Effect of energy dependence of the density of states on pressure-dependent rate constants

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Effect of energy dependence of the density of states on pressure-dependent rate constants

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Abstract: The F_E integral for the normalized Boltzmann-weighted number of molecular states above the threshold energy is the key quantity in computing the collision efficiency in the pressure-dependent unimolecular rate theory developed by Troe, who calls this the energy dependence factor of the density of states. By using the Whitten-Rabinovitch approximation and assuming the Whitten-Rabinovitch $a(E)$ function is independent of energy, F_E can be approximated by an analytic formula by; this approximate formula is widely used because of its convenience and computational efficiency. Here we test its validity by comparing the computed rate constants by using the approximate F_E to the ones given by using the numerically integrated F_E. For small-sized molecules and for reactions with high threshold energies E_0, the differences are negligible at all temperatures, but in other cases the approximate formula tends to underestimate F_E and thus overestimates the collision efficiency, and this leads to smaller pressure falloff. When $a(E)$ at high energies differs appreciably from $a(E_0)$, we find that the underestimation of pressure-dependent rate constants by using the approximate formula can be more than a factor of 5 at high temperatures. The physical insight we draw form this study is that for reactions with threshold energies below about 30 kcal/mol, the rate of collisional energy transfer can be appreciably slowed down by the increase in the density of states at higher energies, and this increases the falloff effect by which finite-pressure rate constants are lower than the high-pressure limit, especially at higher temperatures.

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Predicting the pressure dependence of reaction rate constants is of fundamental importance in combustion[1] and in atmospheric chemistry.[2] For a bimolecular reaction that involves a unimolecular intermediate, in the high-pressure limit, all of the rovibrationally excited unimolecular states (which are generated via chemical activation) are stabilized via nonreactive collisions with the bath gas molecules so that thermal equilibrium is maintained; at lower pressures, such collisions are not strong enough to de-energize all the rovibrationally excited states of the intermediate, and thus the reaction rate constant depends on pressure.[3] Pressure effects are also of central importance in unimolecular reactions, where, at pressures below the high-pressure limit, the thermal activation of the reactant cannot maintain its Boltzmann distribution, and this leads to the falloff of rate constants as pressure is lowered.[4] Similar considerations apply to pressure-dependent association reactions.[5]

Troe developed an approximation to the solution of the master equation[6,7] that is widely used in calculations of rate constants $k(T, p)$ as functions of temperature T and pressure p. The usefulness of this approximation for simulating complex processes and planning experiments has been emphasized by Holbrook et al.[8] The key quantity determining the activation and de-activation rates of energized species and hence the pressure dependence is the collision efficiency β_c, the value of which is between 0 and 1 (where the upper limit is called the strong-collision limit). The collision efficiency β_c is computed from:[7]

$$\frac{\beta_c}{1-\beta_c^{1/2}} = \frac{\left|\langle \Delta E \rangle\right|}{F_E k_B T} \tag{1}$$

where $\langle \Delta E \rangle$ is the average energy transferred per collision in both de-activation and activation processes (it is a negative number), k_B is the Boltzmann constant, and F_E is the energy dependence factor of the density of states. The energy dependence factor of the density of states is a normalized Boltzmann-weighted number of molecular states above the threshold energy, in particular:[7,9]

$$F_E = \int_{E_0}^{+\infty} \frac{\rho(E)}{\rho(E_0)} e^{-(E-E_0)/k_B T} \frac{dE}{k_B T} \tag{2}$$

where $\rho(E)$ is density of states of the unimolecular species at energy E, and E_0 is the threshold energy. Usually, F_E is the only quantity that one computes in order to obtain β_c because in practical applications the average energy transferred is treated as a parameter, and the value of this parameter is obtained from fits to limited experimental data[10,11] or is set equal to the value for a similar system. (There has also been progress in evaluating the energy transfer parameter from trajectories[12] and models.[13])

Troe proposed a very efficient analytic formula[6] for calculating F_E by using the vibrational Whitten–Rabinovitch (WR) approximation[14,15,16] for the density of states. In the vibrational WR approximation, overall rotation and internal rotation are not considered (they can be added at a later stage,9[,17]). Then $\rho(E)$ becomes the vibrational density of states without internal rotations, and in the present article we consider only this case. The WR approximation is a reasonably good approximation for efficiently computing the vibrational density of states without requiring large computations. It is based on a previous semiclassical model proposed by Marcus and Rice[18] and on empirical development by Rabinovitch and coworkers.[19,20,21] The WR approximation only requires the information of vibrational frequencies, and it is computed by the following equations:

$$\rho^{\mathrm{WR}}(E) = \frac{[E + a(E)E_z]^{s-1}}{(s-1)!\prod_{i=1}^{s} h\nu_i} \tag{3}$$

$$a(E) = 1 - \beta\omega \tag{4}$$

in which, for $E \geq E_z$,

$$\log_{10}\omega = -1.0506(E/E_z)^{0.25} \tag{5}$$

and for $E < E_z$,

$$\omega = [\frac{5E}{E_z} + 2.73(\frac{E}{E_z})^{0.5} + 3.51]^{-1} \tag{6}$$

with

$$\beta = \frac{(s-1)^2\sum_{i=1}^{s}\nu_i^2}{s(\sum_{i=1}^{s}\nu_i)^2} \tag{7}$$

where s is number of vibrational degrees of freedom, a is an empirical energy dependence factor, E_z is the zero-point vibrational energy (computed from the frequencies), and ν_i is the vibrational frequency for the i-th mode.

By substituting the Whitten–Rabinovitch density of states $\rho^{\mathrm{WR}}(E)$ into equation (2), one obtains an integral for computing F_E that cannot be evaluated analytically. In order to obtain an analytic approximation, Troe assumed that the E dependence of the $a(E)$ function may be ignored, with its value is fixed at $a(E_0)$. By doing this, the original integrand can be re-written in the form of $x^t\exp(-x)$, and the integral becomes an incomplete gamma function, which leads to the following analytic approximation to the integral:[6,8]

$$F_E = \sum_{i=0}^{s-1} \frac{(s-1)!}{(s-1-i)!} \left[\frac{k_{\mathrm{B}}T}{E_0 + a(E_0)E_{\mathrm{z}}} \right]^i \tag{8}$$

Equations (1)-(8) are the standard equations used in most practical calculations.[22]

Here we test whether or not this widely used approximation is accurate by comparing the final $k(T, p)$ computed by using equation (8) to that by numerically integrating equation (2) with $\rho^{\mathrm{WR}}(E)$. Note that the computed $k(T, p)$ depends on many factors, including the pressure-dependence model itself, the energy transfer parameters, including $<\Delta E>$, and the accuracy of the computed high-pressure-limit rate constants, and we are not examining all these factors in the present work. Our purpose is not to compare the accuracy of the final computed pressure-dependent rate constants to experimental values, but solely to examine the validity of the widely used approximate analytic formula as compared to the numerically integrated Whitten–Rabinovitch F_E. (In a practical application, due to fortuitous or empirical cancellation of errors, the final $k(T, p)$ with the numerical integrated F_E need not agree better than using Troe's approximate analytic formula, but our goal here is to test the effect of applying the Troe model without the unnecessary approximation to the integral because physical insight drawn from a model that works by cancellation of errors may be invalid.)

We pick five examples[23,24,25,26,27] to test the approximation, and they are listed in Table 1.

Table 1 Reactions studied

CHF_3 dissociation:[23] $CHF_3 \rightarrow CF_2 + HF$	(R1)
carbon–carbon double–bond homolysis of C_2F_4:[24] $C_2F_4 \rightarrow CF_2 + CF_2$	(R2)
SO_2 + OH association:[25] $SO_2 + OH \rightarrow HOSO_2$	(R3)
silylene anion isomerization:[26] $(SiH_3)_2SiHSiH^- \rightarrow (SiH_3)_2SiSiH_2^-$	(R4)
H addition to toluene:[27] $C_6H_5CH_3 + H \rightarrow C_6H_6CH_3 \rightarrow C_6H_6 + CH_3$	(R5)

Except for the computations of F_E, the computations for the high-pressure-limit rate constants and the details in the pressure-dependent rate constants using system-specific quantum RRK (SS-QRRK) theory[23,27,28] are the same as reported in the previous work,[23,24,25,26,27] and since they are not the major concerns here, we shall not repeat them. Notice that for long-chain molecules (with or without multiple branches), the Whitten–Rabinovitch approximation itself may not be adequate for computing density of states, since multiple conformational structures and coupled internal torsions[29,30,31] may significantly affect the density of states, and for such cases more exhaustive computational work is needed in order to obtain the density of states; in the present work, we do not consider such cases, and we focus on the above-mentioned systems for which density of states can more reasonably be described by the WR approximation.

First, we examine the validity of approximating $a(E)$ as a constant $a(E_0)$. In SS-QRRK theory the threshold energy E_0 is an effective threshold given by the temperature-dependent high-pressure activation energy $E_a(T)$.[29,30,31] We note that for reaction R3 the threshold energy we need for calculating F_E is $E_a(T)$ of the reverse dissociation reaction, and for reaction R5 it is $E_a(T)$ of the reverse of the addition reaction; for the other three reactions it is $E_a(T)$ for the forward reaction. The resulting temperature-dependent effective threshold energies $E_0(T)$ for calculating F_E for reactions R1–R5 are shown in Table 2. In Figure 1, the $a(E)$ functions for these reactions are plotted as functions of E', which is defined as the total energy E minus the E_0 value at the lowest temperature that we considered for each reaction. The figure shows how the $a(E)$ function increases gradually to the asymptotic value of unity. For reactions R4 and R5, which have relatively small E_0, the variation of $a(E)$ with respect to energy can certainly not be ignored, and in such cases the $a(E)$ values at E′ = 300 kcal/mol (which determine the unimolecular state populations at very high temperatures) differ by 18–20% from $a(E_0)$. As a consequence we shall see that assuming that $a(E)$ equals $a(E_0)$ significantly underestimates of the F_E integral for these reactions at high temperatures.

Table 2 Temperature-dependent effective threshold energies $E_0(T)$ (kcal/mol) for calculating F_E

R1		R2		R3		R4		R5	
T	E_0	T	E_0	T	E_0	T	E_0	T	E_0
298	67.6	1100	62.5	200	27.1	298	24.3	298	26.5
400	72.6	1200	63.8	298	27.8	300	24.4	300	26.6
800	74.2	1400	68.3	300	27.8	400	25.4	600	28.6
1200	74.5	1500	71.4	350	27.6	600	25.9	800	29.3
1600	75.9	1750	81.0	400	28.0	800	26.2	1000	28.9
1800	76.9	2000	92.5	450	29.4	1000	26.7	1400	29.0
2000	77.9					1500	28.5	1800	29.3
2200	79.1							2000	29.6
2400	80.3							2400	30.2

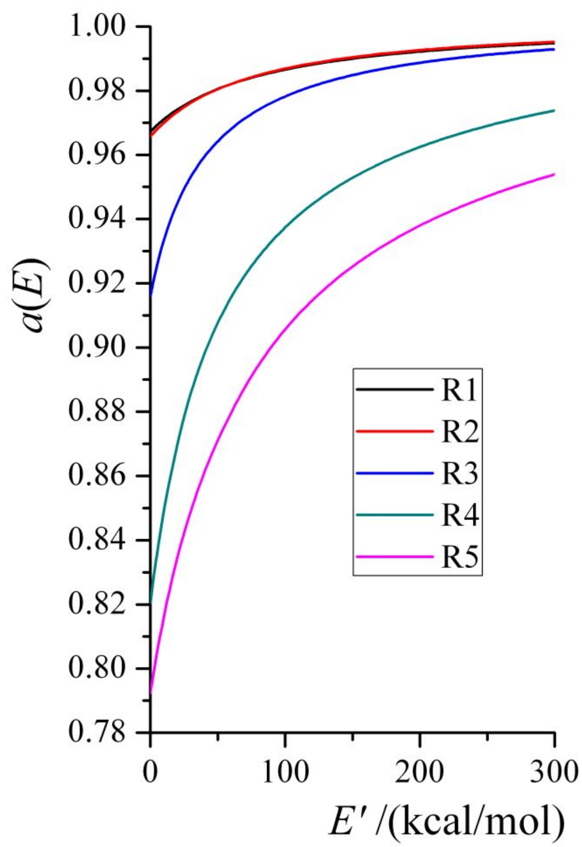

Fig. 1 The $a(E)$ functions for reactions R1–R5 with respect to the energy E', which is defined as the total energy E minus the E_0 at the lowest temperature that we considered for each reaction.

In Table 3, we tabulated the F_E values computed by numerical integration, which are denoted as F_E^{num}, and we also tabulate the ratio $F_E^{\mathrm{app}}/F_E^{\mathrm{num}}$, in which F_E^{app} is the approximate F_E value computed using equation (8). The results are tabulated at various temperatures for each of the reactions R1–R5. For reactions R1–R3, the differences between F_E^{app} and F_E^{num} are entirely negligible at all temperatures. For reactions R4 and R5, however, the difference is as large as a factor of 2 for R4 at 1500 K, and a factor of 2 to 6 for R5 from 1000 K to 2400 K. This means that the approximate analytic formula underestimates the fraction of the rovibrationally excited unimolecular states above the threshold energy, thereby overestimating the collision efficiency and thus underestimating the deviation from the high-pressure limit; the effect is largest at high temperatures.

Table 3 The energy dependence factor of the density of states computed by numerical integration and the reciprocal of its ratio to the analytically approximated energy dependence factor of the density of states as a function of temperature (in K)

R1			R2			R3			R4			R5		
T	F_E^{num}	F_E^{app}/F_E^{num}	T	F_E^{num}	F_E^{app}/F_E^{num}	T	F_E^{num}	F_E^{app}/F_E^{num}	T	F_E^{num}	F_E^{app}/F_E^{num}	T	F_E^{num}	F_E^{app}/F_E^{num}
298	1.061	0.999	1100	1.445	0.998	200	1.089	0.997	298	1.507	0.944	298	1.462	0.922
400	1.078	0.999	1200	1.491	0.997	298	1.134	0.996	300	1.510	0.944	300	1.465	0.922
800	1.163	0.999	1400	1.563	0.997	300	1.135	0.996	400	1.769	0.924	600	2.422	0.817
1200	1.262	0.998	1500	1.589	0.997	350	1.162	0.996	600	2.660	0.863	800	4.070	0.700
1600	1.368	0.998	1750	1.630	0.998	400	1.186	0.995	800	4.621	0.781	1000	8.523	0.551
1800	1.423	0.999	2000	1.646	0.998	450	1.204	0.995	1000	9.508	0.687	1400	86.02	0.288
2000	1.480	0.998							1500	110.0	0.525	1800	1906	0.190
2200	1.539	0.997										2000	9908	0.175
2400	1.598	0.998										2400	261100	0.172

To assess the effect on the rate constant itself, we compared falloff curves computed by using F_E^{app} (represented by dots) to those computed by using F_E^{num} (represented by solid lines); the falloff curves are plotted for reactions R4 and R5 in Figure 2 in the form of $\log_{10}[k(T,p)/k^{HPL}(T)]$ versus p, where k^{HPL} is high-pressure-limit rate constant. For reaction R5, k_{stab} is the formation rate constant of $C_6H_6CH_3$ (which is defined as $(d[C_6H_6CH_3]/dt)/[H][toluene]$), and it is depicted as solid lines; and k_{diss} is the formation rate constant of benzene (which is defined as $(d[C_6H_6]/dt)/[H][toluene]$), and it is depicted as dashed lines. The computed $k(T, p)$ by using F_E^{app} and by F_E^{num} are respectively denoted as $k^{app}(T, p)$ and $k^{num}(T, p)$.

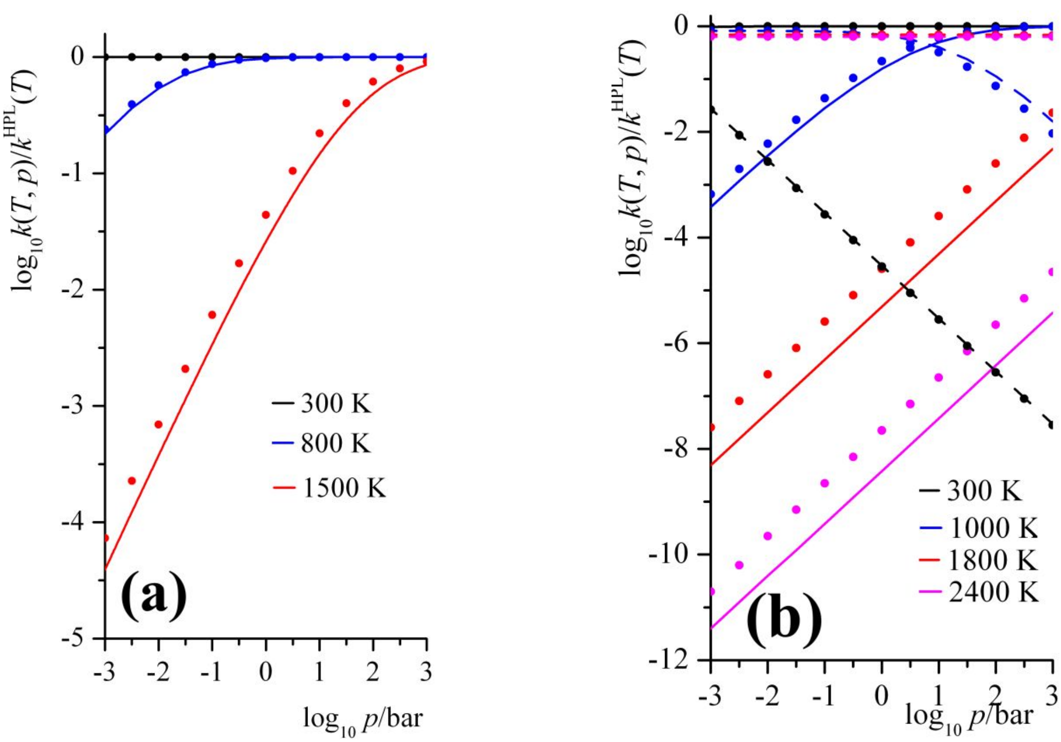

Fig. 2 Computed falloff curves for (a) reaction R4; and (b) reaction R5. The dots are computed by using F_E^{app}, and the lines by using F_E^{num}. In (b), the solid lines are for k_{stab} and the dashed lines are for k_{diss}.

As we can see from Figure 2, using F_E^{app} leads to underestimation of the pressure-dependent effects, and this is particularly noticeable at high temperatures. For reaction R4 and k_{stab} of reaction R5, the falloff effects are underestimated, and the computed $k^{\mathrm{app}}(T, p)$ is larger than $k^{\mathrm{num}}(T, p)$. For reaction R4 at 1500 K and 1.0 bar, $k^{\mathrm{app}}(T, p)$ is a factor of 1.7 larger than $k^{\mathrm{num}}(T, p)$; and at 0.01 bar, it is a factor of 1.8 smaller. For k_{stab} of reaction R5, at 1.0 bar, $k_{\mathrm{stab}}^{\mathrm{app}}(T,p)$ is a factor of 1.4, 5.2 and 5.8 larger than $k_{\mathrm{stab}}^{\mathrm{num}}(T,p)$ at 1000, 1800 and 2400 K respectively. On the other hand, for the further dissociation of the intermediate in reaction R5 which is a chemical activation mechanism, the underestimation of falloff effects lead to smaller k_{diss}, but this effect is relatively smaller than for k_{stab}; at 1.0 bar, $k_{\mathrm{diss}}^{\mathrm{num}}(T,p)$ is only a factor 1.1, 1.0 and 1.0 larger than $k_{\mathrm{diss}}^{\mathrm{app}}(T,p)$ at 1000, 1800 and 2400 K respectively, and at 10.0 bar, this factor is 1.5, 1.0 and 1.0 respectively.

We note that F_E appears as a ratio to $<\Delta E>$ in equation (1); therefore, if experimental data is available, and if $<\Delta E>$ were to be chosen as a function of temperature to match experimental data, there could be some error cancellation (including the error in F_E), although one would obtain an incorrect physical picture by cancelling errors against an incorrect value of the energy transfer parameter. And if $<\Delta E>$ is chosen based on energy-transfer experiments or trajectory calculations of energy transfer, there will be no error cancellation of this type.

We have concluded that the approximate analytic formula tends to underestimate F_E and thus overestimates the collision efficiency, and this leads to smaller pressure effects. For small molecules and for reactions with high threshold energies E_0, the differences are negligible at all temperatures. However, if $a(E)$ at high energies differs appreciably from $a(E_0)$, then the underestimation of pressure-dependent rate constants by using the approximate formula could be about a factor 2 or even higher (we find factors as large as a factor of 5.8) at high temperatures. The physical insight we draw is that for reactions with threshold energies below about 30 kcal/mol, the rate of collisional energy transfer can be appreciably slowed down by the increase in the density of states at higher energies and this increases the falloff effect by which finite-pressure rate constants are lower than the high-pressure limit, especially at higher temperatures.

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