH (4)$$

followed by

$$(CH_{2}CHOCH_{3})H^{+} + CH_{3}OCH_{2}CH_{2}OCH_{3} \xrightarrow{\kappa_{2}} \\ (CH_{3}OCH_{2}CH_{2}OCH_{3})H^{+} + CH_{2}CHOCH_{3} (4a)$$

The normalized intensities given as case II in Figure 1 are taken from a mixture of glyme (0.000 63 mole fraction) in cyclohexane at a total pressure of 1.1 torr at 554 K. k_d is 5.1×10^2 s⁻¹ under these conditions, and k_2 is 4.0×10^{-11} cm³·molecule⁻¹·s⁻¹ on the basis of the reversible kinetics analysis. The reprotonation reaction is, in fact, slightly endothermic and endoergic. Separate measurements in this laboratory have established $\Delta H_{\rm prot}$ of glyme⁴ as -204.7 kcal·mol⁻¹ and vinylmethyl ether (presumed to be the neutral product in reaction 4a) as -206.1 kcal·mol⁻¹.⁸ Glyme also exhibits a negative $\Delta S_{\rm prot}$ of -4.3 cal·deg⁻¹·mol⁻¹. Using the formulation developed in an earlier study⁹ for estimating the effects of ΔH and ΔS on reaction efficiencies for simple particle-transfer reactions, we would predict that the endothermicity (1.4 kcal· mol⁻¹) would lower the efficiency by a factor of 0.28 ($e^{-\Delta H/RT}$) and the negative entropy change (-4.3 eu) would cause a further reduction of 0.12 ($e^{\Delta S/R}$), giving a combined factor of 0.034. In

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Figure 3. Arrhenius plots for the decomposition of protonated glyme and diglyme.

absolute terms, assuming a collision rate constant of 10^{-9} cm³molecule⁻¹·s⁻¹ for reaction 4a, we would then expect a measured value of (3-4) × 10^{-11} cm³·mol⁻¹·s⁻¹ for reprotonation at this temperature, which is in agreement with the experimental value and supports the applicability of the thermochemical formulation to the present systems.

A combination of experimental conditions was achieved in which $k_{\rm d}$ was found to be independent of the pressure of cyclohexane; i.e., the high-pressure limit for the dissociation was reached (see part A of Figure 2). These included temperatures between 540 and 630 K and bath gas pressures up to approximately 2 torr, which is our workable instrumental limit. At temperatures greater than 620 K the high-pressure limit could not be reached at 2 torr of cyclohexane, and below \sim 540 K measurements were complicated by clustering reactions involving protonated glyme. This latter condition precluded accurate evaluation of k_d although the high-pressure limit was attained at low total pressures (Figure 2) because the reversible kinetics analysis required the steady-state ion ratio as well as the time-dependent contour of the MH⁺ decay curve when k_2 (rate constant for the reprotonation reaction) was unknown, as was the case for glyme. Clustering at lower temperatures therefore induced a dual complication in that both the decay contour and the steady-state ratio were affected by slow removal of (CH₃OCH₂CH₂OCH₃)H⁺. Exhaustive checks were performed to ensure that the measured k_d 's were independent of the ether concentration at a given temperature and pressure of the bath gas.

A plot of $\ln k_d$ vs. 1/T (Arrhenius form), where k_d is the high-pressure limiting value, is given in Figure 3. Although the workable temperature range is admittedly restricted, a straight line is obtained with a slope and intercept which give $E_a = 21.1$ kcal-mol⁻¹ and log A = 11.1 when expressing k_d as $k_d = Ae^{-E_a/RT}$. To the best of our knowledge, these are the first data ever recorded for the thermal decomposition of gaseous ions at the high-pressure limit.

Bis(2-methoxyethyl) Ether. This simple triether (diglyme) exhibits irreversible kinetics (case I in Figure 1); i.e., the protonated parent molecule thermally decomposes to yield an unreactive fragment ion:

$$CH_{3}O(CH_{2})_{2}O(CH_{2})_{2}OCH_{3} \cdot H^{+} \rightarrow CH_{3}O(H_{+}O(CH_{2})_{2}OCHCH_{2} \cdot H^{+} (5)$$

The data shown in Figure 1 represent the behavior observed in a mixture of diglyme (0.001 25 mole fraction) in cyclohexane at a total pressure of 1 torr at 602 K. k_d under these conditions is 4.4 (3) × 10² s⁻¹. Again, a set of conditions was achieved under which k_d was found to be independent of the pressure of the bath gas (see Figure 2). A plot of ln k_d vs. 1/T, where k_d is the high-pressure limiting value, is given in Figure 3. As was found for glyme, the high-pressure limit could not be reached at 2 torr of cyclohexane above ~630 K. Although protonated diglyme does not undergo clustering at reduced temperatures, meaningful measurements could not be taken below ~560 K due to the depressed absolute values of k_d (<50 s⁻¹). The slope and intercept of the plot in Figure 3 yield $E_a = 30.7$ kcal-mol⁻¹ and log A =13.7 for reaction 5.

Validity of Arrhenius Parameters. The temperature range over which accurate measurements could be carried out at the highpressure limit was somewhat restricted for both of the ethers investigated (\sim 70 °C). Consequently, the argument might be raised that the data suffer from what might be referred to as observational selectivity; i.e., the Arrhenius plots appear to be linear because the accessible dynamic range of kinetic measurements i limited. However, it is our view that the Arrhenius parameters which we have derived are correct for the systems studied for the following reasons: (i) At a temperature of 620 K, which is at the upper end of our range, a cyclohexane pressure of 2 torr corresponds to a number density of 3.1×10^{16} molecules cm⁻³. If one assumes a rate constant of $\sim 10^{-9}$ cm³·molecule⁻¹·s⁻¹ for collision between the protonated ethers and the bath gas, it follows that the decomposing ions undergo approximately 3×10^7 collisions s⁻¹. At this temperature the measured k_d 's for protonated glyme and diglyme are 5×10^3 and 5.4×10^2 s⁻¹. Therefore, the respective ions collide, on the average, 6000 and 65 000 times with the bath gas prior to dissociation, which is much more than sufficient to ensure that thermal equilibrium is achieved. (ii) We observe the transition between second-order kinetics and the high-pressure limit of unimolecular behavior (Figure 2). The fact that the high-pressure limit is attained at lower number densities of the bath gas at lower temperatures, where the k_d 's are reduced, is also consistent with this model. (iii) The width of the temperature window, \sim 70 °C, is essentially the same as that used in numerous studied⁵ of the acid-catalyzed gas-phase thermal decomposition of various alcohols, esters, ethers, etc. $(80 \pm 20 \text{ °C})$, in which activation energies and A factors were also derived.

Thermochemistry of the Dissociation. The thermal decomposition processes observed here are analogous to the vapor-phase acid-catalyzed decompositions of acetals and monoethers. Acetals yield alcohols and vinyl ethers as products, while ethers generate an alcohol and an olefin:

$$R_2C(OR')_2 + acid \rightarrow VOR' + acid + R'OH$$
 (6)

$$ROR' + acid \rightarrow olefin + acid + R'OH$$
 (6a)

For both classes of molecules, trace products are generally absent, and the catalyst (acid) is regenerated. Activation energies generally fall within the range 22–32 kcal·mol⁻¹, with A factors of 10¹¹–10¹⁴ depending upon the identity of the acid and the alcohol or ether studied. By comparison, the straightforward pyrolysis yields E_a 's of 50-60 kcal·mol⁻¹, with A factors which are similar in magnitude or slightly higher than those associated with the acid-catalyzed decomposition. The present work differs mechanistically to some extent in that the thermal decomposition is initiated by the simplest acid, H⁺, which remains initially bonded to the dissociation product having the highest proton affinity (PA),¹⁰ the vinyl ether (the PA of CH₃OH is 181.9 kcal·mol⁻¹). while the PA's of vinyl ethers are all in excess of 200 kcal·mol⁻¹). Nonetheless, the respective E_a 's of 21.1 and 30.7 kcal-mol⁻¹ found for glyme and diglyme are completely consistent with the range of values associated with the acid-catalyzed decomposition of similar molecules in static systems.

We shall now examine the mechanism of the dissociation in some detail. Glyme exhibits an entropy of protonation, $\Delta S^{\circ}_{\text{prot}}$, of -4.3 cal-mol⁻¹·K⁻¹, indicating the formation of a relatively weak intramolecular hydrogen bond and a quasi-cyclic structure:



⁽¹⁰⁾ Lias, S. G.; Liebman, J. F.; Motevalli-Aliabadi, M.; Levin, R. D. J. Phys. Chem. Ref. Data, in press.

Molecular models show that the two dipoles cannot align themselves with the -0--H+- \cdots O- bond unless the bond angle is distorted to $\sim 120^{\circ}$ from the optimal 180°. Therefore, the unfavorable geometry and rigid skeleton of the ether most likely result in a configuration in which the proton is more tightly bonded to one oxygen, forming a weaker, distended hydrogen bond with the other basic site. The fragment ion produced in the dissociation of I is assumed to be equivalent to protonated vinylmethyl ether (VMO), which has an oxycarbonium ion structure:

$$CH_2 = CH - O - CH_3 + H^+ \rightarrow CH_3 - CH^+ - O - CH_3 \qquad (7)$$

That protonated VMO has this configuration is apparent when one considers that the PA of the saturated analogue, $C_2H_5OCH_3$, which can only undergo oxygen protonation, is only 196.3 kcal·mol⁻¹ (PA(VMO) = 206.1). This difference can only be explained by invoking formation of the highly stabilized oxycarbonium ion, which increases the PA by ~ 10 kcal·mol⁻¹. As discussed earlier, the fragment ion produced in the dissociation of I slowly reprotonates glyme ($k \sim 4 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$). The magnitude of the rate constant at 550-600 K was also shown to be consistent with an endothermicity of ~ 1.4 kcal·mol⁻¹, which is the difference between the PA of glyme (204.7 kcal-mol⁻¹) and VMO (206.1 kcal·mol⁻¹). It follows, therefore, that the fragment ion is VMOH⁺, with the oxycarbonium ion structure, since any other isomer(s) would require incorporation of an OH⁺ site. If this were the case, the reprotonation reaction with glyme would be highly exothermic ($\geq 8 \text{ kcal} \cdot \text{mol}^{-1}$) and proceed with a collision efficiency of unity $(k \sim 10^{-9} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1})$ since the measured PA's of all other neutrals having the empirical formula C_3H_6O are ≤ 197 kcal·mol⁻¹ (propylene oxide, acetone, oxetane, propionaldehyde). Combining the $\Delta H_{\rm f}^{\circ}$ values of the three neutrals, as calculated by the group additivity method,¹¹ with the measured PA's gives an energy requirement of 7.9 kcal·mol⁻¹ for the overall dissociation, which is to be compared with the measured E_a of 21.1 kcal·mol⁻¹. The A factor is low (log A = 11.1), which is typical of a relatively complex fission. The dissociation itself is apparently initiated by electron withdrawal toward the charge donor positive center $(-O-H^+)$, which weakens the -C-O- bond and simultaneously creates a positive hole which is then filled by a two-electron (H⁻) shift, generating the secondary oxycarbonium ion:



The thermochemistry associated with the decomposition of protonated diglyme (reaction 5) is somewhat uncertain, although previous measurements⁴ have established the PA as 218.9 kcal·mol⁻¹ and $\Delta S^{\circ}_{\text{prot}}$ as -13.8 eu. The substantially negative $\Delta S^{\circ}_{\text{prot}}$ apparently results from the formation of an intramolecularly bonded structure which has the form of an eight-membered ring:



This system also exhibits irreversible kinetics; i.e., the fragment ion does not reprotonate diglyme at a detectable rate. Unfortunately, the neutral analogue to VMO, $CH_3O(CH_2)_2OCH=CH_2$,

is unavailable, so that its PA and the corresponding $\Delta H_{\rm f}^{\circ}$ of the fragment cannot be evaluated directly. The fact that reprotonation does not occur again implies a highly stable oxycarbonium ion structure, $CH_3O(CH_2)_2OC^+H-CH_3$, which is produced directly via an electron shift mechanism analogous to that proposed for protonated glyme. Estimates¹² of ΔH°_{f} lead to an energy requirement of approximately 15 kcal·mol⁻¹ for decomposition, which is to be compared with the measured E_a of 30.7 kcal·mol⁻¹. It is pertinent to note that the activation barriers (difference between the endothermicity of the dissociation and E_a) are comparable in both glyme ($\sim 13.2 \text{ kcal} \cdot \text{mol}^{-1}$ and diglyme ($\sim 14.7 \text{ kcal} \cdot \text{mol}^{-1}$), which again suggests a common mechanism. Finally, log A for diglyme is 13.7, while that for glyme is 11.1 ($\Delta \log A = 2.7$). In the Arrhenius expression, $k = Ae^{-E/RT}$, the A (frequency) factor reflects the difference in entropies between the ground-state systems and the transition states associated with the decomposing ions $(A \propto e^{\Delta S/R})$. As already discussed, both glyme and diglyme exhibit negative entropies of protonation due to the formation of intramolecular hydrogen bonds, with diglyme showing a much larger value (-13.8 compared with -4.3 eu). If the assumption is made that the geometric conformation corresponding to the transition state is one in which the hydrogen bond stabilizing the unactivated cyclic structure (I and III) is broken, then the Afactors for the two systems should differ by $e^{9.5/R}$, or 2.1 log A units, with diglyme being the higher. Considering the uncertainties in the absolute values for $\Delta S^{\circ}_{\text{prot}}$ (±1.5 eu), this result is in excellent agreement with the measured difference of $\Delta \log A =$ 2.7 and provides additional support for the formation of the quasi-cyclic structures proposed for these protonated ethers.

Advantages and Limitations of the Technique. The pulsed high-pressure mass spectrometric method can be applied quantitatively to the investigation of the thermally induced unimolecular decomposition of ions provided certain conditions are satisfied. In general, ions are much more reactive than neutrals, and a single fragment can frequently initiate a reaction sequence which may completely mask the most elementary decomposition process. Furthermore, residence time limitations in typical high-pressure ion sources (1-3 ms) restrict the range of k_d values which can be evaluated to $\sim 5 \times 10^{1} - \sim 5 \times 10^{5} \text{ s}^{-1}$, and temperatures in excess of 700 K are very difficult to achieve without special instrumentation. Instrumental limitations also require bath gas pressures \leq a few torr. Fortunately, E_a 's for cation decompositions seem to be substantially lower than those associated with the pyrolysis of neutrals, so that meaningful measurements can be taken under relatively moderate conditions. Given the proper systems, the mass spectrometric technique also affords direct identification of parent-daughter relationships, and an evaluation of k_d at a given temperature can be carried out in a matter of 3-4 min since chemical end-product analysis is not required. In the following article we will explore the application of the pulsed technique to another area of unimolecular kinetics: the determination of thermal activation efficiencies for various bath gases.

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Registry No. $(CH_3OCH_2CH_2OCH_3)H^+$, 38095-34-0; $CH_3O-(CH_2)_2O(CH_2)_2OCH_3$ ·H⁺, 91606-36-9.

⁽¹¹⁾ Benson, S. E. "Thermochemical Kinetics"; Wiley: New York, 1976.

⁽¹²⁾ The energy requirement for reaction 5 was roughly estimated by assuming a PA for CH₃O(CH₂)₂OCH=CH₂ of 212 kcal·mol⁻¹, i.e., 3 kcal·mol⁻¹ higher than that of C₂H₃OCH=CH₂. Using the group additivity method (ref 11) and further assuming that contributions from nonnearest-neighbor interactions in neutral reactants and products are self-canceling, we calculate $\Delta H^{\circ}_{\rm f}$ (diglyme(H⁺)) as 23.9 kcal·mol⁻¹ and CH₃O(CH₂)₂OC⁺H-CH₃ as 87.9 kcal·mol⁻¹. When these are combined with $\Delta H^{\circ}_{\rm f}$ (CH₃OH = -48.0 kcal·mol⁻¹, the overall ΔH for reaction 5 is 16.0 kcal·mol⁻¹. This is likely a lower limit since the PA of CH₃O(CH₂)₂OCH=CH₂ may be higher than the assumed value.