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COMMENTS

Comments on "Proton Affinities of Primary Alkanols: An Appraisal of the Kinetic Method"

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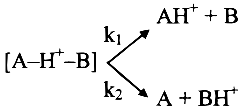
Holmes et al.[1] use the kinetic method[2] (eq 1, where $[A-H^+-B]$ is a proton-bound cluster ion between molecules A and B,



$$\ln\left(\frac{k_1}{k_2}\right) = \frac{\Delta PA}{RT_{eff}} \qquad (1)$$

ΔPA is the difference between their proton affinities, k_1 and k_2 are rate constants for dissociations of the dimer to yield AH^+ and BH^+, normally represented by the fragment ion abundances $[AH^+]$ and $[BH^+]$, and the proportionality factor is the product of R, the gas constant, and the term T_{eff} known as the effective temperature) to measure the relative proton affinities of primary alcohols, although they criticize the technique as being "without a sound physicochemical basis". They particularly criticize the use of the term "effective temperature" and argue that the slope of the correlation line does not relate to a thermodynamic quantity. Previous authors in this area have all noted the approximate nature of these correlations; however, the categorical nature of the claims made in ref 1, their repetition elsewhere,[3] and the logic in the supporting arguments compel this formal response to these authors.

The kinetic method was first described more than 20 years ago,[2a] and the understanding of the method and its physical basis has advanced in the interim.[2c−e] Holmes et al. state repeatedly that systems can only be studied by this method if they are at thermal equilibrium, a contention that repeats previous statements that they are best so studied[4] and that seems to ignore publications that show that microcanonical ensembles can be used in derivations of equations analogous to eq 1.[4b,5] Holmes and co-workers do cite the RRK derivation of a relationship between ln(ion abundance ratio) and ΔPA by Craig et al.,[5c] but we read that work differently. It seems to us that Craig et al. teach not simply that the kinetic method is an approximate method but also that thermal equilibrium is not a precondition for an approximate linear correlation of the type described in eq 1. Considerations such as this suggest to us that the use of the kinetic method to determine relative enthalpic and free energy values not only has a physical basis but that there is information in the slope of kinetic method plots bearing on relative entropies of dissociation, as discussed further below. Both conclusions are at odds with the explicit and implicit conclusions of the authors of ref 1 who express the opinion that in cases in which thermal equilibrium is not satisfied the interpretation of the slope parameter cannot be straightforward or certain. We associate ourselves with the cautions expressed in ref 1 in regard to the use of the kinetic method but not with the more categorical injunctions made.

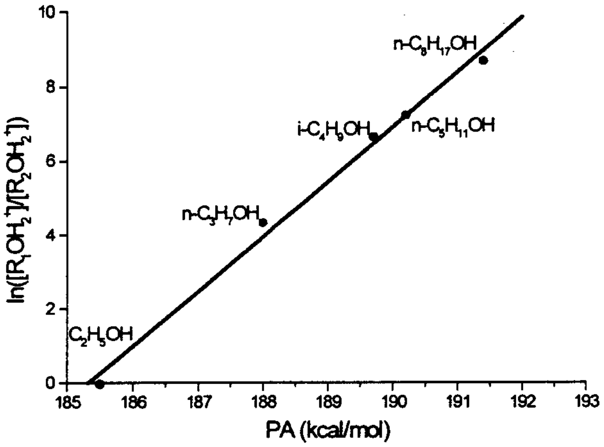


Figure 1. Plot of $\ln([R_1OH_2^+]/[R_2OH_2^+])$ vs PA calculated by the MassKinetics program.[9] Experimental conditions were as described by Holmes.[1] The activation energy was 30 kcal/mol and the frequency factor 10^{15}, again as described by Holmes.[1] The data are shown in the same form as in Figure 2 of ref 1.

Holmes et al. concede that the existence of a straight-line correlation of the type described by eq 1 for metastable ion dissociations is remarkable but conclude that it is "unlikely to have any physicochemical significance" because no change in the fragment ratios (and hence effective temperature) was detected upon varying source conditions. This observation is nothing more than an (approximately true) consequence of the metastable time window constraint,[6] which requires that the observed products of metastable ion dissociation always arise from parent ions lying in the same narrow internal energy range. Unless the energy distribution has very sharp features, changing it will simply alter the absolute abundances of the metastable peaks (as was indeed observed).

The authors of ref 1 also believe that "a single temperature-like term is unsuitable for describing both metastable channels simultaneously". Their analysis of the energetics of competitive metastable dissociation, derived from the calculations summarized in their Figure 1, leads them to suggest that the two processes take place from two populations of ions with nonoverlapping internal energies. However, the case they present in their Figure 1 does not take into account the fact that the higher energy ion population will be undergoing the *lower* energy reaction so rapidly as to have completely fragmented prior to reaching the metastable region. As shown by Bojesen,[4b]

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in such circumstances, the two populations actually do merge, although for systems with a large energy difference (e.g., 0.2 eV ≈ 4 kcal/mol) between the two channels the peaks of the distributions will not coincide exactly.

Recent data from Drahos and Vékey[7] indicate that the effective temperature is related to the energy distribution of the decomposing ions and not to the distribution of the whole ion population. These results have parallels with the proposals of both Beauchamp and Brauman that T_{eff} is related to the excess energy per active oscillator for the dissociating cluster.[5a,c] These studies have cast T_{eff} (really the product RT_{eff}) in the role of an energy parameter characteristic of the particular system under study (cluster binding strength, activation conditions, experimental time scale, etc.). To summarize this point, the conclusion of Holmes et al., that it is clearly unsound to relate the slope of the ln(ion abundance ratio) vs PA plot to a single *thermodynamic* temperature is true and has been stated in the past. It does not follow that relating the slope to a single *effective* temperature is unsound. Klots' use of a single temperature-like term to calculate thermodynamic properties of populations of ions with non-Boltzmann distributions of internal energy[8] would appear to offer general support for the use of an effective temperature description of a *single population* of ions.

Holmes et al. claim that the linearity of kinetic method plots is merely due to the fact that a logarithmic quantity, $\ln([B_1H^+]/[B_2H^+])$, is used to deduce proton affinity values. To show that the linearity of kinetic method plots is not simply an empirical feature, we have calculated the branching ratios of some of the alcohol clusters studied by Holmes et al. and show these data in Figure 1 in the same form as given in Figure 2 in their paper.[1] The data have been calculated by the MassKinetics program[9] using a direct state count RRKM approach with frequencies calculated by the MNDO molecular orbital method. The source temperature, experimental conditions, assumption of the activation energy (30 kcal/mol), a loose transition state, and proton affinities have all been taken from Holmes et al.[1] The data in Figure 1 show a very good linear fit, very similar to that obtained experimentally by Holmes et al. Note that *no empirical fitting* was used in the calculations, *only* data given in ref 1 were used, and the reaction kinetic calculations do *not* use the concept of "effective temperature". The "effective temperature" can be *derived* from the calculations either for individual clusters or from the slope in Figure 1. Note also that the effective temperature derived by Holmes (342 K) is very similar to that obtained from the slope in Figure 1 (341 ± 12 K). (Although the nearly exact agreement is likely a coincidence, we reiterate that no fitting procedure was used in our calculations.)

A significant amount of space is devoted by Holmes et al. to considering the quality of metastable ion, mixed metastable and collision-induced dissociation (CID), and pure collision-induced dissociation data. By use of their particular instrument and with this chemical particular system, there are some unexplained differences in the quality of the straight lines obtained by kinetic method plots when metastable ions are compared with those dissociating by CID. While there are some interesting questions here for the practicing mass spectroscopist, they are less fundamental than the other issues raised in the paper. Indeed, one should note that a large number of kinetic method studies have been done on multiple quadrupole or ion trap instruments that do not show significant signals in the absence of added gas and where these criticisms therefore cannot apply.

We turn now to the issue of changing collision conditions in order to change the internal energy distribution sampled in a CID experiment. Holmes et al. did not observe a dependence of the CID branching ratio on the choice of collision gas when steps were taken to remove contributions from metastable decays. The use of different target gases to change the effective temperature in kiloelectronvolts CID experiments has been a key facet of the work of Wesdemiotis et al.[10] The heavier gas gives rise to a higher center-of-mass energy, thus depositing a higher average internal energy into a proton- (or other ion-) bound dimer. This should, in turn, affect the effective temperature and the resulting branching ratio. Keeping in mind that center-of-mass energies are very large in kiloelectronvolt collisions, different targets cause small changes in the branching ratio, necessitating abundance measurement with high precision; nevertheless, such small changes have unequivocally been detected (also after separation of metastable ion (MI) and CID data).[10d] Related experiments, e.g., those of Fenselau and coworkers,[11] use different collision energies to achieve similar results. Branching ratio dependence on center-of-mass energy in kiloelectronvolts collisions has also been documented by Jennings et al.[12] It is important to note that a target of higher mass increases both the center-of-mass collision energy and the probability of scattering losses. The latter is instrument-dependent and may obstruct the accurate measurement of small differences in branching ratios; this is just one factor that could account for the failure of Holmes et al.[1] to observe a target effect.

Holmes, Aubry, and Mayer conclude their paper with three recommendations/conclusions: (i) that the use of a temperature-type term derived from kinetic method investigations be discontinued; (ii) that the use of different target gases in order to observe different internal energy distributions appears to be unjustified, and (iii) that only isolated CID mass spectra, free of metastable ion contributions, be recorded for kinetic method data analysis. We assume that conclusion i refers not simply to nomenclature but to the underlying enterprise of learning something about relative entropy changes accompanying cluster ion fragmentation from a kinetic method treatment, most clearly evident in the publications of Fenselau and co-workers[11] and Wesdemiotis and co-workers.[10] The available literature would suggest that the method, like those applications of the kinetic method to determine relative enthalpic or free energy quantities, is too valuable to discard, although we would join in a plea for caution, recognizing the fact that there are important approximations and assumptions underlying this treatment. It is likely that differences in experimental procedures and instrumentation lead Holmes et al. not to observe target gas effects seen by others[10] and hence to conclusion ii. Conclusion iii may similarly be tied to peculiarities of particular instruments; however, most kinetic method measurements are performed with nonsector mass spectrometers, so an issue like this is appropriately resolved before a narrower audience. We agree with Holmes[1] that separating metastable and CID contributions is indeed advantageous and that either could be used to obtain plots by the kinetic method. We note, however, that in our experience the use of "mixed" metastable/CID peaks does not lead to significant errors.

In conclusion, we are convinced that the kinetic method has a strong physicochemical basis. However, this is not to be confused with a basis in *equilibrium* thermodynamics, and we and other authors have carefully noted that the method is approximate. Furthermore, we have here demonstrated that the linear free energy relationship used in the kinetic method can be derived a priori using reaction rate calculations without any assumption whatsoever about the effective temperature. Therefore, we think that use of a temperature-type term derived from the slopes measured in kinetic method investigations can be continued cautiously for the purpose of providing relative entropic information on competing reactions. Finally, while we contest the notion that the kinetic method is simply based on an empirical correlation, we find that the application of the method by Holmes et al. to derive thermochemical data is an impressive achievement.

Note Added in Proof. P. B. Armentrout (personal communication, December 1999 and *J. Am. Soc. Mass Spectrom.*, in press) has recently demonstrated the usefulness of the slope-derived effective temperature and gone on to use it in van't Hoff like plots to draw conclusions about the entropy change associated with proton-transfer reactions.

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