

# A Fitting Formula for Pressure and Temperature Dependence of Unimolecular Reaction Rate Constants

Peng Zhang and Chung K. Law\*

Department of Mechanical and Aerospace Engineering  
Princeton University, Princeton, New Jersey 08544, USA

## Abstract

A five-parameter fitting formula is proposed to approximate the pressure and temperature dependence of unimolecular reaction rate constants. Compared with the widely adopted fitting formula of Troe, the present formula is mathematically simpler and free of empirical constants. Eight test cases from VariFlex program package were used to examine the present formula, showing improved performance as compared to previous fitting formulas.

## Introduction

Unimolecular and the reverse recombination reactions are important components of many chemical reaction mechanisms in combustion and atmospheric chemistry [1]. At present, theoretical chemistry is capable to precisely calculate the pressure- and temperature-dependent rate constants of these reactions, provided accurate quantum mechanical parameters of the participating molecules are known. Since directly performing such calculation in large reaction systems is computationally demanding, approximate formula of high accuracy is still needed for the evaluation of unimolecular (recombination) reaction rate constants in the simulation of chemical reaction systems.

As the earliest unimolecular reaction rate expression, the Lindemann-Hinshelwood formula [1,2] can be also considered as the simplest, parameter-free fitting formula, in which the high-pressure limit rate constant  $k_\infty$  and the low-pressure limit rate constant  $k_0$  are assumed to be given Arrhenius functions of temperature; the rate constant  $k$  in the pressure fall-off region is expressed by  $k/k_\infty = P_r/(1+P_r)$  where  $P_r = k_0[M]/k_\infty$  is the reduced pressure. Since this formula usually results in large systematic deviation of the rate constants from their theoretical values in the pressure fall-off region, a number of fitting formulas with adjustable parameters have been proposed to reduce the deviation in the fitting. Among these formulas, those with a single parameter [3-9] have not been widely used because they still result in significant fitting errors. The most widely used multi-parameter fitting formula is that of Troe [7-9], which substantially improves the accuracy of the Lindemann-Hinshelwood formula by introducing a four-parameter correction term called the Lorentzian broadening factor. In an attempt to further improve the accuracy of fitting, Wang & Frenklach [10, 11] modified the broadening factor from the Lorentzian type to the Gaussian type.

However, this formula has not been widely used, ostensibly because it requires six additional parameters to fit the temperature dependence of the rate constants. Adopting an approach that is different from those of Troe and of Wang & Frenklach, Prezhdo [12] proposed a five-parameter formula, which has a simpler functional form and shows good performance for the single test case of ethane decomposition. No other reactions were tested.

The objective of the present study was to postulate and derive an alternate fitting formula that is not only more accurate than the existing ones, but it is also more facilitating in the computational simulation of large-scale reaction systems. To meet this goal, we note that, firstly, the formula should be mathematically simple and contain as few as possible the transcendental functions, such as the exponential and logarithmic functions, because their computational evaluation is very time consuming. Secondly, the formula should contain as few fitting parameters as possible, and these parameters should vary in a relatively small range so that optimal fitting can be easily achieved. Finally, the formula should always result in high fitting accuracy, validated against as many reactions as possible, and for as wide a range of temperature and pressure as possible.

In view of the above considerations, we shall propose in Section 2 a new five-parameter fitting formula and compare it with the formulas of Troe and of Prezhdo.. Eight cases from four representative pressure-dependent reactions will be used to test these fitting formulas, in Section 3.

## Fitting Formulas

Troe's fitting formula [7-9] expresses the scaled rate constant  $k/k_\infty$  as the product of the Lindemann-Hinshelwood formula and a broadening factor,  $F$ , which is used to reduce the systematic errors associated with the Lindemann-Hinshelwood formula in the pressure fall-off range:

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\* Corresponding author: cklaw@princeton.edu  
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$$\frac{k}{k_\infty} = \frac{P_r}{1+P_r} F, \quad (1)$$

$$\log F = \frac{\log F_c}{1 + \{(\log P_r + c) / [N - d(\log P_r + c)]\}^2},$$

where

$$c = -0.4 - 0.67 \log F_c, \quad (2)$$

$$N = 0.75 - 1.27 \log F_c,$$

$$d = 0.14,$$

and  $F_c$  is fitted as a function of temperature by

$$F_c = (1 - \alpha) \exp(-T/T^{***}) + \alpha \exp(-T/T^*) + \exp(-T^{**}/T). \quad (3)$$

Expression (1) is a four-parameter fitting formula with the adjustable parameters  $\alpha$ ,  $T^*$ ,  $T^{**}$  and  $T^{***}$ , and can degenerate to a single-parameter fitting formula with the only adjustable parameter  $F_c$  when the rate constants are fitted at each temperature. Previous studies have shown that (1) usually results in fitting errors of more than 10% [12] and even as much as a factor of two [10], and that the empirical constants in (2) are not likely the universal constants for all reactions [12]. Furthermore, (1) contains a large number of exponential and logarithmic functions and therefore could result in a substantial increase of the computational load if a large number of pressure-dependent reactions are involved in the calculation.

From a different approach, Prezhdo proposed his fitting formula as [12]

$$\frac{k}{k_\infty} = \frac{P_r F(P)}{1 + P_r F(P)}, \quad (4)$$

$$F(P) = \frac{1 - \tanh\{a[\log(P) - b]\}}{2},$$

where  $P$  is the pressure,  $\tanh x = (e^x - e^{-x}) / (e^x + e^{-x})$  is a hyperbolic tangent function, and  $a$  and  $b$  are fitted polynomials of temperature:

$$a = a_1 T^2 + a_2 T + a_3, \quad (5)$$

$$b = b_1 T + b_2,$$

which makes (4) to be a five-parameter fitting formula with the adjustable parameter  $a_1$ ,  $a_2$ ,  $a_3$ ,  $b_1$  and  $b_2$ . When the rate constants are fitted for each temperature, (4) degenerates to a two-parameter formula with the parameters  $a$  and  $b$ .

Compared with Troe's formula, Prezhdo's formula has a simpler functional form and does not contain any empirical constants, although the hyperbolic tangent function can be still computational demanding. Furthermore, we note that the pressure  $P$ , instead of the dimensionless reduced pressure  $P_r$ , is used as an independent variable in the correction term  $F(P)$ . As a result, the range of the fitting parameter  $b$  (or  $B$ ) varies with the unit of pressure and therefore could result in difficulty in looking for optimal fitting.

After extensive exploration based on the physical requirements of such a fitting formula, the following expression has been found to largely satisfy the criteria mentioned above,

$$\frac{k}{k_\infty} = \frac{P_r}{P_r + \exp\left[\beta\left(1 - \frac{1}{\chi(P_r)^\delta + 1}\right)\right]}. \quad (6)$$

where  $\beta$ ,  $\chi$  and  $\delta$  are positive adjustable parameters that satisfy  $\beta > 1$ ,  $\chi \leq 1$  and  $\delta < 1$ . Several importance characteristics of the fall-off curve of unimolecular reaction rates have been taken into account in (6). First, (6) properly degenerates to the low and high pressure limits, with  $k = k_0$  when  $P_r \rightarrow 0$  and  $k = k_\infty$  when  $P_r \rightarrow \infty$ .

Secondly, the parameter  $\beta$  plays a similar role of  $F_c$  in Troe's formula to adjust the rate constant at  $P_r = 1$  for different temperatures. Consequently, a second-order polynomial in the form of

$$\beta = \beta_1 T^2 + \beta_2 T + \beta_3 \quad (7)$$

can approximate well the temperature dependence of the rate constants for a large temperature range. Finally, the parameters  $\chi$  and  $\delta$  are introduced to adjust the fall-off curve whose width and curvature usually change for different reactions. Compared to Troe's and Prezhdo's formulas, (6) has a simpler functional form and better fitting performance, as demonstrated in the next section.

## Results and discussion

To test and compare the fitting formulas in the preceding section, we used the pressure-dependent reaction rate data provided in the sample test runs of VariFlex [13], a program package developed at the Argonne National Laboratory for estimating rate constants of several types of gas-phase reactions. The eight test cases used in the present study are summarized in Table 1. The data were least-square fitted using the Microsoft Excel's Solver Add-in, which is an excellent tool for optimization and equation solving.

By using Case 1, we test the performance of the fitting formulas (1), (4) and (6) at each temperature, as shown in Figures 1-3. The fitting parameters that result in the least square errors are listed in Appendix 1. The maximum relative errors for (1) and (4) are respectively about 14% and 6%, which are basically consistent with the reported fitting precision [12]. The present formula shows improved performance in that the maximum relative error is only 2% and the most fitting errors are below 1%. We note that even (6) contains three adjustable parameters while (1) and (4) contain only one and two, respectively, the high accuracy of (6) is nevertheless still quite impressive.

Table 1: Summary of test cases

Case	Reaction	Energy transfer parameter $\alpha_0$ ( $\text{cm}^{-1}$ )	Pressure (Torr)	Temperature (K)	Total number of fitting data
1	CN + NO	25	$1\sim 10^5$	102~740	42
2		100			42
3		400			42
4	CH <sub>3</sub> + OH	100	7.66~678	290~700	32
5		400			32
6		800			32
7	C <sub>3</sub> H <sub>6</sub> + H	230	2.72~25.6	720~880	69
8*	CH <sub>3</sub> + CH <sub>3</sub>	N/A	$0.1\sim 3\times 10^5$	200~2500	168

\* [14]

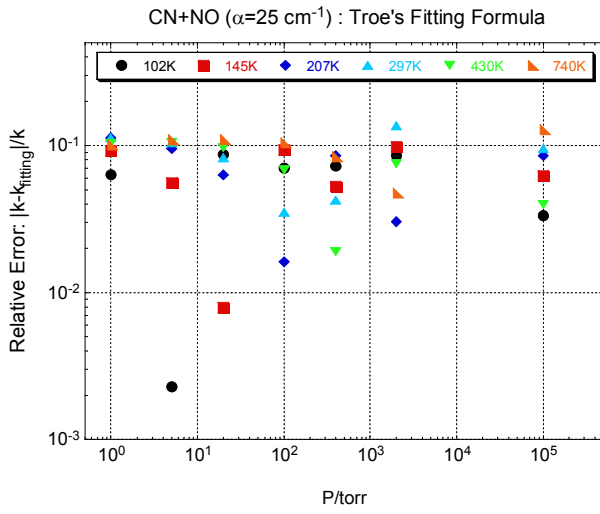


Figure 1. Relative errors for Troe's fitting formula in Case 1. The adjustable parameter  $F_c$  is fitted at each temperature.

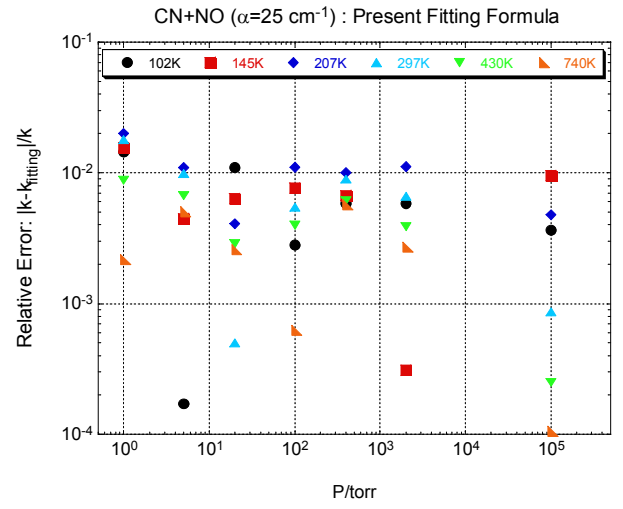


Figure 3. Relative errors for the present fitting formula in Case 1. The adjustable parameters  $\beta$ ,  $\chi$  and  $\delta$  are fitted at each temperature.

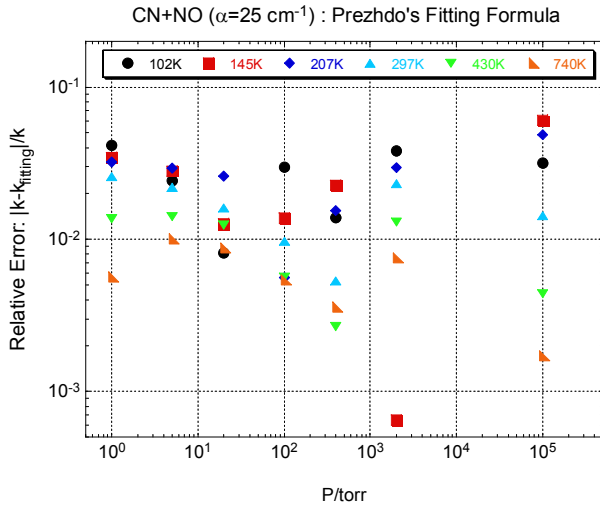


Figure 2. Relative errors for Prezhdo's fitting formula in Case 1. The adjustable parameters  $A$  and  $B$  are fitted at each temperature.

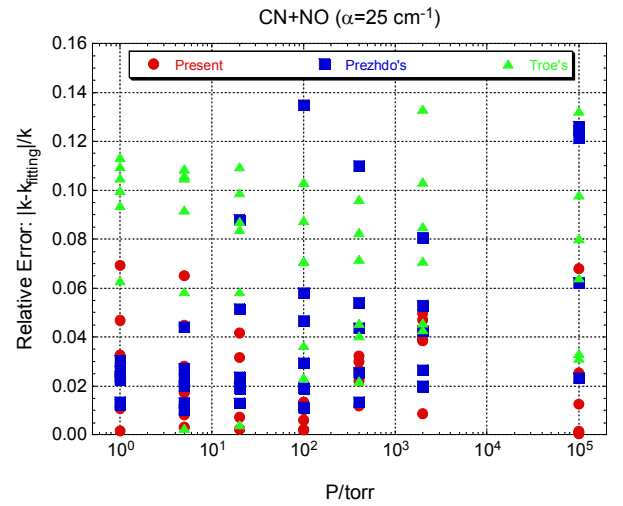


Figure 4. Relative errors for the fitting formulas (1), (4) and (6) in Case 1. The adjustable parameters are fitted as functions of temperature.

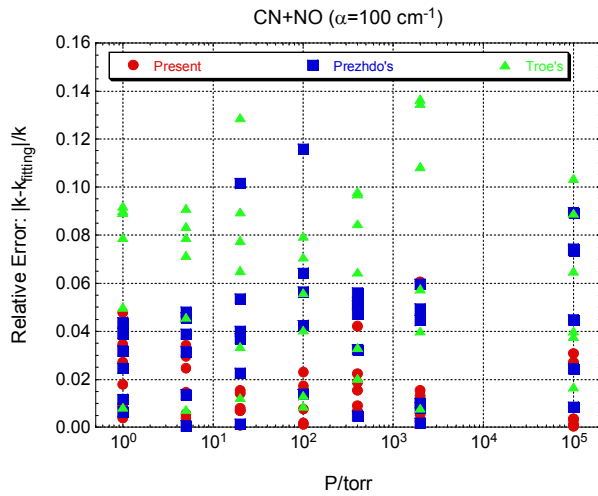


Figure 5. Relative errors for the fitting formulas (1), (4) and (6) in Case 2. The adjustable parameters are fitted as functions of temperature.

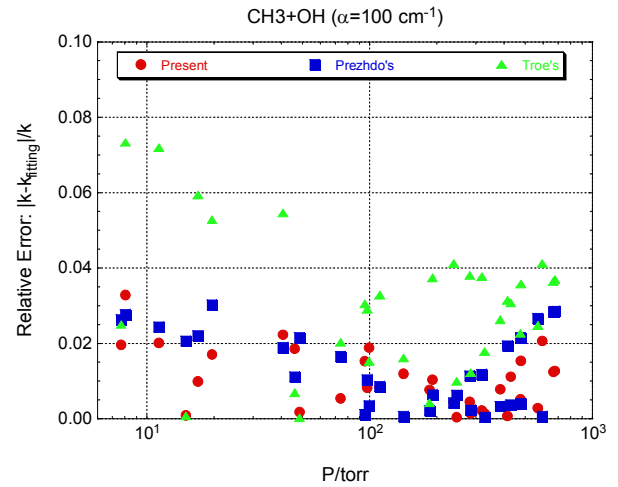


Figure 7. Relative errors for the fitting formulas (1), (4) and (6) in Case 4. The adjustable parameters are fitted as functions of temperature.

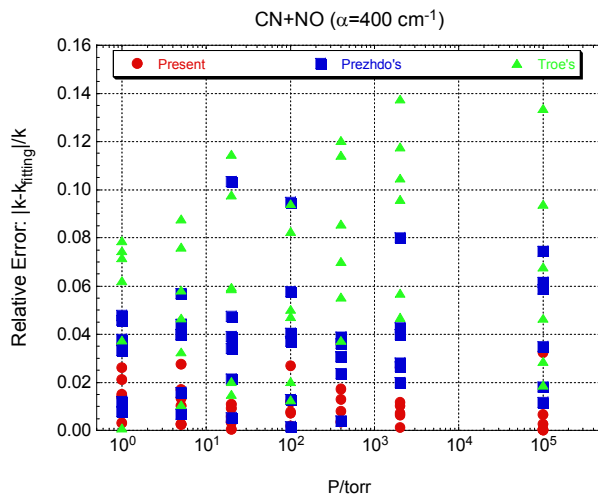


Figure 6. Relative errors for the fitting formulas (1), (4) and (6) in Case 3. The adjustable parameters are fitted as functions of temperature.

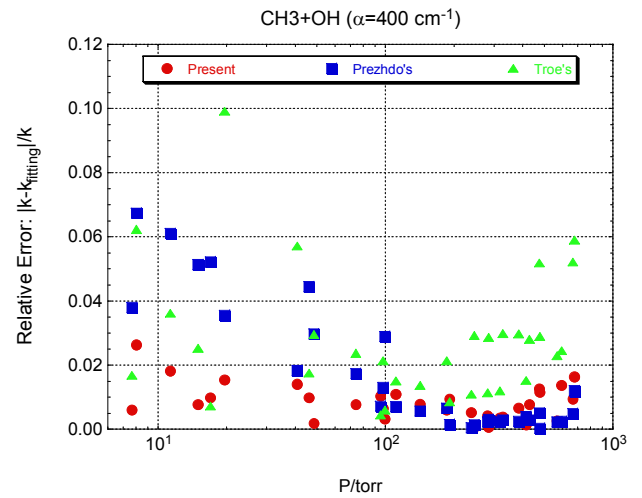


Figure 8. Relative errors for the fitting formulas (1), (4) and (6) in Case 5. The adjustable parameters are fitted as functions of temperature.

Since the fitting errors usually increase if the adjustable parameters are fitted as functions of temperature, we used Case 1 to test the performance of (1), (4) and (6) in such condition, as shown in Figure 4. The maximum relative error of (1) is found to not change much while that of (4) substantially increases to be about 13%. The present fitting formula (6) again shows better performance in that the maximum relative error is only about 7%.

For a wider range of case studies, we further tested the present fitting formula and compared it with the other two by using Cases 2-7. The fitting parameters that result

in the least square errors are listed in Appendix 2. In all six test cases, shown in Figures 5-10, (6) shows better fitting accuracy than (1) and (4), with the only exception of Case 4, for which the maximum relative error for (6) is about 3.5%, which is slightly larger than the 3% of (4). Recognizing that the temperature range in Cases 1-7 is relatively narrow and that it is very important to test the fitting formulas in a wider range of temperature and pressure, we use Case 8 [14], which was designed for such a purpose. Figure 11 shows that, while the maximum relative error of Troe's and Prezhdo's formulas can be as high as about 20%, it is only about 11% for the present formula.

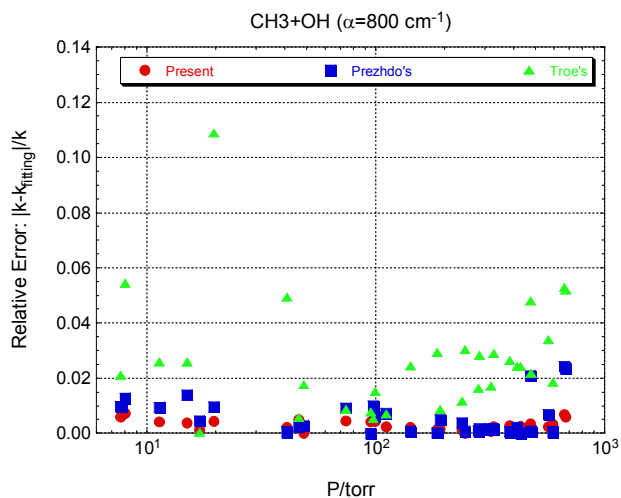


Figure 9. Relative errors for the fitting formulas (1), (4) and (6) in Case 6. The adjustable parameters are fitted as functions of temperature.

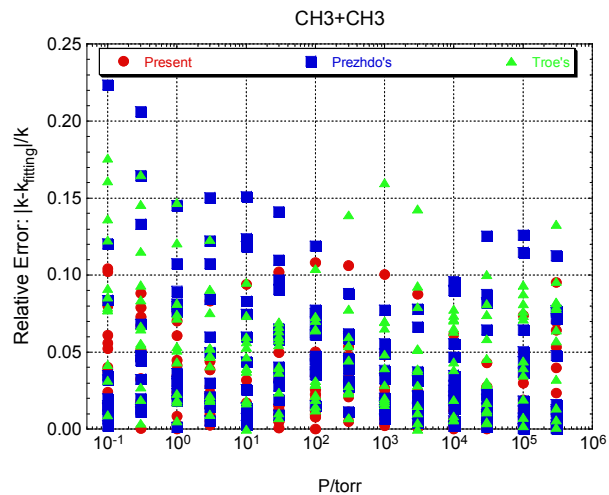


Figure 11. Relative errors for the fitting formulas (1), (4) and (6) in Case 8. The adjustable parameters are fitted as functions of temperature.

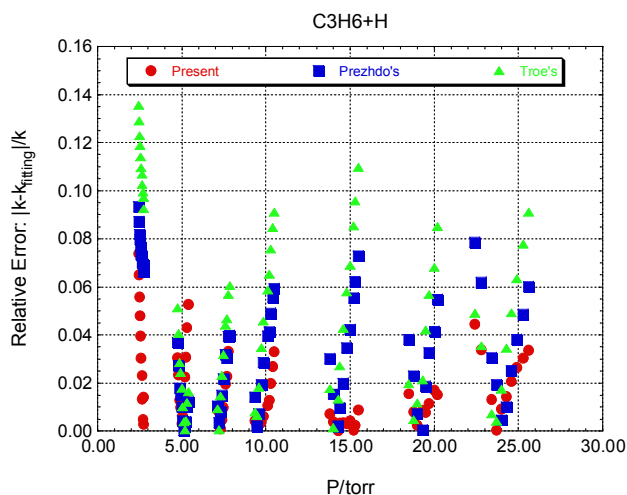


Figure 10. Relative errors for the fitting formulas (1), (4) and (6) in Case 7. The adjustable parameters are fitted as functions of temperature.

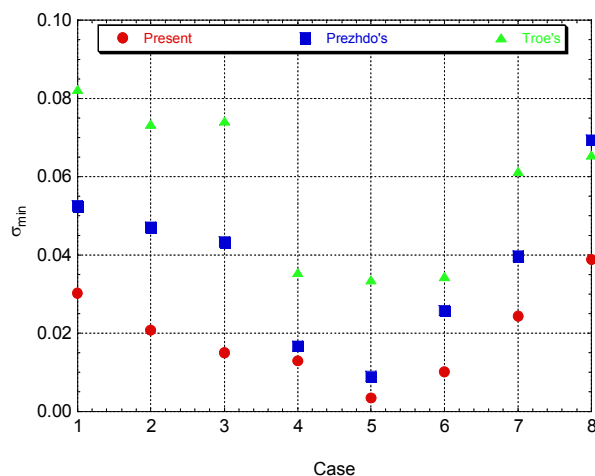


Figure 12. Comparison of the least-square errors of the fitting formulas (1), (4) and (6) in Cases 1-8.

We further recognize that the maximum relative error is not the best measure for the quality of a fitting formula, which can be directly measured by the least square error. Consequently, in order to compare different cases, we defined an average least square error by

$$\sigma_{\min} = \sqrt{\min \left\{ \frac{1}{n} \sum_{i=1}^n \left( \frac{k_i - k_{i,fitting}}{k_i} \right)^2 \right\}}, \quad (8)$$

where  $n$  is the total number of fitting data,  $k_i$  and  $k_{i,fitting}$  are respectively the  $i$ th theoretical and fitting rate

constant. The average least-square errors of the three formulas for Cases 1-8 are shown in Figure 12. The comparison again shows that the present fitting formula produces much better fitting accuracy for all cases, even for the Case 4, in which it has a slightly larger maximum relative error than that of Prezhdo's formula. We also note that while Prezhdo's formula is able to substantially improve Troe's formula in most cases, it usually needs much effort to find the optimal fitting parameters by trial and error.

### Concluding Remarks

A new five-parameter fitting formula for the pressure- and temperature-dependence of unimolecular reaction

rate constants was proposed and tested in the present study. Compared to Troe's and Prezhdo's fitting formulas, the present one shows much improvement of fitting precision in all test cases. Since the present formula has a mathematically simpler form, it is believed to be of higher computational efficiency, which is important for large-scale computation of combustion chemistry. In view of the promising fitting accuracy demonstrated herein, more testing for other reactions and wider parametric ranges is merited.

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Appendix 1. Fitting parameters for Case 1.

T(K)	Troe's	Prezhdo's		Present		
	$F_c$	$A$	$B$	$\beta$	$\chi$	$\delta$
102	0.55108	0.45207	0.44998	1.92194	0.95129	0.54884
145	0.49448	0.45411	0.27261	2.14717	0.98759	0.52022
207	0.44217	0.43880	0.17351	2.59890	0.86974	0.47678
297	0.42004	0.43360	0.11325	2.51646	1.14177	0.47265
430	0.39926	0.42613	0.07350	2.12521	1.81667	0.47089
740	0.35564	0.39889	0.04728	1.30741	4.73918	0.46900

Appendix 2. Fitting parameters for Cases 1-8.

Troe's fitting formula				
Case	$\alpha$	$T^*$	$T^{**}$	$T^{***}$
1	0.456	3034.444	12360.880	64.036
2	0.519	3584.414	12360.780	67.727
3	0.565	6700.771	12360.370	51.240
4	0.410	642.758	2634.838	1.000
5	0.602	558.565	1755.333	1.000
6	0.479	728.824	2524.479	69.180
7	1.000	1108.672	15416.300	1.000
8	0.316	2482.303	6371.283	107.638

Prezhdo's fitting formula					
Case	$a_1$	$a_2$	$a_3$	$b_1$	$b_2$
1	-5.48E-07	1.74E-04	0.49429	0.005378	1.60978
2	0.00E+00	2.55E-05	0.47448	0.003859	1.57452
3	0.00E+00	-2.09E-05	0.48372	0.003489	1.49804
4	6.19E-07	-7.70E-04	0.67719	0.002964	-1.70664
5	0.00E+00	7.97E-05	0.42633	0.003689	-2.52882
6	1.11E-07	3.60E-10	0.42633	0.003689	-2.52882
7	-5.85E-07	-1.50E-04	1.32123	0.002085	-0.69072
8	4.84E-04	-1.94E-02	0.59546	0.219254	-2.72916

Case	Present fitting formula				
	$\beta_1$	$\beta_2$	$\beta_3$	$\chi$	$\delta$
1	-0.03176	0.60129	1.72780	0.66615	0.42303
2	-0.02775	0.42570	1.42985	0.76406	0.45391
3	-0.00979	0.16859	1.45326	0.94959	0.49885
4	0.00120	0.39955	6.06391	0.36907	0.22915
5	-0.03756	0.54788	3.56996	0.53045	0.28405
6	-0.00906	0.36277	4.71560	0.45089	0.25463
7	0.00000	0.78381	-3.85256	1.00000	0.77252
8	-0.00680	0.25553	5.22494	0.41186	0.24051

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