Pressure-Dependent Rate Constant Predictions Utilizing the Inverse Laplace Transform: A Victim of Deficient Input Data

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ABSTRACT: $k(E)$ can be calculated either from the Rice–Ramsperger–Kassel–Marcus theory or by inverting macroscopic rate constants $k(T)$ for understanding combustion, atmospheric chemistry, and chemical vapor deposition. Apart from direct experimental measurements, $k(T,p)$ is obtained from microscopic balancing, employing the master equation (ME) approach, using microcanonical rate constant data as an indispensable ingredient.

The prediction of $k(E)$ has been a central aspect in chemical kinetic research for almost a century, starting with the landmark work on the Rice–Ramsperger–Kassel–Marcus (RRKM) theory. Variants of this theory were used to estimate pressure dependence and laid the foundation for automatically determining $k(T,p)$ prediction schemes used in, e.g., reaction mechanism generator software of Green and co-workers. The present research focuses on properly including reaction mechanism generator software of Green and co-workers.

The prediction of $k(E)$ from inaccurate/incomplete $k(T)$ information that yields more accurate $k(E)$ reconstructions. The present work suggests that accurate representation of experimental and theoretical $k(T)$ data in a broad temperature range could be used to obtain $k(T,p)$. Thus, purely temperature-dependent kinetic models could be converted into fully temperature- and pressure-dependent kinetic models.

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Table 1. Considered Reactions with Their Abbreviation, Type, and Adiabatic Activation Energy $E_A$ in kJ mol$^{-1}$

| reference | equation | type | $E_A$ (kJ mol$^{-1}$) |
|-----------|----------|------|----------------------|
| 39, 40    | CH$_2$O $\rightarrow$ CH$_2$OH (1) | iso, H-tr | 123.3 |
| 39, 40    | CH$_2$OH $\rightarrow$ CH$_3$O (2) | iso, H-tr | 162.8 |
| 39, 40    | CH$_3$O $\rightarrow$ CH$_3$O + H (3) | dec, H-abs | 103.2 |
| 39, 40    | CH$_2$OH $\rightarrow$ CH$_3$O + H (4) | dec, H-abs | 167.2 |
| 41        | CH$_2$OCHO $\rightarrow$ CH$_2$OCHO (5) | iso, H-tr | 165.7 |
| 41        | CH$_2$OCHO $\rightarrow$ CH$_2$OCHO (6) | iso, H-tr | 163.2 |
| 41        | CH$_2$OCHO $\rightarrow$ CH$_2$O + CO (7) | dec, non-H-tr | 91.2 |
| 41        | CH$_2$OCHO $\rightarrow$ CH$_2$O + CO$_2$ (8) | dec, non-H-tr | 60.3 |
| 41        | CH$_2$OCHO $\rightarrow$ CH$_2$O + CHO (9) | dec, non-H-tr | 139.3 |
| 42        | NNH $\rightarrow$ N$_2$ + H (10) | dec, H-abs | 26.7 |

For the corresponding $\ln[k_\infty(T)]$ for 1–10, see the Supporting Information; Table S1. $^b$Reaction type: “iso” denotes an isomerization reaction, “dec” denotes a decomposition reaction, “H-tr” and “H-abs” denote the transfer and abstraction of the H-atom, respectively, and “non-H-tr” denotes the reactions where no H transfer/abstraction happens.

Table 2. Considered Models for an Approximation of $k_\infty(T)$ Data

| name          | expression | parameters | RMSD $^b$ |
|---------------|------------|------------|-----------|
| Arhenius      | $\ln[k_\infty(T)] = A + B/T$ **(11)** | A, B       | 2.96      |
| mod. Arhenius | $\ln[k_\infty(T)] = A + B/T + C \ln(T)$ **(12)** | A, B, C    | 1.00      |
| red. van’t Hoff | $\ln[k_\infty(T)] = A + B/T + DT$ **(13)** | A, B, D    | 1.40      |
| van’t Hoff    | $\ln[k_\infty(T)] = A + B/T + C \ln(T) + DT$ **(14)** | A, B, C, D | 0.42      |
| s-Arhenius    | $\ln[k_\infty(T)] = A + B/T$ **(15)** | A, B, s    | 0.63      |
| d-Arhenius    | $\ln[k_\infty(T)] = A + \ln(1 + dB/T)/d$ **(16)** | A, B, d    | 0.45      |
| d-e-Arhenius  | $\ln[k_\infty(T)] = A + B \exp(C/T)$ **(17)** | A, B, C    | 0.40      |
| exothermic$^c$ | $\ln[k_\infty(T)] = A + B \ln(T + l/C) - D(T - C)/(T^2 + C^2)$ **(19)** | A, B, C, D | 0.11      |
| endothermic$^c$ | $\ln[k_\infty(T)] = A + B \ln(T) - D(T + C)/(T^2 + C^2)$ **(20)** | A, B, C, D | 0.11      |

ILT was conducted using the inverse temperature $\beta = (kT)^{-1}$ expressed in cm. The corresponding equations and parameters can be found in the Supporting Information (see Table S2 and below). $^b$Normalized average root mean squared deviation between the reference and approximated $\ln[k_\infty(T)]$. The modified Arhenius equation was selected as the reference since this format is the frequently used format to represent kinetic data. $^c$Note, an absolute value of the parameter C was used under natural logarithm to prevent the failure during ILT.

RESULTS AND DISCUSSION

Before we move to the assessment of the input data quality for the ILT, a brief introduction to the ILT method for $k(E)$ computation will be considered together with tests of chemical reactions and mathematical models for approximation of the kinetic input data. We start with the mathematical expression for $k(E)$ for unimolecular reactions

$$k(E) = \frac{L^{-1}[k_\infty(T)Q(T)]}{L^{-1}[Q(T)]}$$

In this expression, the ILT, denoted by $L^{-1}$, needs to be applied to a reactant’s partition function, $Q(T)$, and to the product of $Q(T)$ with the high-pressure limit rate constant, $k_\infty(T)$. The advantage of the ILT concerning RRKM theory is that no prior information on the transition state is required. This information is implicitly available from $k_\infty(T)$. Therefore, providing an accurate and complete description of $k_\infty(T)$ is highly relevant not only within the experimental range of temperatures but also outside this range, i.e., in the limits $T \rightarrow 0$ and $T \rightarrow \infty$. For simplicity, we specifically focus on various mathematical descriptions of the raw $k_\infty(T)$ data and will not discuss different approximations for $Q(T)$ but confine to the rigid-rotor harmonic-oscillator (RRHO) approximation. The reference $k(E)$ data, $k(T,p)$, and $k_\infty(T)$ have been calculated for each reaction with RRKM theory, conducting multiple well and multiple channel ME simulations employing MESS software $^{37}$ (see Computational Methods). Note, all results presented here are computed in the nonvariational single-structural harmonic-oscillator-based RRKM approximation to prove the concept and advocate the ILTs. The benchmarking of ILT using either experimental results or the state-of-the-art SS-QRRK and variational transition state theories will be conducted in a future work.

As the next step, we select a set of 10 reactions simulated previously in our group$^{38}$ see Table 1. For simplicity, we thoroughly reconstructed $k(E)$ into the ME approach provides accurate $k(T,p)$ predictions. Ultimately, the present work aims at convincing researchers to revisit well-established automated $k(T,p)$ prediction schemes and reassess the functional form for $k(T)$ input data representation.
consider one possible reaction path per reactant only. The reactions considered in the test set cover a broad range of adiabatic activation energies from 26 to 167 kJ mol\(^{-1}\). Among these 10 reactions, 4 reactions are radical isomerization reactions and 6 reactions are radical decomposition reactions. On the other hand, seven reactions (1 to 6 and 10) are H-atom transfer/abstraction reactions, where tunneling plays an important role, which is not so important for 7 to 9. Thus, these two test sets allow to verify the ILT performance not only for the different reaction types but also to check whether the ILT can account for possible tunneling from provided \(k_{\infty}(T)\).

Before employing the ILT, it is necessary to represent \(k_{\infty}(T)\) data in a condensed format by applying various models. Ten models were considered to fit \(k_{\infty}(T)\) data, with a maximum of four adjustable parameters (see Table 2). The simplest model for representing \(k_{\infty}(T)\) is the Arrhenius equation (eq 11) with two parameters \(A\) and \(B\). These parameters can be quickly obtained by applying linear regression for \(\ln[k_{\infty}(T)]\) on the basis of one descriptor, the inverse temperature, \(T^{-1}\). The Arrhenius equation could be further modified by including \(\ln(T)\) or/and \(T\) descriptors and applying multilinear regression. These changes lead to the modified Arrhenius (eq 12), the reduced van’t Hoff (eq 13), and the van’t Hoff (eq 14) equations.\(^{43}\) Because of their simplicity, linear and multilinear regressions were and will be a standard practice for representing \(\ln[k_{\infty}(T)]\) data and their representation in tables and databases.\(^{44}\)

The convenience and simplicity of \(k_{\infty}(T)\) data representation via one of the first four equations in Table 2 has its price, providing results that deviate noticeably from the reference after ILT (see Figure 1A,B). Therefore, we consider modifications of the Arrhenius equation, which are not linear in the parameters (see eqs 15 to 18), expecting that these models could perform better. The application of nonlinear regression techniques is not as challenging as it was several decades ago but nowadays are readily available in most popular data processing packages. The first investigated modification of the Arrhenius equation is the stretching of the exponential function \(\exp(-x) \approx \exp(-x^s)\) with \(s\) close to unity (eq 15). This modification is referred to as the stretched Arrhenius or s-Arrhenius equation. The second modification is the Aquilanti–Mundim deformed Arrhenius equations or d-Arrhenius equations (eq 16). This modification represents the exponent in the Arrhenius equation as the Euler limit \(\exp(-x) \approx (1 - d\cdot x)^{1/d}\) with a finite value of \(d\) close to zero. These nonlinear modifications of the Arrhenius equation coincide with it at \(s = 1\) or, respectively, in the limit \(d \to 0\). The s- and d-Arrhenius equations allow to account for the deviations from the Arrhenius equation that are related to tunneling effects and the temperature dependence of the prefactor. An alternative functional form that could also account for tunneling is eq 17. This equation is named as the exponentially modified Arrhenius or e-Arrhenius equation. The deformed exponentially modified Arrhenius (d-e-Arrhenius) equation was considered (eq 18). This equation includes the features of d- and e-Arrhenius equations and contains four adjustable parameters. To the best of our knowledge, eqs 15, 17, and 18 have not been considered before for raw \(\ln[k_{\infty}(T)]\) data approximation and are proposed here for the first time in this context. Finally, we included two physically motivated nonlinear four-parameter equations for fitting \(\ln[k_{\infty}(T)]\) for exothermic (eq 19) and endothermic (eq 20) reactions suggested by Truhlar and co-workers.\(^{46,47}\)

Note, the functional form of eqs 17 to 20 provides a nonzero value of \(k_{\infty}(T)\) at \(T \to 0\) contrary to other equations considered here.

Now, to assess the input data quality, we consider the average of the root mean square deviations (RMSDs) normalized to the RMSD of the modified Arrhenius equation listed in the last column in Table 2. The normalization reference is chosen to be the modified Arrhenius equation since this equation is the most popular format for kinetic data representation. The complete tables with raw and normalized RMSDs for each reaction are given in the Supporting Information (see Tables S3 and S4). The RMSD of the modified Arrhenius and reduced van’t Hoff equations is one-

Figure 1. Reconstructed \(k(E)\) obtained from \(k_{\infty}(T)\) for 1 described via linear (A) and nonlinear (C) fitting functions and corresponding detailed views (B, D). The vertical black dashed lines correspond to the adiabatic activation energy. Results for 2 to 10 are presented in the Supporting Information in Figures S1 to S9.
considered nonlinear functional forms significantly improve the quality of reconstructed $k(E)$. The next, we consider the results of the ILTs of the canonical data represented by Eqs. 11–20 for $k_{\infty}(T)$, using the RRHO approximation for $Q(T)$, as mentioned before. Since the conclusions remain the same for all considered reactions, we present the results of only the 1 (for the results for 2–10, see the Supporting Information). Among various methods available for ILT, we employed the second-order steepest descent algorithm.\(^{38–51}\) In this method, the knowledge of the derivatives of $\ln[Q(T)exp(E/k_{\infty})]$ and $\ln[k_{\infty}(T)]$ functions up to fourth order is required with respect to $(k_{\infty})^{-1}$. The computation of the derivatives was done applying symbolic derivatives using MATLAB.\(^{52}\)

The reconstructed $k(E)$ is presented in Figure 1 in a logarithmic scale versus energy. The striking difference between the ILT of the linear (A and B) and nonlinear models (C and D) is immediately noticed. Arrhenius, modified Arrhenius, and reduced van’t Hoff equations provide systematic underestimation below the activation barrier. A breakdown of the numerical procedure above the activation energy barrier for the van’t Hoff equation appears in all cases (1–10) due to nonphysical asymptotic behavior at high temperatures (see Figures S10–S19 in the Supporting Information).

In contrast to the linear models, the $k(E)$ reconstructed from nonlinear models are in better agreement with the reference RRKM data. First, a significantly improved description of $k(E)$ is achieved below the adiabatic activation energy. Second, all nonlinear equations have proved stable when applying the numerical inversion procedure except the exothermic equation. For this equation (eq 19), the $C$ parameter was enforced to be positive under the natural logarithm to achieve numerical stability. Finally, a systematic decrease of the RMSD for $\ln[k(E)]$ was found in the s-, d-, e-, d-e-Arrhenius, exothermic, and endothermic equations (see the Supporting Information, Table S5). On the basis of this, it appears that a decrease in the raw $k_{\infty}(T)$ data fitting RMSD improves the reconstructed $k(E)$ (see Figure 2). Switching from the s-Arrhenius equation to the e-Arrhenius equation reduces the RMSD for $\ln[k(E)]$ up to 7 orders of magnitude. Subsequently, employing the e-Arrhenius and d-e-Arrhenius equations further decreases RMSD for $\ln[k(E)]$ for 1 order, providing more accurate reconstruction of the RRKM $k(E)$ data for reactions considered here. A further decrease of RMSD can be achieved by applying exothermic and endothermic fitting formulas but only for 5 out of 10 reactions. However, even this improvement does not lead to better $k(T,p)$ after ME simulations from computed $k(E)$ (see below).

The next important point is the temperature interval and the number of points for the initial model fitting. So far, all results were obtained from data in the temperature range 300–2000 K with 10 K steps, i.e., 171 equidistant data points were used for the fitting. In many cases, it might be problematic to get sufficient data points, especially in the low-temperature region. Thus, we consider scenarios for 1 where the data points are sparse (50 K step) and cover the whole region 300–2000 K, low-temperature region 300–700 K, intermediate region 700–1200 K, and high-temperature region 1200–2000 K. The sparsity of the initial data does not influence the final $k(E)$ (see Figure S20 in the Supporting Information). However, narrow data ranges decrease the completeness of $k(E)$ reconstruction. Moving from low- to high-temperature ranges, the information on $k(E)$ at low $E$ systematically disappears. Also, at the low-temperature region underestimation of the reference $k(E)$ can be noticed. Thus, the completeness of $k(E)$ reconstruction highly depends on the input $k_{\infty}(T)$ and ideally requires the temperature range as large as possible.

As we have shown above, the application of nonlinear models for fitting raw $k_{\infty}(T)$ data brings a dramatic improvement of $k(E)$ obtained with the ILT. Thus, the application of such nonlinear models is highly advisable for fitting the raw $k_{\infty}(T)$ data. The majority of $k_{\infty}(T)$ data available in the literature, however, has been originally fitted via the modified Arrhenius equation and going back to the raw $k_{\infty}(T)$ data is often not easy, if possible at all. Therefore, it is desirable to avoid using the raw $k_{\infty}(T)$ data and instead to refit the rate constants available in the modified Arrhenius format using nonlinear models. This makes out of initially loose input data a much better source for the ILT approach. To this end, we consider the nonlinear models (Eqs. 15–20) for refitting $[k_{\infty}(T)]$ data provided in the modified Arrhenius equation format. The refitted nonlinear models were then used as input for ILT to obtain $k(E)$. The results for 1 are presented in Figure 3. As one can see, for s-, d-, and e-Arrhenius equations, the results of the refitting of the modified Arrhenius equation match the results obtained from the original data both at low-
and high-energy regions, whereas d-e-Arrhenius together with exo- and endothermic equations performs poorly compared with the original results. This poor performance appears to be due to the bad performance of the modified Arrhenius equation at low temperatures. The actual behavior at such conditions could not be recaptured once it is lost during the initial fitting. Despite this small drawback, refitting the modified Arrhenius equation by nonlinear models and the subsequent inversion of them provides much better \( k(E) \) recovery than direct inversion of the modified Arrhenius equation. This emphasizes that the newly proposed functional forms not only allow for better initial fitting of \( k_\infty(T) \) but are physically more meaningful when being used to reconstruct \( k(E) \) via ILT.

Finally, we considered the results of the computation of \( k(T,p) \) from reconstructed \( k(E) \) employing ME simulations. These \( k(T,p) \) were obtained from the molecular data employing RRKM/ME simulations and from the reactant’s \( Q(T) \) and \( k(E) \) employing ILT/ME simulations. The resulting \( k(T,p) \) at various temperatures for 1 is presented in Figure 4 (results for 2−10 are given in the Supporting Information, Figures S21−S29). The linear models presented by eqs 11−13 (see Figure S30 in the Supporting Information) indicate that the smallest deviation between ILT/ME and RRKM/ME can be achieved at 2000 K. This shows once again that use of eqs 15−20 for ILT/ME simulations is highly promising for predicting the pressure-dependent reactions.

To provide quantitative results for the performance of ILT/ME approach, we computed normalized average RMSDs between ILT/ME and RRKM/ME \( k(T,p) \) at 300, 500, and 2000 K.

| T and reaction type | s-A | d-A | e-A | d-e-A | exo | endo |
|---------------------|-----|-----|-----|-------|-----|-----|
| 300 K, iso, H-tr     | 73  | 43  | 36  | 2.7   | 13  | 13  |
| 500 K, iso, H-tr     | 16  | 15  | 12  | 1.3   | 8.4 | 8.2 |
| 2000 K, iso, H-tr    | 6.6 | 4.8 | 4.5 | 1.0   | 7.9 | 7.8 |
| 300 K, dec, H-abs    | 27  | 19  | 11  | 11    | 28  | 28  |
| 500 K, dec, H-abs    | 12  | 6.0 | 4.2 | 4.1   | 25  | 25  |
| 2000 K, dec, H-abs   | 4.4 | 1.1 | 1.0 | 1.0   | 27  | 27  |
| 300 K, dec, non-H-abs| 2.6 | 106 | 9.1 | 41    | 20  | 20  |
| 500 K, dec, non-H-abs| 8.2 | 55  | 5.0 | 11    | 7.4 | 7.4 |
| 2000 K, dec, non-H-abs| 2.6| 4.0 | 1.6 | 1.0   | 0.7 | 0.7 |

| T and reaction type | s-A | d-A | e-A | d-e-A | exo | endo |
|---------------------|-----|-----|-----|-------|-----|-----|
| 300 K, dec, non-H-abs| 2.6 | 4.0 | 1.6 | 1.0   | 0.7 | 0.7 |

The normalization is done to the d-e-Arrhenius equation at 2000 K for each reaction type.

Table 3. Normalized Average RMSDs between ILT/ME and RRKM/ME \( k(T,p) \) at 300, 500, and 2000 K.

Figure 3. \( k(E) \) reconstruction from the refitted modified Arrhenius equation. A vertical dashed line is the reaction energy barrier. The left side (A) contains the comparison of the s- and d-Arrhenius equations, whereas the right-hand side (B) contains the comparison of the e- and d-e-Arrhenius equations.

Figure 4. \( k(T,p) \) computed from reference RRKM/ME (points) and ILT/ME simulations (solid lines) for the 1. Black, red, blue, green, and orange points and lines correspond to simulations at 300, 400, 500, 900, and 2000 K, respectively. Top left (A), top right (B), middle left (C), middle right (D), bottom left (E), and bottom right (F) parts of the figure represent the results for the s-, d-, e-, d-e-Arrhenius, exothermic, and endothermic equations as the input data for ILT/ME simulations, respectively. Results for 2−10 are presented in the Supporting Information in Figures S21−S29.
deviation between RRKM/ME and ILT/ME results increases for all considered reaction types. The d-e-Arrhenius equation performs the best for the isomerization reactions with the proton transfer (1, 2, 5, and 6) followed by exo- and endothermic equations and e-, d-, and s-Arrhenius equations. For the decomposition reactions with the proton abstraction (3, 4, and 10), the best performance showed e- and d-e-Arrhenius equations, followed by d-, s-Arrhenius, exothermic, and endothermic equations. Finally, the decomposition reactions without proton abstraction (7–9) could be described more accurately by exothermic and endothermic equations at 2000 K, whereas at lower temperatures, e-Arrhenius provides much better results. Our results indicate that it is essential to provide a very accurate, physically motivated fitting formula for the initial \( k_\text{sp}(T) \) input data. The fitting formula should consider both quantum tunneling and the nonlinear temperature dependence of the activation energy at low temperatures. More interestingly, the models with a finite limit at \( T \to \infty \), i.e., e- and d-e-Arrhenius equations, provide the best performance compared with the physically motivated exo- and endothermic equations. Thus, we can conclude that the finite limit at \( T \to \infty \) is an additional condition for providing better physically motivated fitting formula.

## CONCLUSIONS

The present work provides a sophisticated comparison and testing of different \( k(T) \) representations as input to the ILT approach for \( k(E) \) reconstruction. This comparison reveals that the ILT approach is highly sensitive to the \( k(T) \) input data quality, which directly affects the \( k(T,p) \) predictions based on reconstructed \( k(E) \) data. It is found to be essential to provide a very accurate, physically motivated fitting formula for fitting the experimental or theoretical \( k(T) \) input data. This formula should consider both quantum tunneling and the nonlinear temperature dependence of the activation energy in the low-temperature region (\( T < 500 \) K), as well as the finite limit for \( T \to \infty \).

The endothermic and exothermic equations are designed to reproduce the correct low-temperature behavior, whereas the presently proposed e- and d-e-Arrhenius equations always have a finite limit for \( T \to \infty \). Using the e- and d-e-Arrhenius equations largely improves the quality of \( k(T) \) representation and makes ILT a robust alternative to RRKM theory for \( k(E) \) computation. With these findings, we want to encourage researchers to revisit well-established \( k(T,p) \) prediction schemes and to consider the presently proposed \( k(T) \) representations as the input for \( k(E) \) reconstruction via ILT.

The e- and d-e-Arrhenius equations can further be used to regain microcanonical information from \( k(T) \) literature data provided in the modified Arrhenius form. Although \( k(T,p) \) prediction via ILT/ME with input in the modified Arrhenius form would be practically useless, using the e- or d-e-Arrhenius equations to refit the aforementioned input data provides reliable \( k(T,p) \). Therefore, the present work is a first step toward estimating completely pressure-dependent chemical kinetic models from available high-pressure literature data.

## COMPUTATIONAL METHODS

Temperature- and pressure-dependent rate constants for the unimolecular reactions are calculated via the master equation (ME) using MESS software package version 2016.3.23.\(^5\) Also, the microcanonical rate constants are calculated employing the nonvariational single-structural harmonic-oscillator-based RRKM approximation in MESS software package. Three and two rotational degrees of freedom were included in computing the \( Q \)s for nonlinear and linear molecules, respectively. Because of the classical treatment of the rotational degrees of freedom, \( 1 - D \ k(E) \) in the master equation calculation was used without imposing \( J \) conservation. Tunneling is considered via one-dimensional Eckart potentials obtained from the deep wells and imaginary frequencies of the transition states. The energy transfer via collisions is modeled via the weak collider bath nitrogen using \( \langle \Delta E_{\text{down}} \rangle = 200 \) cm\(^{-1} \) (\( T/300 \))^\(^{0.85} \); the Lennard-Jones collision frequency was taken from Dönggen et. al.\(^{33} \) The temperature range considered in these studies was from 300 to 2000 K with a 10 K increment, whereas the pressure was considered from \( 10^{-3} \) to \( 10^{8} \) bar with a 0.2 increment in the common logarithmic scale.

The ILT/ME simulations were conducted by providing the number of states for the reactants and transition states in separate files computed from 1 to 40,000 cm\(^{-1} \) with 1 cm\(^{-1} \) steps. The MESS.2016.3.23 version of code needs to be modified at line 5045 in the file model.cc from static const double rotd_n_tol = 1. to static const double rotd_n_tol = 1.e-300 to enable the direct reading of the number of states obtained from the ILT/ME simulations. Since the computation was time consuming due to the missing libraries, we multiply the number of states of reactant and transition state to \( 10^{30} \). All values less than 1.01 after scaling were enforced to be 1.01. These changes of the input data do not change the final results.

The reading of the files with the number of states was activated with the “Core Rotid” keyword. The number of states for the reactant was computed by inverting the reactant’s partition function divided by \( \beta = 1/(k_BT) \). The number of states for the transition state was computed by inverting \( k(\beta) \cdot Q(\beta) \) and multiplying with the Planck constant expressed in the appropriate units, i.e., in cm\(^{-1} \).

The inverse Laplace transform is given by the Bromwich integral

\[
f(E) = \frac{1}{2\pi i} \int_{γ−i∞}^{γ+i∞} F(β) e^{βT} dβ
\]

where \( γ \) is a vertical contour in the complex plane chosen so that all singularities of \( F(β) \) are to the left of it. \( β \) and \( E \) are the inverse temperature and energy expressed in cm and cm\(^{-1} \), respectively. To evaluate this integral, the integrand is assumed to have a maximum at a position \( β^* \). Using the auxiliary function \( φ(β) = \ln[F(β) e^{βT}] \), the maximizer \( β^* \) is computed as a solution of \( φ'(β) = 0 \). Finally, the maximizer \( β^* \) for a fixed \( E \) is used to compute a continuous approximation of the original function \( f(E) \)

\[
f(E) ≈ \frac{e^{β^*(φ(β^*)})}{\sqrt{2πφ'(β^*)}} \left[ 1 + \frac{φ′(β^*)}{8(φ''(β^*))^2} - \frac{5(φ''(β^*))^2}{24(φ'(β^*))^4} \right]
\]

\( Q(β) \) and \( k(β) \cdot Q(β) \) functions were used to get \( ρ(E) \) and \( ρ(E) \cdot k(E) \) functions, respectively. From these functions, the target \( k(E) \) was computed.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00311.

MATLAB input files (ZIP)
Coefficients for linear and nonlinear models (XLS)
Tables with \( k_{\infty}(T) \), coefficients for the eqs 11–20, complete tables with scaled and unscaled RMSDs for test case reactions 1–10, plots of \( k(E) \) vs \( E \) and \( \ln(k_{\infty}(T)) \) vs \( T^{-1} \) for reactions 2–10, reduced \( k(T,p) \) against pressure plots (PDF)
MESS input files (ZIP)

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Notes
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