COMMENTS

Comment on “Branching Ratios in Activated Systems”

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Received: February 27, 1997

Craig et al.[1] have recently discussed branching ratios in the context of unimolecular reactions. They consider a molecule with total energy E which can dissociate via two channels with rate constants k_1 and k_2 and Arrhenius activation energies $E_1{}^a$ and $E_2{}^a$. Suppose that these two energies are taken as initially equal and equal to $E_0{}^a$. They are then respectively raised and lowered such that their arithmetic average remains constant. Craig et al. summarize the empirical evidence for (and present ad hoc calculations supporting) the relation

$$\partial \ln(k_1/k_2)/\partial(E_1{}^a - E_2{}^a) = -\text{const} \qquad (1)$$

This apparently useful relation is in fact a rigorous consequence of unimolecular reaction theory. Further the constant can be identified as

$$\text{const} = (k_B T^{\ddagger})^{-1} \qquad (2)$$

where the temperature is defined by

$$E = \bar{E}(T^{\ddagger}) + E_0{}^a - k_B T^{\ddagger} \qquad (3)$$

where $\bar{E}(T^{\ddagger})$ is the canonical energy of the parent molecule. This result follows from the relation[2]

$$\partial \ln k_i/\partial E_i{}^a = -(k_B T^{\ddagger})^{-1} \qquad (4)$$

itself an example of a more general theorem. The effects of variations in energy and angular momentum on a branching ratio are implicit in these relations and have already been discussed.[3]

Craig et al. also consider the case where only one of the activation energies is changed. This limit is more directly realizable in the laboratory, as in the competition between thermionic emission and dissociation. The relevant ionization potential can be continuously varied with a power supply,[4] whereas the barrier for dissociation is left unaffected. Now, however, one must consider higher order terms when integrating eq 4; the temperature defined in eq 3 will change as the activation energy which appears there itself changes. One obtains

$$\ln(k_i/k_i{}^0) = -(\delta E_i{}^a/k_B T^{\ddagger}) - (\delta E_i{}^a/k_B T^{\ddagger})^2/2C... \qquad (5)$$

for the first few terms, where C is one less than the heat capacity (in units k_B) of the parent molecule. The second term on the right-hand side is exactly canceled when both activation energies change oppositely. Its effect is noticeable, however, in the model calculations of Craig et al. whenever only one activation energy is permitted to change. In particular, the heat capacity subtends in a compact manner the role of molecular size which they report.

Thus, it is straightforward to account for the calculations of Craig et al. and also to think of a real-life circumstance when eq 4 is directly applicable. Nevertheless, it is remarkable that the other “real-life” applications cited by Craig et al. also exist. Note that the relations above were written as partial derivatives; something else, in this case an Arrhenius preexponential factor, was being held constant. When comparing a series of homologous reactions, it suffices that the ratio of two such factor be constant. All deviations from expectations will arise solely from a violation of that condition.

References and Notes

(1) Craig, S. L.; Zhong, M.; Choo, B.; Brauman, J. I. *J. Phys. Chem. A* **1997**, *101*, 19.

(2) Klots, C. E. *Int. Rev. Phys. Chem.* **1996**, *15*, 205. Also in: *Unimolecular and Bimolecular Reaction Dynamics*; Ng, C., Baer, T., Powis, I., Eds.; Wiley: London, 1994.

(3) Klots, C. E. *J. Phys. Chem.* **1995**, *99*, 1748.

(4) Klots, C. E.; Compton, R. N. *Phys. Rev. Lett.* **1996**, *76*, 4092.

S1089-5639(97)00729-9 CCC: $14.00