

THE EFFECT OF REAGENT VIBRATIONAL ENERGY ON MEASURED REACTION RATE CONSTANTS*

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Summary

The effect of reagent vibrational energy E_{vib} on experimentally measured rate constants for reactions between neutral species at thermal kinetic energies is reviewed. The vibrational acceleration of chemical reactions has recently been characterized by a parameter α describing the efficiency of the usage of the internal energy in overcoming the Arrhenius activation energy, E_a . For reactions of vibrationally excited H_2 , HCl , OH , and O_3 studied to date, α is generally less than 0.6, and is uncorrelated with E_a , E_{vib} , the excess vibrational energy, or the reaction exothermicity. It is concluded that the utility of this conversion efficiency parameter is limited to the phenomenological description of the vibrational acceleration of rate processes or to the role of an adjustable parameter in calculations involving reactions of excited species.

Introduction

The effect of reactant energy in specific degrees of freedom on the rates of chemical reactions has received a great deal of attention recently. It has sometimes been proposed that the presence of vibrational energy E_{vib} in the reactants would be completely effective in cancelling the Arrhenius activation energy, E_a , determined for thermal reagents, and that therefore the rate constant k^\ddagger for reaction of vibrationally excited reagents would be increased by a factor of $\exp[E_{\text{vib}}/RT]$ above the value k for the overall reaction measured with the reagents in thermal equilibrium at temperature,

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T. Indeed, in a few cases, this limiting vibrational acceleration has been observed [1]; however, the accelerating effect of reagent vibrational energy on chemical reaction rates is generally less than this limit [2 - 12], sometimes no vibrational acceleration is observed [13], and in at least one case [14], vibrational excitation of one of the collision partners actually decelerates the reaction. It is therefore of interest to examine the systematics of the vibrational acceleration results obtained to date to see if there is any correlation between the magnitude of the vibrational enhancement of rate processes and identifiable physical variables.

At this time there are insufficient data available to rigorously test detailed microscopic treatments [15, 16] of the dependence of reaction rates on internal and translational energy. Furthermore, there is no immediately clear way to formulate the vibrational acceleration of rate processes in terms of readily measured microscopic or macroscopic variables. In the absence of detailed knowledge about the kinetics of vibrationally excited species, it is not unreasonable to assume that k^\ddagger can be characterized by an Arrhenius expression. Indeed, in the two cases for which the temperature dependence of k^\ddagger has been determined [11, 12], Arrhenius behavior has been displayed. In an operational representation of k^\ddagger that has been used recently [1, 8 - 10] the activation energy E_a^\ddagger for the vibrationally excited reagents is related to E_a and E_{vib} via a vibrational efficiency factor ' α ' as*:

$$E_a^\ddagger = E_a - \alpha E_{\text{vib}} \quad (\text{I})$$

Making the assumption that the Arrhenius pre-exponential factor A^\ddagger is unaffected by reactant vibrational excitation, it is possible then to calculate α from the ratio k^\ddagger/k as:

$$\alpha = \frac{RT}{E_{\text{vib}}} \ln(k^\ddagger/k) \quad (\text{II})$$

There is no theoretical foundation for assuming that $A^\ddagger = A$, and this simplification has been motivated primarily by the lack of data on the bulk temperature dependence of k^\ddagger . Also, it must be emphasized that, at this point, α is strictly a phenomenological parameter that should not be given great physical significance. In this paper, we examine the systematics of the influence of reagent vibrational energy on experimentally measured rate constants for reactions between neutral species at thermal kinetic energies by seeking a correlation between α and readily measured quantities. For a discussion of the effect of reagent energy on ion-molecule reactions, see ref. [17].

Table 1 gives values of k^\ddagger/k and α for a number of reactions. Also given are E_{vib} , E_a , the exothermicity ΔH for non-vibrationally excited reactants, and the temperature at which the observations were made. Several comments are in order. For reaction (1) between O and H₂ the values of (k^\ddagger/k) and α

*Equations introduced in the text and in Table 1 are labelled with Roman and Arabic numerals, respectively.

reported by Birely *et al.* [10] are upper bounds to the true values of these quantities. In the H + H₂ system (2) it is not clear [4] what fraction of H₂ (1) destruction collisions proceed by atom exchange. The brackets around the values of (k^\dagger/k) and α for the H + HCl results of Arnoldi and Wolfrum [7] indicate an uncertainty as to the branching ratio between processes (3) and (4), although these authors give evidence in favor of the predominance of channel (3). The results of Arnoldi and Wolfrum [7] and of Brown *et al.* [11] on k^\dagger for the O + HCl (1) system represent a sum of the contribution from the reactive channel (5) and the non-reactive vibrational deactivation of HCl (1) by O atoms to yield O + HCl (0), although the former authors give evidence for some reaction.

In the reaction between O₃[‡] and NO to give NO₂^{*} (electronically excited NO₂) Braun *et al.* [8] give evidence to support the assertion that it is the ²B₂ state of NO₂, rather than the generally accepted ²B₁ state [18], *i.e.* the emitting species and the analysis here assumes emission from NO₂ (²B₂). Interpretation of the O₃[‡] + NO results is complicated by the recent observation by Redpath and Menzinger [19] that NO(²π_{3/2}) reacts to yield mainly NO₂^{*} whereas NO(²π_{1/2}) reacts to give mostly NO₂ (²A₁). In their treatment of reactions (7) - (11) involving O₃[‡], the authors of refs. [1, 6, 8, 9] have made the assumption, based on experimental observations of Gordon and Lin [6] that the reactive species in the O₃[‡] + NO reaction is O₃ in its (0,1,0) vibrational level, and the values of α for the O₃[‡] reactions in Table 1 have been calculated for O₃ (0,1,0). Subsequent experiments have shown [12, 20], however, that other vibrationally excited modes of ozone may also have contributed significantly to the production of NO₂^{*}.

The OH + O₃ system is a striking example of a reaction in which vibrational energy is highly inefficient in promoting chemical reaction. Coltharp *et al.* [3] studied this system for OH with $v = 2 - 9$, and the value of $\alpha = 0.019$ in Table 1 characterizes the acceleration of the reaction involving OH (2). Although the rate constant increases monotonically with v , the ratio k^\dagger/k for OH (9) having $E_{\text{vib}} = 74.9$ kcal/mol is only 7.7, which corresponds to $\alpha = 0.016$. While the relative importance of processes (12) - (14) is not known, a review of rate constants for the OH + O₃ reaction by Hampson *et al.* [21] suggests that the process:



makes only a minor contribution to k even though this is the only exothermic reaction for OH (0).

In addition to the results given in Table 1, Odiorne *et al.* [2] have carried out a molecular beam study of the vibrational energy dependence of the reaction:



and found that the cross-section ratio $\sigma(1)/\sigma(0)$ for HCl in its $v = 1$ and $v = 0$ levels was about 10². For their experimental conditions, the most probable relative velocity is $\approx 8 \times 10^4$ cm/s [22] and setting this equal to $(2kT/\mu)^{1/2}$

TABLE 1
Measured vibration acceleration of rate processes

Reaction	Vibrationally excited reagent	E_{vb} (kcal/mol)	E_a (kcal/mol)	ΔH (kcal/mol)	k^\dagger/k	T (K)	α
(1) $O + H_2 \rightarrow OH + H$	$H_2(1)$	11.9 ^a	10 ^d	1.8 ⁱ	$< 3.8 \times 10^4$ ^j	300	$< 0.3^i$
(2) $H + H_2 \rightarrow H_2 + H$	$H_2(1)$	11.9	7.5 ^e	0	1.5×10^3 ^e	300	0.33
(3) $H + HCl \rightarrow H + HCl$	$HCl(1)$	8.2 ^a		0	58 ^f	300	0.29
(4) $H + HCl \rightarrow H_2 + Cl$	$HCl(1)$	8.2	3.5 ^f	-1.1 ⁱ	4×10^3 ^{fx}	300	0.60 ^{fx}
(5) $O + HCl \rightarrow OH + Cl$	$HCl(1)$	8.2	4.5 ^f , 4.8 ^s	0.7 ⁱ	7.1×10^3 st	300 ^f , 298 ^t	0.64 st
(6) $F + HCl \rightarrow HF + Cl$	$HCl(1)$	8.2	~ 1.0 ^g	-32.7 ⁱ	3.1 ^k	1700	0.45 ^k
(7) $O_3 + NO \rightarrow NO_2(^2A_1) + O_2$	$O_3(0,1,0)$	2.0 ^b	2.3 ^h	-48.0 ^{b,i}	$17.1^i, 9.5^q$	300 ⁱ , 350 ^q	0.85 ⁱ , 0.78 ^q
(8) $O_3 + NO \rightarrow NO_2(^2B_1) + O_2$	$O_3(0,1,0)$	2.0	4.2 ^h	-20.0 ^{b,i}	5.6 ^m	300	0.51 ^m
(9) $O_3 + NO \rightarrow NO_2(^2B_2) + O_2$	$O_3(0,1,0)$	2.0		-8.0 ^{b,i}		300	
(10) $O_3 + O_2(^1\Delta_g) \rightarrow 2O_2 + O$	$O_3(0,1,0)$	2.0		1.4 ^{a,b,i}	38 ^m	300	1.08
(11) $O_3 + SO \rightarrow SO_2(^1B_1) + O_2$	$O_3(0,1,0)$	2.0	4.2 ^u	-25 ^{b,o}	2.5 ^p	300	0.27
(12) $OH + O_3 \rightarrow HO_2 + O_2$	$OH(2)$	19.9 ^c		-38 ^c		300	
(13) $OH + O_3 \rightarrow H + 2O_2$	$OH(2)$	19.9		8.7	1.9 ⁿ	300	0.019 ⁿ
(14) $OH + O_3 \rightarrow OH + O_2 + O$	$OH(2)$	19.9		25.4		300	

^a G. Herzberg, Spectra of Diatomic Molecules, Van Nostrand, Princeton, 1973.

^b G. Herzberg, Electronic Spectra of Polyatomic Molecules, Van Nostrand, Princeton, 1966.

^c Ref. [21].

^d Calculated from data in D. L. Baulch, D. D. Drysdale, D. G. Horne and A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions, Vol. 1, Homogeneous Reactions of the H_2/O_2 System, Butterworths, London, 1972.

^e Ref. [4].

^f Ref. [7].

^g L. J. Kirsch and J. C. Polanyi, J. Chem. Phys., 57 (1972) 4498.

^h Ref. [25].

- i A. E. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall, London, 1968.
- j This value of α was given in correctly as 0.3 in ref. 10.
- k Calculated from the ratio $k(v)/k(0) = 1 + 2.7 v$ given in Ref. [5].
- l Ref. [8].
- m Ref. [1].
- n Calculated from k^\ddagger for OH (2) from ref. [3] and k determined by Kaufman as reported in ref. [21].
- o J. C. D. Brand and R. Nanes, *J. Mol. Spectros.*, 46 (1973) 194.
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where μ is the reduced mass, the effective translational temperature is ≈ 700 K. Therefore, the vibrational conversion efficiency for this reaction can be taken as ≈ 0.8 .

Our attempts to establish a correlation between α and the energetics of the systems studied to date are shown in Figs. 1 - 4. The average of the two determinations of α is used for reactions (5) and (7). Theoretical considerations [23] imply that reagent vibration is generally more effective than translation in promoting endothermic reactions, while for exothermic systems, the converse is indicated. The data in Table 1 are mostly for exothermic or essentially thermoneutral systems and, in the sense that α is less than 1.0 for the exothermic systems, the results obtained to date are qualitatively in agreement with this generalization; however, as shown in Fig. 1, there is no strong correlation between α and ΔH .

Figure 2 shows a slight tendency toward decreasing α with increasing E_{vib} ; however, the wide range of values of α for the families of reactions involving O_3^\ddagger and HCl^\ddagger demonstrates that E_{vib} alone does not determine α . It is interesting to note the general trend toward increasing α with increasing mass of the atomic reagent for the HCl^\ddagger reactions.

The results given in Fig. 3 show that there is no strong correlation between vibrational conversion efficiency and the magnitude of the activation energy. There does appear to be a slight trend toward decreasing α with increasing E_a . This effect is particularly noticeable for the two product channels in the $\text{O}_3^\ddagger + \text{NO}$ reaction, but is completely lacking in the processes involving HCl^\ddagger .

Rather than a simple correlation between α and the absolute magnitude of ΔH , E_{vib} or E_a , a review of theoretical studies of the influence of reagent energy or reaction probability [23] suggests that the crucial parameter is the energy in excess of that required to cross the potential barrier separating products and reactants. Although the activation energies in Table 1 represent

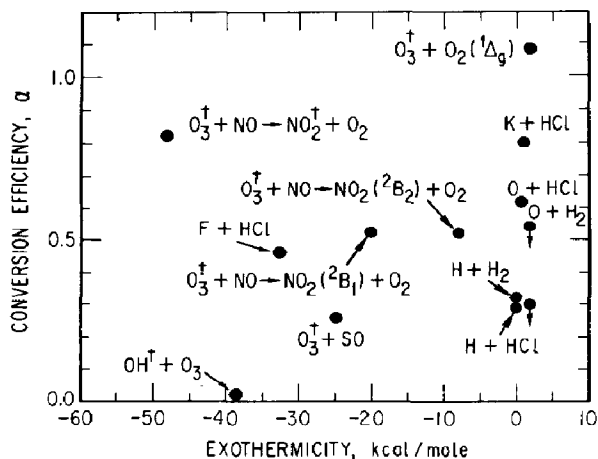


Fig. 1. Dependence of conversion efficiency on reaction exothermicity.

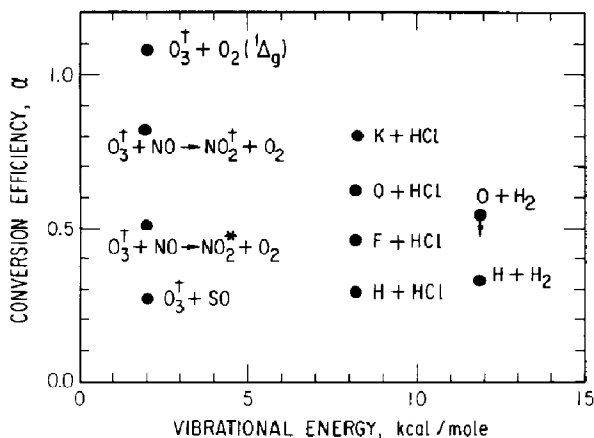


Fig. 2. Dependence of conversion efficiency on reagent vibrational energy.

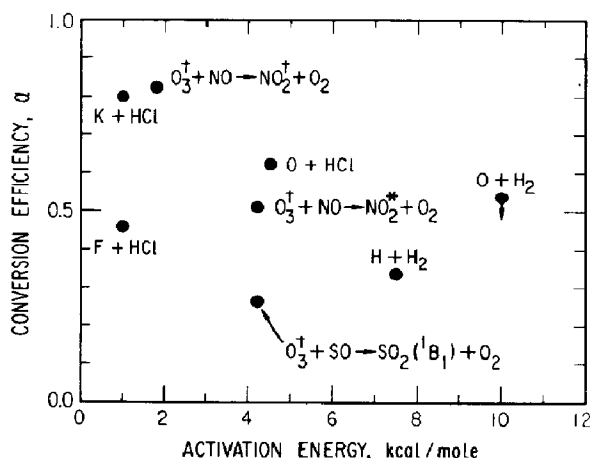


Fig. 3. Dependence of conversion efficiency on activation energy.

macroscopic averages of the barriers over all degrees of freedom, it is nonetheless worthwhile to see if a correlation exists between α and $(E_{\text{vib}} - E_a)$. Figure 4 addresses this question, and from these results, it appears that no strong correlation exists between α and the excess energy or between α and the ratio E_{vib}/E_a .

It is clear from the results in Figs. 1-4 that α is almost always less than 0.6.* Furthermore, the analysis given in Table 1 assumes that k^\ddagger follows an Arrhenius relationship, that the pre-exponential factors A^\ddagger and A are identical, and that α is temperature-independent. The temperature depen-

*If one is to attach literal significance to the parameter α in eqn. (1) then in the spirit of the Arrhenius representation of the rate constant, the energy $(E_a - \alpha E_{\text{vib}})$ would never be negative. This in turn implies that α should never exceed a maximum value of E_a/E_{vib} . Inspection of the results in Table 1 indicates that, within experimental error, this criterion is fulfilled in all reactions for which it can be tested except process (6).

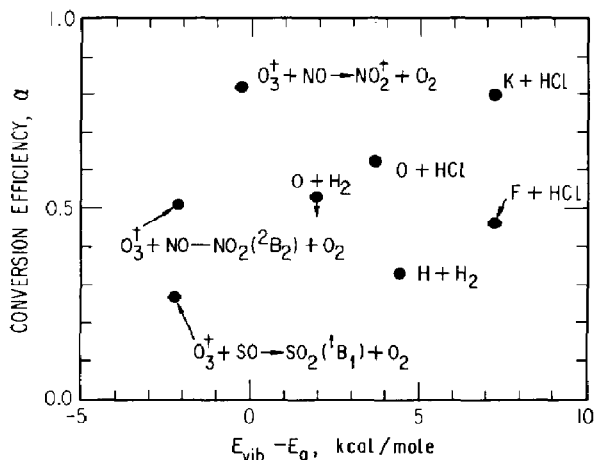


Fig. 4. Dependence of conversion efficiency on excess energy $E_{\text{vib}} - E_a$.

dence of k^\ddagger has recently been determined for two reactions. Brown *et al.* [11] have shown that the $\text{O} + \text{HCl}$ (1) reaction can be characterized by an Arrhenius relationship over the 196 - 397 K temperature range they employed; however, taken together with the temperature dependence of k reported by Brown and Smith [24] the five-fold increase in k^\ddagger over this interval implies that A^\ddagger/A is about 15 and that α is ≈ 0.45 rather than 0.64.

Kurylo *et al.* [12] have studied the temperature dependence of the $\text{O}_3^\ddagger + \text{NO}$ reaction over the range 153 - 373 K. Although three separate deconvolution schemes displaying Arrhenius behavior fit their data, Kurylo *et al.* favor one for which the reaction rate constant k^\ddagger for O_3 in each of the fundamental modes ν_1 , ν_2 , and ν_3 is equal to $2.0 \times 10^{-11} \exp[-1525/T$ ($^\circ\text{K}$)] $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These authors feel that the reaction proceeds primarily through the non-chemiluminescent reaction (7) to give $\text{NO}_2(^2\text{A}_1)$ and that their results should be compared with the value of $k = 7.1 \times 10^{-13} \exp[-1180/T$ (K)] $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for this process involving reagents at thermal equilibrium reported by Clough and Thrush [25].

It is clear from a comparison of A^\ddagger and E_a^\ddagger with A and E_a that the major accelerating effect on the rate constant for the analysis of the $\text{O}_3^\ddagger + \text{NO}$ reaction given by Kurylo *et al.* is associated with an increased pre-exponential factor rather than with a decreased activation energy. In fact, the value of $E_a^\ddagger = 3.0 \text{ kcal/mol}$ exceeds the value of $E_a = 2.3 \text{ kcal/mol}$ reported by Clough and Thrush*.

*Huie and Herron [26] have recently redetermined the activation energy for the overall reaction between thermally equilibrated ozone and nitric oxide to be 3.0 kcal/mol. This is slightly larger than the value of 2.46 kcal/mol reported by Clyne *et al.* [27] and used by Clough and Thrush [25] in their determination of E_a for reaction (7). Use of the newer result of Huie and Herron in analysis of the data of Clough and Thrush would imply that $E_a^\ddagger \approx E_a$ for reaction (7).

Although it is unrealistic to make a generalization on the basis of only two reactions, these experiments support the assumption of Arrhenius behavior of k^\ddagger but do not support the simplified treatment for which $A^\ddagger = A$.

The lack of a simple relationship characterizing the influence of reagent vibrational energy in terms of Arrhenius parameters is not unexpected when one considers the results of several recent studies on the relative influence of reagent translational and vibrational energy. Jaffe and Anderson [28] studied collisions of HI with DI in the energy range 40 - 215 kcal/mol and were unable to detect HD formation even though the activation energy for the reaction:



is only 44 kcal/mol. Redpath and Menzinger [29] determined the kinetic energy dependence of the chemiluminescent reaction:



and found that the reaction threshold of 3.0 kcal/mol was significantly less than the value of $E_a = 4.2$ for this process. Pruett *et al.* [30] have studied the effect of translational kinetic energy on reaction (III) over a range of relative energy $\approx 2 - 12$ kcal/mol. When the reactants had relative kinetic energy equal to E_{vib} for HCl, the enhancement of the reaction cross-section was about an order of magnitude less than that observed in the same laboratory by Odierne *et al.* [2] for the reaction of K with HCl (1). These studies clearly demonstrate that for some chemical reactions reagent vibrational energy is far more effective than translational kinetic energy in promoting chemical reactions. Furthermore, in the $\text{AlO} + \text{O}_2$ reaction*, for which vibrational excitation of AlO led to no enhancement of the reaction rate [13], and possibly for the $\text{CN} + \text{O}_2$ reaction where vibrational excitation of CN led to a deceleration of the rate [14], the reagent vibrational energy was contained in a bond that was not broken during the reaction. The latter two observations and the indication [6] of possibly different reactivities with NO of O_3^\ddagger with the ν_1, ν_2 or ν_3 vibrational modes excited suggest that simply supplying reagent vibrational energy is not sufficient to promote chemical reactions. The vibrational energy may have to be present in a specific mode in order to lead to efficient rate acceleration, and, when neither of the reagents is an atom, vibrational energy in one of the collision partners may be far more effective in promoting reaction.

The utility of the conversion efficiency parameter α is limited to the phenomenological description of vibrational acceleration of rate processes or to its role as an adjustable parameter in calculations involving reactions of excited species. This treatment appears to have little predictive value beyond the result that the mean value of α for the reactions given in Table 1

*As pointed out in ref. [13], a potential complication in the study of the $\text{AlO}^\ddagger + \text{O}_2$ reaction is the possibility that rapid vibrational equilibration between $\text{AlO}(1)$ and $\text{AlO}(0)$ causes the measurements of k^\ddagger and k to be equivalent.

is 0.47 and the average deviation from the mean is 0.23. Furthermore, reliable conclusions about the effect of reagent vibrational energy on the dynamics of a bimolecular reaction cannot be drawn from the value of the parameter α as it has been used to date for several reasons.

The assumption that the pre-exponential factor is the same for reaction from all vibrational states is not necessarily valid. Also, for a reaction having a low threshold and a large vibrational efficiency factor, a negative activation energy can result for the vibrationally excited species. If these were the only shortcomings of this treatment, a reformulation including the vibrational energy dependence of the pre-exponential factor could remove these objections as more data on the temperature dependence of k^\ddagger became available.

One may be tempted to assume that $k^\ddagger/k = k^\ddagger/k(0)$ or that α is automatically a good indication of the acceleration of the reaction rate over that for the reagents in the ground vibrational state. This assumption, however, may not be good for all reactions. As the following simple analysis demonstrates, under certain circumstances vibrationally excited species can contribute significantly to k . The thermal rate constant is given in terms of rate constants $k(v)$ for reactions of the v th vibrational level as:

$$k = \sum_v f(v) k(v) \quad (\text{V})$$

where $f(v)$ is the fraction of molecules in the v th vibrational level having energy $E_{\text{vib}}(v)$. If one assumes Arrhenius behavior for $k(v)$ and that an equilibrium distribution of vibrational states is maintained during the determination of k , then

$$k(v) = A(v) \exp[-E_a(v)/RT] \quad (\text{VI})$$

and, by definition,

$$f(v) = f(0) \exp[-E_{\text{vib}}(v)/RT] \quad (\text{VII})$$

Consider the limiting case in which:

$$A(v) = A(0) \quad (\text{VIII})$$

for all v and:

$$E_a(v) = \begin{cases} E_a(0) - E_{\text{vib}}(v), & E_{\text{vib}}(v) \leq E_a(0), \\ 0, & E_{\text{vib}}(v) > E_a(0) \end{cases} \quad (\text{IX})$$

For the states with $E_{\text{vib}}(v) < E_a(0)$, the rate constant becomes in this limit:

$$\begin{aligned} k(v) &= f(0) A(0) \exp[-E_a(0)/RT] \\ &= f(0) k(0) \end{aligned} \quad (\text{X})$$

i.e., all vibrational states having energy less than or equal to $E_a(0)$ would contribute equally to k . If $f(0) \approx 1$, it follows from eqns. (V) - (X) that

$$k \approx v^* k(0) \quad (\text{XI})$$

where v^* is the number of vibrational states with $E_{\text{vib}}(v) \leq E_a(0)$. (There

would, of course, be a small contribution to k from higher states.) Consider for instance reaction (8) in Table 1. There are five vibrational states of ozone with $E_{\text{vib}}(\nu)$ less than the 4.2 kcal/mol activation energy for this process* but at $T = 300$ K, the vibrational partition function of O_3 is 1.05. Therefore, if the assumptions made in eqns. (VIII) and (IX) were correct for reaction (8) (which they probably are not) then k would be $\approx 5 k(0)$ and $k^+/k(0)$ would be 28 in comparison with the observed $k^+/k = 5.6$. While this is clearly a contrived example, it should serve to point out that α is not necessarily a reliable indication of vibrational acceleration.

A better understanding of the effect of reagent vibrational energy can be had by considering its influence, through the potential energy surface, on the molecular mechanics of chemical reactions [5, 22, 31, 32]. It is anticipated that the application of information-theoretical methods [33, 34] to characterize the selectivity of reactant energy consumption in chemical reactions will be particularly instructive.

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*It follows from eqn. (XI) that $E_a = E_a(0)$ in this limiting case.

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