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

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The $F_E$ integral for the normalized Boltzmann-weighted number of unimolecular states above the threshold energy is the key quantity for 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–Rabinovich approximation and assuming that the Whitten–Rabinovich $a(E)$ function is independent of energy, $F_E$ can be approximated by an analytical formula; this approximate formula is widely used because of its convenience and computational efficiency. Here we test its validity by comparing the rate constants computed by using the approximate $F_E$ to the ones determined 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 greater than a factor of 5 at high temperatures. The physical insight we draw from this study is that, for reactions with threshold energies below about 30 kcal mol$^{-1}$, 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 become lower than the high-pressure limit, especially at higher temperatures.

Prediction of 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 the rate constants as the pressure is lowered.$^4$ Similar considerations apply to pressure-dependent association reactions.$^5$

Troe developed an approximation to the solution of the master equation$^6$, that is widely used in the 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 $\beta_c$, the value of which is between 0 and 1 (where the upper limit is called the strong-collision limit). The collision efficiency $\beta_c$ is computed from:

$$\beta_c = \frac{1}{1 + (\Delta E)^2}$$

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:

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

where $\rho(E)$ is the density of states of the unimolecular species at energy $E$, and $E_0$ is the threshold energy. The unimolecular species may be a reactant or an intermediate. Usually, $F_E$ is the only quantity that one computes in order to obtain $\beta_c$ 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\textsuperscript{10,11} or is set equal to the value for a similar system. (There has also been progress in the evaluation of the energy transfer parameter from trajectories\textsuperscript{12} and models.\textsuperscript{13})

Troe proposed a very efficient analytical formula\textsuperscript{6} for calculating \( F_E \) by using the vibrational Whitten–Rabinovitch (WR) approximation\textsuperscript{14–16} 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\textsuperscript{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 semi-classical model proposed by Marcus and Rice\textsuperscript{18} and on empirical development by Rabinovitch and coworkers.\textsuperscript{19–21} The WR approximation only requires the information of vibrational frequencies, and it is computed by the following equations:

\[
\rho_{\text{WR}}(E) = \frac{[E + a(E)E_2]^{s-1}}{(s-1)!} \prod_{i=1}^{n} \hbar \nu_i
\]

in which, for \( E \geq E_2, \)

\[
\log_{10} \omega = -1.0506(E/E_2)^{0.25}
\]

and for \( E < E_2, \)

\[
\omega = \left[ \frac{5E}{E_2} + 2.73 \left( \frac{E}{E_2} \right)^{0.5} + 3.51 \right]^{-1}
\]

with

\[
\beta = \frac{(s-1)^2}{s} \sum_{i=1}^{n} \nu_i^2
\]

where \( s \) is the number of vibrational degrees of freedom, \( a \) is an empirical energy dependence factor, \( E_2 \) is the zero-point vibrational energy (computed from the frequencies), and \( \nu_i \) is the vibrational frequency for the \( i \)-th mode. Note that \( E \) is the energy above the zero-point level.

By substituting the Whitten–Rabinovitch density of states \( \rho_{\text{WR}}(E) \) into eqn (2), one obtains an integral for computing \( F_E \) that cannot be evaluated analytically. In order to obtain an analytical approximation, Troe assumed that the \( E \) dependence of the \( a(E) \) function may be ignored, with its value being fixed at \( a(E_0) \). By doing this, the original integrand can be re-written in the form of \( \chi \exp(-\chi) \), and the integral becomes an incomplete gamma function, which leads to the following analytical approximation to the integral:\textsuperscript{6,8}

\[
F_E = \sum_{i=0}^{s-1} (s-1)! \left( \frac{k_B T}{E_0 + a(E_0)E_2} \right)^{s-1-i} E_0^{i (s-1-i)!}
\]

Eqn (8) is the standard equation used in most practical calculations.\textsuperscript{22}

Here we test whether or not this widely used approximation is accurate by comparing the final \( k(T, p) \) computed by using eqn (8) to that computed by numerically integrating eqn (2) with \( \rho_{\text{WR}}(E) \). Note that the computed \( k(T, p) \) depends on many factors, including the pressure-dependence model itself, the energy transfer parameters including \( \langle \Delta E \rangle \), 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 the experimental values, but solely to examine the validity of the widely used approximate analytical 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 analytical 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\textsuperscript{23–27} to test the approximation, and they are listed in Table 1.

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 the system-specific quantum RRK (SS-RRQR) theory\textsuperscript{23,27,28} are the same as reported in the previous work\textsuperscript{23–27} 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 the density of states, since multiple conformational structures and coupled internal torsions\textsuperscript{29–31} may significantly affect the density of states, and for such cases, more exhaustive computational work is needed in order to determine the density of states; in the present work, we do not consider such cases, and we focus on the above-mentioned systems for which the 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 the SS-RRQR theory, the threshold energy \( E_0 \) is an effective threshold given by the temperature-dependent high-pressure activation energy \( E_a(T) \).\textsuperscript{29–31} 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 Fig. 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 certainly cannot be ignored, and in such cases the $a(E)$ values at $E' = 300$ kcal mol$^{-1}$ (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 the $F_E$ integral for these reactions at high temperatures.

As shown in Table 3, we tabulated the $F_E$ values computed by numerical integration, which are denoted as $F_E^{\text{num}}$, and we also tabulated the ratio $F_E^{\text{app}}/F_E^{\text{num}}$, in which $F_E^{\text{app}}$ is the approximate $F_E$ value computed using eqn (8). The results at various temperatures are tabulated for each of the reactions R1–R5. For reactions R1–R3, the differences between $F_E^{\text{app}}$ and $F_E^{\text{num}}$ 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 analytical 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.

To assess the effect on the rate constant itself, we compared the falloff curves computed by using $F_E^{\text{app}}$ (represented by dots) to those computed by using $F_E^{\text{num}}$ (represented by solid lines); the falloff curves are plotted for reactions R4 and R5 and shown in Fig. 2. The $F_E^{\text{app}}$ is the approximate $F_E$ value computed using eqn (8). The results at various temperatures are tabulated for each of the reactions R1–R5. For reactions R1–R5, the differences between $F_E^{\text{app}}$ and $F_E^{\text{num}}$ 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 analytical 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.

As we can see from Fig. 2, using $F_E^{\text{app}}$ leads to underestimation of the pressure-dependent effects, and this is particularly noticeable at high temperatures. For reaction R4 and the $k_{\text{stab}}$ of reaction R5, the falloff effects are underestimated, and the computed $k^{\text{app}}(T, p)$ is larger than $k^{\text{num}}(T, p)$. For reaction R4 at 1500 K and 1.0 bar, $k^{\text{app}}(T, p)$ is a factor of 1.7 larger than $k^{\text{num}}(T, p)$; and at 0.01 bar, it is a factor of 1.8 larger. For the $k_{\text{stab}}$ of reaction R5 at 1.0 bar, $k^{\text{app}}(T, p)$ is a factor of 1.4, 5.2 and 5.8 larger than $k^{\text{num}}(T, p)$ 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 mecha-

This table lists the temperature-dependent effective threshold energies $E_0(T)$ for calculating $F_E$ for reactions R1–R5.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_0$ at 1500 K</th>
<th>$E_0$ at 1800 K</th>
<th>$E_0$ at 2000 K</th>
<th>$E_0$ at 2100 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1500 K</td>
<td>1800 K</td>
<td>2100 K</td>
<td>2400 K</td>
</tr>
<tr>
<td>R2</td>
<td>1500 K</td>
<td>1800 K</td>
<td>2100 K</td>
<td>2400 K</td>
</tr>
<tr>
<td>R3</td>
<td>1500 K</td>
<td>1800 K</td>
<td>2100 K</td>
<td>2400 K</td>
</tr>
<tr>
<td>R4</td>
<td>1500 K</td>
<td>1800 K</td>
<td>2100 K</td>
<td>2400 K</td>
</tr>
<tr>
<td>R5</td>
<td>1500 K</td>
<td>1800 K</td>
<td>2100 K</td>
<td>2400 K</td>
</tr>
</tbody>
</table>

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.
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 of 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$^{-1}$, 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 become lower than the high-pressure limit, especially at higher temperatures.

Conflicts of interest

There are no conflicts to declare.

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References


