Temperature and Molecular Size Dependence of the High-Pressure Limit

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In kinetic models, gas-phase reactions involving large molecules (of more than about a dozen atoms) are often assumed to be in the high-pressure limit, that is, to not exhibit significant falloff or chemical activation effects. However, cases are known where rather large molecules are indeed involved in chemically activated, pressure-dependent reactions particularly at high temperatures. Here, we present simple formulas giving guidance for deciding whether a particular reaction's rate can be accurately approximated using the high-pressure limit rate constant $k_\infty(T)$. We find that under practical combustion conditions for liquid and gaseous fuels, few reactions are truly in the high-pressure limit, regardless of the size of the molecules involved.

I. Introduction

It is well-known that the rate constants for elementary-step gas-phase reactions of the form A + B → C, C → A + B, or C → D are dependent on both temperature and pressure.[1] Depending on the nature of the reaction, this phenomenon is known as "fall-off" or "chemical activation." A reaction in which the rate constant is dependent on temperature (T) and pressure (P) in a particular region of (T,P) space is said to be "pressure-dependent" or "in the fall-off regime." If one fixes the temperature and increases the pressure toward infinity, the reaction eventually reaches a regime in which the rate constant is no longer sensitive to pressure. In other words, as the pressure is increased, $k(T,P) \rightarrow k_\infty(T)$ where $k_\infty(T)$ is known as the high-pressure limit rate constant.

Calculation of the rate constant $k(T,P)$ as an explicit function of temperature and pressure can be complex and demanding, sometimes involving a large network of interconnected pressure-dependent pathways.[2,3] In addition, the preferred methods of evaluating $k(T,P)$ (for example, a Rice−Ramsperger−Kassel−Marcus/Master-Equation (RRKM/MEQ) calculation) for any reaction will require detailed information about the transition state, potential energy surface, and the internal vibrational and rotational modes of all the species involved; a single pressure-dependent reaction network is often the subject of many years' work. Such demands are strong incentives for many kinetic modelers, especially those studying high-temperature pyrolysis, combustion, or partial oxidation systems, to assume that a pressure-dependent reaction is in its high-pressure limit whenever this is reasonable. That is, it is very convenient for the builders of large, gas-phase kinetic models to assume, for a great many reactions

$$k(T,P) \approx k_\infty(T) \tag{1}$$

When is such an assumption reasonable? In the literature it is almost universally assumed the high-pressure limit approximation, eq 1, is true for reactions involving large molecules (more than 8−10 heavy atoms[4]). The justification is as follows:

Falloff and chemical-activation effects can clearly be neglected when the stabilization rate due to collisions with the bath gas M, $\beta k_s[M]$, is significantly faster than the microcanonical reaction rate $k(E)$ of the activated species

$$\beta k_s[M] \gg k(E) \tag{2}$$

where k_s is the collision rate and $1/\beta$ is roughly the average number of collisions required to thermalize the activated species.[5] The microcanonical RRKM reaction rate $k(E)$ (neglecting energy associated with any conserved quantum numbers such as J) can be written

$$k(E) = N_{TS}(E)/(h\rho(E + E_{AB})) \tag{3}$$

where E is the energy relative to the zero-point energy of A + B, E_{AB} is the threshold for the reaction C → A + B, $N_{TS}(E - E_{AB})$ is the sum of states at the transition state from 0 to E, h is Planck's constant, and ρ is the accessible density of states of the molecule or adduct undergoing reaction. The density of states ρ increases exponentially with the number of atoms in the adduct;[1] therefore, the argument goes, $k(E)$ must rapidly drop below $\beta k_s[M]$ in eq 2 with increasing molecule size. The exponential dependence of ρ on molecular size is so strong that, by this argument, pressure dependence will only be relevant when the reacting molecules or adducts have less than about 10 heavy atoms; otherwise, it is acceptable to assume $k(T,P) \approx k_\infty(T)$ at any temperature.

However, there are several indications in the literature that this common assumption is incorrect—even reactions through very large adducts are strongly pressure-dependent. For example, we have recently found the reaction $C_{10}H_7 + C_2H_2$, where the initially formed energized 21-atom adduct has an enormous density of states ($\rho > 10^{14}$ states/cm^{-1}), is dominated by chemically-activated product channels instead of the expected stabilization product over the whole range of pressures and temperatures relevant for combustion.[6] Others have shown chemical activation dominates for the recombination of cyclopentadienyl radicals ($C_5H_5 + C_5H_5$)[7] and for reactions involving even larger molecules.[8] In addition, the microcanonical argument given above is qualitatively inconsistent with the predictions of even a simple Lindemann model (see the Supporting

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Information). In short, eq 1 is not true merely because the reacting species are large, as the microcanonical argument given above would suggest; in fact, kinetic modelers can (and do) incur serious errors using eq 1 for large species, especially under high-temperature combustion or pyrolysis conditions. A more detailed treatment is given in this paper which identifies the source of these discrepancies and presents a better criteria for determining when eq 1 is valid.

In this work, we demonstrate the validity of the assumption $k(T,P) \approx k_\infty(T)$ depends far more on temperature than on molecular size especially at higher temperatures. We present a fast, reliable, and convenient method for determining whether the approximation of eq 1 will be valid, without performing a precise $k(T,P)$ calculation. The point of the calculations presented is to show temperature is the overwhelmingly important variable in assessing the validity of eq 1, and molecular size is a relatively small correction except at lower temperatures. The purpose is not to resolve the many open questions regarding how best to accurately calculate $k(T,P)$ a priori for complex reactions in different bath gases, nor to improve the existing literature on the specific reactions presented as illustrative examples.

To aid builders of kinetic models, we present a formula for P_{switch} as a function of T and adduct size where P_{switch} is the pressure at which $k(T,P)$ begins to approach $k_\infty(T)$, within a user-specified tolerance. Given a temperature T, the kinetic modeler can be confident of eq 1 at pressures above P_{switch} but should carry out a pressure-dependent estimate of $k(T,P)$ below it. Analytical and numerical results are presented which validate the formula for P_{switch} and show how it can be used in practice. Based on these examples we present rough guidelines for when whole reaction classes should or should not be treated as true pressure-dependent systems.

II. A Simple Model for Estimating the Onset of the High-Pressure Limit

For any fall-off or chemically-activated reaction through an energized adduct C*, we define the transition to the high-pressure limit to occur when the rate of formation of thermalized C, $k_{A+B \to C}$, is given by

$$k_{A+B \to C}(T,P) = k_{\infty,A+B \to C}(T)/(1 + \epsilon) \quad (4)$$

where ϵ is a tolerance. For a chosen ϵ, eq 4 defines a curve on a (T,P) grid such that the rate constant in (T,P) space well above the curve (i.e., at higher P and/or lower T) may be considered "in the high-pressure limit". Similarly, the rate constant would be pressure-dependent in regions of (T,P) space well below this curve (at lower P and/or higher T). Only rarely would one know $k_\infty(T)$ to better than a factor of 2; therefore, $\epsilon \approx 1$ is a reasonable choice. For $\epsilon = 1$, the error incurred by assuming $k(T,P) \approx k_\infty(T)$ for the main channel $A + B \to C$ at any T and P above the curve defined by eq 4 will be less than a factor of 2 (This criterion ensures most of the flux into C* will form thermalized C, as it should in the high-pressure limit. In some situations one is concerned with even very minor chemically-activated channels; to predict their yields accurately, much tighter tolerances may be required).

In terms of the microcanonical quantities, the microscopic reversibility relation[1] gives

$$\rho_{A+B}(E)k_{A+B}(E) = \rho_C(E + E_{AB})k_C(E + E_{AB}) \quad (5)$$

where ρ_{A+B} and ρ_C are the densities of states of $A + B$ and C, respectively, and k_{A+B} and k_C are the rates of $A + B \to C$ and

$C \to A + B$ correspondingly. Equation 4 becomes

$$\int_0^\infty \rho_{A+B}(E)k_{A+B}(E)\phi(E + E_{AB})e^{-E/k_BT}dE =$$
$$\frac{1}{1 + \epsilon}\int_0^\infty \rho_{A+B}(E)k_{A+B}(E)e^{-E/k_BT}dE \quad (6)$$

$$\int_{E_{AB}}^\infty \rho_C(E)k_C(E)\phi(E)e^{-E/k_BT}dE =$$
$$\frac{1}{1 + \epsilon}\int_{E_{AB}}^\infty \rho_C(E)k_C(E)e^{-E/k_BT}dE$$

where E_{AB} is the threshold (barrier height) for the reverse reaction $C \to A + B$ whose microcanonical rate is $k_C(E)$, and $\phi(E)$ is the fraction of C*(E) that is stabilized to C. To arrive at a simple general formula for $P_{\text{switch}}(T)$, we approximate $\phi(E)$ by the modified strong collision formula

$$\phi(E) = \frac{\beta k_s[M]}{\beta k_s[M] + \sum_i k_i(E)} \quad (7)$$

where the sum is over all the open reaction (dissociation and isomerization) channels for C*(E). Assuming simple Arrhenius forms suffice to describe all high-pressure limit rates $k_\infty(T)$ and using the inverse-Laplace transform[9] expression for the corresponding microcanonical rates yields

$$k_{\infty,i}(T) = A_i e^{-E/k_BT} \quad (8)$$

$$k_i(E) = A_i \frac{\rho_C(E - E_i)}{\rho_C(E)} H_{Ei}$$

where H_{Ei} is the Heaviside function $H_{Ei} = H(E - E_i)$. The density of vibrational−rotational states for a large molecule can be approximated by the semiclassical expression[1] (cf. eq 4.78, neglecting the factor of β_R)

$$\rho(E) = \frac{(E + Z)^{m-1}}{\Gamma(m)\prod_i^s h\nu_i}\prod_j^r\left(\frac{8\pi^3 I_j}{h^2}\right)^{1/2} \quad (9)$$

where Z is the zero-point energy, m is the number of degrees of freedom ($m = N_{\text{vibrations}} + N_{\text{rotors}}/2 = s + r/2$), I_j is the moment of inertia of the jth rotor, and ν_i is the frequency of the ith oscillator. Note that all the constants in eq 9 cancel when ρ is substituted into eq 8. With these approximations, and after some manipulation (see the Supporting Information) we obtain

$$\int_a^\infty \frac{w^{m-1}e^{-(m-1)w}}{1 + \frac{1}{\beta k_s[M]}\sum_i A_i H_{Ei}\left[1 - \frac{E_i}{w(m-1)k_BT + E_{AB}}\right]^{m-1}}dw =$$
$$\frac{1}{1 + \epsilon}\int_a^\infty w^{m-1}e^{-(m-1)w}dw \quad (10)$$

where $w = (E + Z - E_{AB})/((m-1)k_BT)$, $Z = hc\langle\omega\rangle s/2$, $a = (hc\langle\omega\rangle/2k_BT)(s/(m-1))$, and $H_{Ei} = H((m-1)wk_BT + E_{AB} - Z - E_i)$. Typical values of the mean vibrational frequency for organics $\langle\omega\rangle$ range from about 800 cm^{-1} to 1200 cm^{-1}; here, $\langle\omega\rangle$ was fixed to 1000 cm^{-1}. To this level of accuracy, one can

approximate the dimensionless variable a (roughly the ratio of zero-point energy to available thermal energy) by $a \approx hc\langle\omega\rangle/(2k_BT)$, the same for all molecules.

This integral equation can be solved numerically to find the (T,P) locus which defines the region where the high-pressure limit approximation is accurate. However, analytic results are more useful for our purposes. One can notice immediately if

$$\sum_i A_i \ll \epsilon\beta k_s[M] \qquad (11)$$

the equation has no solution; at these high [M], the system can always be approximated as being in the high-pressure limit. For large m, the integrand on the right-hand side is sharply peaked (like a Dirac δ function) at $w = 1$, and numerical quadrature is not really necessary. In fact, in eq 10 both integrands can be replaced by simple function evaluations at $w = (1 + a^4)^{1/4}$; i.e., $\int_a^\infty w^{m-1}e^{-(m-1)w}dw \approx (1 + a^4)^{(m-1)/4}e^{-(m-1)(1+a^4)^{1/4}}(\Delta w)$, where Δw is the width of the sharp peak. A similar substitution can be made for the integral on the left-hand side using an identical Δw element without significantly affecting the computed (T,P) locus. In this approximation (see the Supporting Information), which has been verified numerically, the equation defining the (T,P) locus becomes

$$\sum_i A_i H_{Ei}\left(1 - \frac{E_i}{E_{AB} + (m-1)(1 + a^4)^{1/4}k_BT}\right)^{m-1} \cong$$

$$\epsilon\beta k_s[M] = \frac{\epsilon\beta k_s P}{RT} \quad (12)$$

where

$$H_{Ei} = H((m-1)(1 + a^4)^{1/4}k_BT + E_{AB} - Z - E_i)$$

Equation 12 requires only estimates of the A's and E_a's for each reaction channel from the initial adduct, the collision rate, and the $\langle\Delta E\rangle_{all}$ used to compute β as inputs. It does not require many of the details required for a detailed master equation (e.g., the vibrational frequencies or heat capacities of all the isomers or transition states) nor all the multiple-well inputs required for a QRRK calculation. Consequently, it is very convenient to use eq 12 to compute the switchover pressure as a function of the temperature (for any specified tolerance ϵ), to assess whether a more detailed $k(T,P)$ calculation is necessary. A simple MATLAB computer program to perform this calculation is available.[10]

Why the Simple Microcanonical Argument Is Incorrect. Before proceeding with a general discussion of eq 12 and its implications, we once again reconsider the misleading argument based on eq 3 which concluded that large molecule reactions are never pressure-dependent. This incorrect argument implicitly assumes E is fixed, independent of molecular size or T. However, in the real system, the reactants A and B are typically thermalized before they combine, so the initially formed adduct C* has an average energy $\langle E\rangle \approx mk_BT + E_{AB}$ where for large m and high T the first term can significantly exceed the second. More precisely, making the substitution $\langle E\rangle = (1 + (hc\langle\omega\rangle/(2k_BT))^4)^{1/4}(m-1)k_BT - Z + E_{AB}$ in the microcanonical expression of eq 3 gives

$$k(\langle E\rangle) = \frac{N_{TS}\left(\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_BT}\right)^4\right]^{1/4}(m-1)k_BT - Z\right)}{h\rho\left(\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_BT}\right)^4\right]^{1/4}(m-1)k_BT - Z + E_{AB}\right)} \quad (13)$$

The number of quantum states in the transition state for a large molecule can be approximated by the semiclassical expression[1] (cf. eq 4.75, neglecting the factor of β_R)

$$N_{TS}(E - E_{AB}) = \frac{(E - E_{AB} + Z)^{m-1}}{\Gamma(m)\prod_i^{s-1} h\nu_i^{TS}}\prod_i^r\left(\frac{8\pi^3 I_i^{TS}}{h^2}\right)^{1/2} \quad (14)$$

where TS indicates vibrational frequencies and moments of inertia of the transition state. Using this approximation and the expression for the density of states in eq 9, the criteria for describing the system as being in the high-pressure limit becomes

$$\beta k_s[M] \gg k(\langle E\rangle) =$$

$$\left(1 - \frac{E_{AB}}{E_{AB} - Z + k_BT(m-1)\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_BT}\right)^4\right]^{1/4}}\right)^{m-1} \times$$

$$\frac{(\prod_i^s \nu_i)(\prod_i^r (I_i^{TS})^{1/2})}{(\prod_i^{s-1} \nu_i^{TS})(\prod_i^r (I_i)^{1/2})} \quad (15)$$

In the products over the frequencies and the moments of inertia, the denominator has one fewer frequency because the reaction coordinate is not included. The ratio of these products is a frequency itself, presumably not very sensitive to the size of the molecule, so eq 15 can be written in the form

$$\ln(\beta k_s[M]) \gg \ln(\nu) + (m-1) \times$$

$$\ln\left(1 - \frac{E_{AB}}{E_{AB} - Z + k_BT(m-1)\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_BT}\right)^4\right]^{1/4}}\right) \quad (16)$$

Expanding the second logarithm on the right and keeping the first term in the series[11] yields

$$\ln(\beta k_s[M]) \gg \ln(\nu) - \frac{E_{AB}}{k_BT}\left\{\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_BT}\right)^4\right]^{1/4} + \frac{E_{AB}}{2(m-1)k_BT} - \frac{Z}{(m-1)k_BT}\right\}^{-1} \quad (17)$$

For low temperatures, the term in square brackets in eq 17 is approximately $hc\langle\omega\rangle/(2k_BT) = Z/(mk_BT)$, roughly canceling with the last term, and the leading terms in the expansion for eq 17 are

$$\ln(\beta k_s[M]) \gg \ln(\nu) - 2(m-1) \text{ (low } T) \quad (18)$$

According to this very rough model, the [M] required to achieve the high-pressure limit will be exponentially dependent

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TABLE 1: $k(T, P)/k_\infty(T)$ Ratios for Important Large-Molecule ($m = 60$) Reactions as Predicted by eq 12

	laboratory 400 K, 1 atm	cool flame/reactor 800 K, 10 atm	engine ignition 1200 K, 20 atm	flame 2000 K, 10 atm
β-scission of R•: R• → R′• + alkene[21]	0.999	0.998	0.954	0.103
β-scission of RO•: RO• → RO + R′•[23]	0.863	0.770	0.227	0.004
R• + O_2 → ROO•[24]	0.995	0.974	0.479	0.002
2R• → R−R[25]	1.000	1.000	1.000	0.379
ROOH → RO. +.OH[26]	1.000	0.997	0.846	0.006
•OH + aromatic[27]	0.613	0.447	0.074	0.001
C_2H_2 + aryl radicals[6]	0.991	0.986	0.876	0.029

on the size of the adduct at very low T. However, for higher temperatures, the first term in braces is close to unity, and for large m and T it dominates the sum; therefore, the leading terms in the expansion for eq 17 are

$$\ln(\beta k_s[\text{M}]) \gg \ln(\nu) - \frac{E_{\text{AB}}}{k_{\text{B}}T} \text{ (high } T\text{)} \qquad (19)$$

In this rough approximation, the required [M] to achieve the high-pressure limit does not depend significantly on molecular size but has a strong Arrhenius temperature dependence (which arises because the initial energy of the adduct depends on the thermal energy of A + B). The microcanonical rate constant will likewise be sensitive to T, but relatively independent of molecular size at high temperatures. This improved microcanonical argument based on eq 2 agrees qualitatively with the more precise eq 12.

Implications of the Simple Model. Although eq 12 can be easily evaluated numerically, it is complex enough that it may be hard to see the fundamental physics. Judicious approximations make the physical behavior of large-adduct pressure-dependent reactions more transparent. For a reaction with large m, the channel with the smallest E_i will often dominate the sum. Let the Arrhenius parameters for the lowest energy exit channel be A_{lowest} and E_{lowest}. Keeping only this term and rearranging, this approximation gives

$$\ln(P_{\text{switch}}) \cong \ln\left(\frac{A_{\text{lowest}}RT}{\epsilon\beta k_s}\right) + (m - 1) \times$$
$$\ln\left\{1 - \frac{E_{\text{lowest}}}{E_{\text{AB}} + k_{\text{B}}T(m - 1)\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_{\text{B}}T}\right)^4\right]^{1/4}}\right\} \qquad (20)$$

Expanding the term in braces and keeping the first term in the series yields

$$\ln(P_{\text{switch}}) \cong \ln\left(\frac{A_{\text{lowest}}RT}{\epsilon\beta k_s}\right) - \left[\frac{E_{\text{lowest}}}{2E_{\text{AB}} - E_{\text{lowest}}}\right] \times$$
$$\left\{\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_{\text{B}}T}\right)^4\right]^{1/4}\frac{k_{\text{B}}T}{2E_{\text{AB}} - E_{\text{lowest}}} + \frac{1}{2(m - 1)}\right\}^{-1} \qquad (21)$$

The first term in square braces contains the energy difference between the entrance and exit channels and accounts for the fact that chemically activated reactions are further from the high-pressure-limit than the corresponding "fall-off" reaction through the same adduct. For the special case of fall-off where there is only a single channel for C*(E) back to A + B, eqs 20 and 21 trivially reduce to eqs 22 and 23, respectively:

$$\ln(P_{\text{switch}}) \cong \ln\left(\frac{ART}{\epsilon\beta k_s}\right) + (m - 1) \times$$
$$\ln\left\{1 - \frac{E_{\text{AB}}}{E_{\text{AB}} + k_{\text{B}}T(m - 1)\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_{\text{B}}T}\right)^4\right]^{1/4}}\right\} \qquad (22)$$

$$\ln(P_{\text{switch}}) \cong \ln\left(\frac{ART}{\epsilon\beta k_s}\right) -$$
$$\left\{\left[1 + \left(\frac{hc\langle\omega\rangle}{2k_{\text{B}}T}\right)^4\right]^{1/4}\frac{k_{\text{B}}T}{E_{\text{AB}}} + \frac{1}{2(m - 1)}\right\}^{-1} \qquad (23)$$

Equations 21 and 23 make it easier to see how temperature and molecular size contribute to the switchover pressure. At low temperature, the term in braces is sensitive to the last term, and increasing the size of the adduct reduces the switchover pressure. At higher temperature, the first term in braces dominates, and the molecular size dependence is greatly reduced. For any temperature, because of the $1/m$ dependence, the switchover pressure reaches the "large-molecule-limit" when $m \gg E_{\text{AB}}/(k_{\text{B}}T)$.

Testing the Simple Model. We compare the results of eq 12 against well-established methods[12−14] as implemented in a substantially improved multiwell version of CHEMDIS.[15] This improved CHEMDIS approximates the effective collision parameter β using a complex form suggested by Gilbert et al.[16] We have found our expression for $P_{\text{switch}}(T)$ agrees quite well with CHEMDIS even when the collision efficiency β used in our expression (eq 12) was evaluated from the simple Troe[5] expression $\beta/(1 - \beta^{1/2}) = -\langle\Delta E\rangle_{\text{all}}/(F_E k_{\text{B}}T)$. In our expression, F_E was assumed to be 1.15 (cf. Table 2 of ref 16); the value of the average energy transferred $(-\langle\Delta E\rangle_{\text{all}})$ was taken from Gardiner.[17] In both CHEMDIS and our expressions, Lennard-Jones collision rates[18] for an argon bath gas were used for k_s; values for collision diameters and well depths were taken from Hippler et al.[19] The densities of states $\rho(E)$ required by CHEMDIS come from the heat capacities fitted to the three-frequency form proposed by Bozzelli et al. using their THERFIT software.[20]

III. Results

The contour plot of $k(T,P)/k_\infty(T)$ in Figure 1 demonstrates the quality of these expressions for the chemically-activated reaction $C_{10}H_7 + C_2H_2$ including all the multiple-channel and low-barrier isomerization pathways proposed by Richter et al.[6] An interesting feature of this strongly chemically-activated reaction is the presence of several isomerization channels which have barriers much lower (~150 kJ lower) than the decomposition back to $C_{10}H_7 + C_2H_2$. These low-barrier isomerization channels compete with collisional stabilization and so determine where the reaction is in its high-pressure-limit. Despite the complexity of the system, our approximate calculation for P_{switch} via eq 12 accurately locates the "transition regime" (gray area)
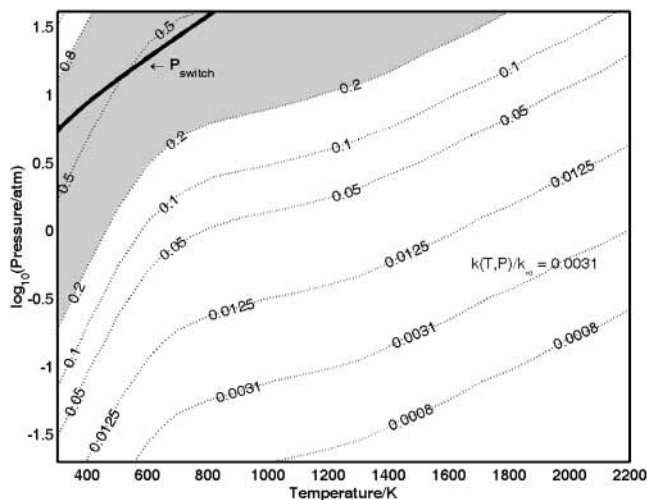
Figure 1. Switchover pressures [pressures where $k(T,P)/k_\infty(T) = {}^1\!/_2$] predicted by eq 12 for $C_{10}H_7 + C_2H_2 \rightarrow C_{10}H_7CHCH$ plotted over contours of $k(T,P)/k_\infty(T)$ as calculated by CHEMDIS (including multiple competing chemically activated channels). In the region of (T,P) space above the P_{switch} curve, this rate can be approximated by the high-pressure limit. Our approximate calculation for P_{switch} via eq 12 accurately locates the "transition regime" (gray area) between the pressure-dependent and pressure-independent regions of (T,P) space.
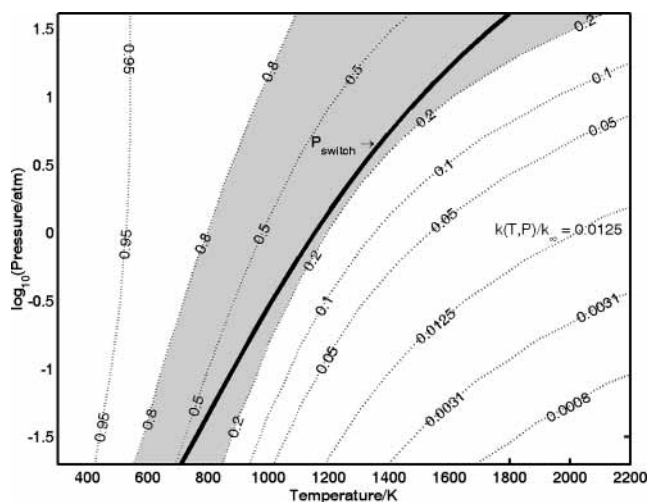

Figure 2. Switchover pressures [pressures where $k(T,P)/k_\infty(T) = {}^1\!/_2$ due to falloff] predicted by eq 12 for $C_4H_9 \rightarrow C_2H_4 + C_2H_5$ plotted over contours of $k(T,P)/k_\infty(T)$ as calculated by CHEMDIS.

between the pressure-dependent and pressure-independent regions of (T,P) space, using minimal inputs. The contour plot of $k(T,P)/k_\infty(T)$ in Figure 2 illustrates the same method applied to the single-well dissociation of C_4H_9 using the parameters of Knyazev et al.[21] Similar accuracy is seen in plots for several other important reaction classes, both chemical-activation cases and falloff cases with quite different potential energy surfaces, presented in the Supporting Information.

All the equations presented here as well as the CHEMDIS calculations are only approximations to the full master equation treatment. The ratios $k(T,P)/k_\infty(T)$ predicted by our simple model and CHEMDIS are compared with detailed master equation calculations in the Supporting Information for the multi-well, multichannel chemically activated reaction of $C_6H_5 + C_2H_2$ at 1000 K. The potential energy surface and values for the input parameters for MultiWell[22] were taken from Richter et al.[6] All methods agree within a factor of 3; similar good agreement between master equation and modified strong collision models has been observed in several other cases.[3,12–14] (Any calculation
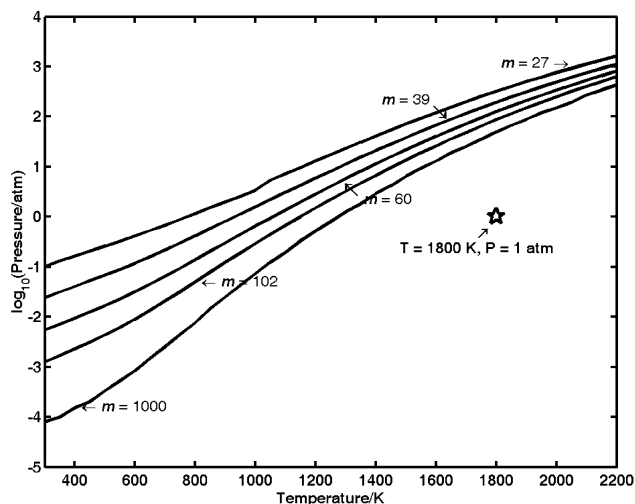

Figure 3. Switchover pressure [pressure where $k(T,P)/k_\infty(T) = {}^1\!/_2$] plots using different values of m ($= N_{vibrations} + N_{rotors}/2$), the number of degrees of freedom in the adduct. Other parameters of eq 12 are identical to those used for $C_6H_5 + C_2H_2 \rightarrow C_6H_5CHCH$. The switchover pressure is only weakly dependent on adduct size $m \approx 3N - 6$ above 800 K, and at typical combustion conditions indicated by the star ($T = 1800$ K, $P = 1$ atm), even a reaction that forms a very large adduct can be pressure-dependent.

will have substantial uncertainties in the rate and collisional energy transfer parameters; likely, the true uncertainty in predicted $k(T,P)$ will be larger than this factor of 3 variation).

For a given temperature, the switchover pressure is weakly dependent on the adduct size m, particularly at high temperatures, as shown in Figure 3. It is clearly demonstrated in Figure 3 that the ratio $k(T,P)/k_\infty(T)$ is largely a function of temperature and to a lesser extent the molecular size of the adduct. The spread of this ratio between a small molecule (11 atoms, $m = 27$) and a very large one ($m = 1000$) varies between 3 orders of magnitude at low temperatures to less than an order of magnitude at high temperatures. For reactions involving large molecules (more than 8–10 heavy atoms), the high-pressure limit approximations used in ref 4 are valid at low temperatures; however, these assumptions can incur serious errors if applied to high-temperature conditions. Under typical flame conditions ($T = 1800$ K, $P = 1$ atm) the important reaction between very large aryl radicals and acetylene to form polycyclic aromatics and other soot precursors is not in the high-pressure limit. Virtually all existing soot-formation models may have to be reexamined.

In Table 1 we list some important reaction classes, and indicate the ratio $k(T,P)/k_\infty(T)$ ($= 1/(1 + \epsilon)$) for a 22-atom adduct ($m = 60$) as predicted by our approximations in various pressure–temperature ranges of technological importance. The required A's and E_a's for all the channels of each reaction were taken from literature sources indicated in the table. In general, if $k(T,P)/k_\infty(T) < 1/2$, pressure dependence cannot be ignored.

IV. Conclusions

At high temperatures, the switchover pressure for reactions through polyatomic energized adducts depends only weakly on molecular size. The common belief that falloff and chemical activation can be ignored for reactions of large molecules in all temperature ranges is incorrect.

Our simple formula for $P_{switch}(T)$, eq 12, requires as inputs only estimates of the A's and E_a's for each reaction channel, of the collision rate, and $\langle\Delta E\rangle_{all}$. A user-friendly code for computing the switchover pressure using eq 12 is available.[10] These

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rough estimates of the switchover pressure are sufficient since the transition from "pressure-dependent" to "in the high-pressure limit" is not very sharp (cf. Figure 1). However, if it is necessary to accurately predict minor channel yields, much tighter tolerances will be needed. Furthermore, if the estimated switchover pressure given by our approximation is within a factor of 10 of the pressure of interest, it is advisable to perform a more detailed $k(T,P)$ calculation using a more precise $\rho(E)$ than the simple generic expression used here (eq 9).

Our analysis of the molecular size dependence of falloff and chemical activation indicates many types of reactions are pressure-dependent even for very large molecules and even under relatively high-pressure conditions. Notably, β-scission reactions of alkoxy radicals, additions of OH to aromatics, and additions of O_2 to radicals are pressure-dependent under most conditions. Under typical flame conditions, most reactions through adducts are not in the high-pressure limit even at 10 atm, even if the adducts are quite large. Essentially all existing flame models for fuels heavier than methane have neglected this effect and will need to be reexamined.

Supporting Information Available: Comparison of $k(T,P)/k_\infty(T)$ ratios at $T = 1000$ K for the reaction $C_6H_5 + C_2H_2 \rightarrow C_6H_5CHCH$ predicted by several models and contour plots of $k(T,P)/k_\infty(T)$ for all of the reactions listed in Table 1, some intermediate steps in the derivations, and a Lindemann model showing the approximate molecular size and T-dependence of the high-pressure limit. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*, 2nd ed.; John Wiley & Sons: New York, 1996.

(2) Matheu, D. M.; Lada, T. A.; Green, W. H.; Dean, A. M.; Grenda, J. M. *Comput. Phys. Commun.* **2001**, *138*, 237.

(3) Matheu, D. M.; Green, W. H.; Grenda, J. M. *Int. J. Chem. Kinet.* **2003**, *35*, 95.

(4) See, for example: (a) Larson, C. W.; Patrick, R.; Golden, D. M. *Combust. Flame* **1984**, *58*, 229. (b) Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. *Combust. Flame* **1998**, *114*, 149.

(5) Troe, J. *J. Phys. Chem.* **1979**, *83*, 114.

(6) Richter, H.; Mazyar, O. A.; Sumathi, R.; Green, W. H.; Howard, J. B.; Bozzelli, J. W. *J. Phys. Chem. A* **2001**, *105*, 1561.

(7) Dean, A. M. *J. Phys. Chem.* **1990**, *94*, 1432.

(8) Richter, H. Private communication.

(9) Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, 1973.

(10) See: http://web.mit.edu/greengp/software/.

(11) Gradshteyn, I. S.; Ryzhik, I. M. *Tables of Integrals, Series, and Products*, 4th ed.; Academic Press: San Diego: 1980 (cf. eq 1.512.2).

(12) Dean, A. M. *J. Phys. Chem.* **1985**, *89*, 4600.

(13) Westmoreland, P. R.; Howard, J. B.; Longwell, J. P.; Dean, A. M. *AIChE J.* **1986**, *32*, 1971.

(14) Westmoreland, P. R.; Dean, A. M.; Howard, J. B.; Longwell, J. P. *J. Phys. Chem.* **1989**, *93*, 8171.

(15) Chang, A. Y.; Bozzelli, J. W.; Dean, A. M. *Z. Phys. Chem.* **2000**, *214*, 1533.

(16) Gilbert, R. G.; Luther, K.; Troe, J. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 169.

(17) Gardiner, W. C., Jr. *Gas-Phase Combustion Chemistry*; Springer-Verlag: New York, 2000.

(18) Troe, J. *J. Chem. Phys.* **1977**, *66,* 4758.

(19) Hippler, H.; Troe, J.; Wendelken, H. J. *J. Chem. Phys.* **1983**, *78*, 6709.

(20) Bozzelli, J. W.; Chang, A. Y.; Dean, A. M. *Int J. Chem. Kinet.* **1997**, *29*, 161.

(21) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem.* **1996**, *100*, 5318.

(22) Barker, J. R. *Int. J. Chem. Kinet.* **2001**, *33*, 232.

(23) Batt, L. *Int. Rev. Phys. Chem.* **1987**, *6*, 53.

(24) Wagner, A. F.; Slagle, I. R.; Sarzynski, D.; Gutman, D. *J. Phys. Chem.* **1990**, *94*, 1853.

(25) Dean, A. M. *J. Phys. Chem.* **1985**, *89*, 4600.

(26) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Hayman, G.; Just, Th.; Kerr, J. A.; Murrells, T.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1994**, *23*, 1004.

(27) Lay, T. H.; Bozzelli, J. W.; Seinfeld, J. H. *J. Phys. Chem.* **1996**, *100*, 6543.