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Computational Study of the Reactions of H Atoms with Chlorinated Alkanes. Isodesmic Reactions for Transition States

Vadim D. Knyazev

Research Center for Chemical Kinetics, Department of Chemistry, The Catholic University of America, Washington, D.C. 20064, and National Institute of Standards and Technology, Physical and Chemical Properties Division, Gaithersburg, Maryland 20899

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Reactions of H atoms with methane, ethane, and chlorinated methanes and ethanes were studied by computational methods. An approach to estimating reaction rate constants based on the use of isodesmic reactions for transition states was developed and implemented. Reactions of H atoms with CH_4 and CCl_4 (clear cases of H and Cl abstraction, respectively) were used as reference reactions. Rate constants of all other reactions from the series were calculated using the isodesmic reactions approach. For the seven reactions for which directly obtained experimental data are available, the resultant calculated temperature dependences of the rate constants demonstrate agreement with experiment. Average deviations between calculations and experiment are 17−24%, depending on the quantum chemical method used, although channel-specific rates show larger divergence. Rate constants of all 30 reaction members of the H + chloromethane and H + chloroethane classes are calculated as functions of temperature using the described approach. Individual channels of H and Cl abstraction and the corresponding reverse reactions are quantitatively characterized. In a separate part of the investigation, it is demonstrated that correlations between the energy barriers and reaction enthalpies do not provide a good predictive tool for evaluating temperature dependences of the reaction rate constants of the H + chloroalkanes class.

I. Introduction

Use of incineration as a method of disposal of hazardous industrial wastes, including chlorinated hydrocarbons (CHCs), has stimulated the research directed at mechanistic and kinetic modeling of chlorinated hydrocarbon combustion. Fundamental knowledge of mechanisms, specific pathways, and rate constants of important elementary reactions is of key importance to the success of such modeling. Among the most important and sensitive reactions involved in the currently used mechanisms of CHC combustion are the reactions of H and Cl atoms with the main compounds that are being burned.[1−9] In CHC/O_2 and CHC/hydrocarbon/O_2 flames, reactions of Cl and H atoms with CHCs together with unimolecular decomposition are the major channels of consumption of CHCs.[1−5,7−14] The results of numerical kinetic simulations demonstrate that the rates of CHC destruction and concentrations of active species are highly sensitive to the rates of H + CHC and Cl + CHC reactions.

In two recent articles,[15,16] we reported our direct experimental studies of the reactions of H atoms with methane, four chlorinated methanes, ethane, and three chlorinated ethanes. Although the rate constants of these nine reactions were obtained experimentally over wide temperature ranges, the temperature range of practical interest (extending to the temperatures of combustion, i.e., up to 2000−2500 K) is much larger. Accurate extrapolation of rate constants to higher temperatures requires application of theory and modeling. Such modeling is complicated by the fact that the reactions of H atoms with partially chlorinated alkanes can proceed through the abstraction of both chlorine and hydrogen atoms; different sites of abstraction are possible for chloroalkanes larger than C_1 species. At present, experimental data are limited to the temperature dependences of the overall rate constants, which includes all abstraction channels, of both H and Cl atoms at all possible sites. Therefore, computational tools are needed to separate the experimental rate constant values into those of the individual elementary reactions and to extrapolate these values to higher temperatures. Finally, it can be noted that it is in general unrealistic to attempt to obtain rate coefficients of all the important reactions in direct experiments. Instead, extensive sets of reliable experimental data should be used as benchmarks to identify computational tools capable of predicting the desired rate constants of cognate reactions of interest. In the current work, the body of kinetic information on the reactions of H atoms with methane, ethane, and chlorinated methanes and ethanes obtained in our earlier direct experimental studies[15−17] as well as in direct experimental studies of other groups[18,19] is used to develop and validate a computational approach to the evaluation of kinetics of reactions of this type.

This article reports the results of a computational study of the kinetics of the reactions of H atoms with C_1 and C_2 chlorinated alkanes. The study has two interrelated objectives: (1) to develop computational tools suitable for accurate description of reactions of this type and to validate these tools against the existing directly obtained experimental data and (2) to use these tools to separate the existing experimental rate temperature dependences into channel-specific ones and to predict the rates of H + chloroethanes reactions for which no experimental data are available.

In our earlier experimental study of the reactions of H atoms with methane and chlorinated methanes,[15] a correlation was observed between the experimental activation energies and enthalpies of the chlorine abstraction channels of these reactions.

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This correlation motivated our use of the Marcus equation

$$E_R = {}^1/_2\Delta H_R + E^\circ\left\{1 + (\ln 2)^{-1} \ln\left[\cosh\left(\frac{\Delta H_R \ln 2}{2E^\circ}\right)\right]\right\} \quad \text{(I)}$$

for gas-phase reactions of atom transfer[20] (relating the reaction barrier E_R and the 0 K energy of reaction ΔH_R via E°, the "intrinsic barrier" for a series of reactions of similar type) to estimate the rate constants and branching fractions of the channels of abstraction of H atoms in the H + chloromethanes reactions. The resultant transition-state-theory models of these reactions demonstrated internal coherence and agreement with the experimental data.

This prior successful application of the Marcus equation (eq I) directed the initial attempt of the current work to investigate the correlation between E_R and ΔH_R and its potential predictive use in modeling. As will be demonstrated in this article, the results of quantum chemical analysis of the reaction potential energy surfaces (PES) indicate that such predictive use is, at best, limited to the case of chloromethanes and, even there, cannot be assured. Thus, a second approach was used to evaluate the transition state properties of the reactions of interest, that of the isodesmic reactions.

Isodesmic reactions, i.e., (usually) fictitious reactions that conserve the types of chemical bonds and their numbers, are often used in computational thermochemistry. Enthalpies of these reactions are usually obtained in quantum chemical calculations and it is expected that computational errors that are specific to a particular bond type will, to a large extent, cancel on both sides of the chemical equation. Despite the widespread use of the formalism of isodesmic reactions for evaluation of reaction enthalpies, it has not seen any extensive application in assessing the properties of the transition states. It is demonstrated in this article that this approach, when applied to the reactions of the H + chloroalkane class, results in very good agreement with the experimental data. Rate constants of 30 reactions of the H + chloromethane and H + chloroethane classes are calculated using the isodesmic reactions approach.

This article is organized as follows. This section is an Introduction. The computational methods and results are described in section II. Section III is a Discussion and a Summary of the method and the results is given in section IV.

II. Computational Methods and Results

In this section, first the computational efforts to assess potential correlations between the enthalpies of reactions and the reaction barriers are described. Second, the computational formalism of isodesmic reactions as applied to the study of the properties of transition states and reaction kinetics is introduced. Third, the application of this formalism to a series of reactions of H and Cl abstraction from chloroalkanes by an H atom and comparison of the results with the experimental data are presented. Finally, this formalism is used for predictive purposes for a series of reactions of the same class for which no experimental data are available.

II.1. Correlations between the Reaction Enthalpy and Energy Barrier. Several computational methods of quantum chemistry were applied to analyze the correlation between the 0 K enthalpies (energies) and energy barriers of a series of reactions of H atoms with chlorinated methanes and ethanes (abstraction of both H and Cl atoms). The following techniques were used for geometry optimization and vibrational frequency analysis: UMP2/6-31G(d,p), UMP2/6-311G(2d,2p), B3LYP/6-311G(d,p), BH&HLYP/6-311G(d,p), and QCISD/6-311+G(d,p) (ref 21 can be consulted for the description of methods). The version of the BH&HLYP functional[22,23] implemented in the Gaussian 98 program[24,25] was used. In addition to the enthalpy and energy values obtained with these methods, higher level single-point energy calculations were used with the molecular geometry optimized at two of the above methods: spin projected PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p), QCISD(T)/6-311+G(2d,2p)//UMP2/6-311G(2d,2p), and QCISD(T)/6-311+G(2d,2p)//BH&HLYP/6-311G(d,p). The choice of these higher level and the corresponding geometry optimization methods is explained in subsection II.2, where the isodesmic reactions approach is described. The Gaussian 98[24] suite of programs was used in all quantum chemical calculations.

Although some of the methods employed, especially those used for the geometry optimization, cannot be expected to yield accurate values of reaction barriers and energetics, they still can be used to confirm or refute the existence of the correlation in question. In that respect, use of a variety of computational methods helps to understand whether the potentially observed correlation is specific to a particular method or, if observed independently of the particular combination of the methods and basis set, is determined by the underlying physical principles and thus is real.

For the reactions of H atoms with methane and chlorinated methanes a correlation between the reaction barrier E_R and the 0 K energy of reaction ΔH_R was observed at all computational levels used (Figure 1). For the data obtained using the UMP2/6-31G(d,p), B3LYP/6-311+G(2d,2p), BH&HLYP/6-311G(d,p), and QCISD/6-311+G(d,p) optimized geometries and electronic energies obtained at the same levels, these E_R vs ΔH_R dependences (filled symbols) can be well reproduced with the Marcus equation (eq I), as indicated by the fitted lines in Figure 1a. It is interesting to note that inclusion of zero-point vibrational energies (ZPE) in reactants, products, and transition states worsened the conformance of the correlation to eq I for the H-abstraction channels (open symbols and lines in Figure 1a). When a larger 6-311G(2d,2p) basis set was used with the UMP2 method for the geometry optimization and energy calculation and when higher level PMP4(SDTQ)/6-311++G(3df,2p) and QCISD(T)/6-311+G(2d,2p) energies were calculated with these optimized geometries, the agreement between the resultant E_R vs ΔH_R dependences and the Marcus equation (I) worsened (Figure 1b).

When reactions of H atoms with ethane and chlorinated ethanes are included into consideration, the results demonstrate a significant deterioration of the observed E_R vs ΔH_R correlation compared to the case of the H + chloromethanes reactions (Figure 2). For the data obtained using the higher level methods (Figure 2b), the "spread" of the obtained values of E_R around the lines drawn through the data according to eq I is, on average, 3.5 kJ mol^{-1} and reaches 19 kJ mol^{-1} in its maximum.

For reactions of chlorinated hydrocarbons larger than methanes, the deterioration of the correlation between E_R and ΔH_R observed for the reactions of H atoms with ethane and chlorinated ethanes has negative implications for the potential predictive use of such correlations, in general, and of the Marcus equation (I), in particular. The resultant uncertainty in the reaction barriers is clearly outside the limits of the desired chemical accuracy. However, although the results obtained with several different quantum chemical methods yield similar results, a slight possibility that the observed scatter of the barrier values is caused by an artifact of the computational approach cannot be ruled out completely. Another factor that makes a practical

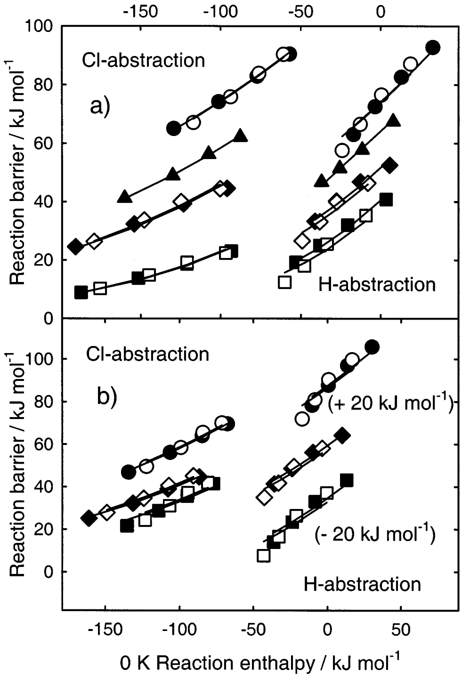

Figure 1. Correlation between the 0 K reaction enthalpies and energy barriers for the reactions of H and Cl abstraction by an H atom from methane and chlorinated methanes. Different series of data correspond to different computational methods. In each series, different points correspond to different members of the CH$_x$Cl$_{4-x}$ class. Filled symbols display values of electronic energy only, and open symbols show energies with ZPE included. Lines are fits with formula I (Marcus equation). (a) UMP2/6-31G(d,p) (circles); B3LYP/6-311+G(2d,2p) (squares); QCISD/6-311+G(d,p) (triangles); BH&HLYP/6-311G(d,p) (diamonds). (b) UMP2/6-311G(2d,2p) (circles); PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) (squares); QCISD(T)/6-311+G(2d,2p)//UMP2/6-311G(2d,2p) (diamonds). The QCISD(T)/6-311+G(2d,2p)//BH&HLYP/6-311G(d,p) E_R vs ΔH_R dependences are similar to those obtained at the QCISD(T)/6-311+G(2d,2p)//UMP2/6-311G(2d,2p) level and thus are not displayed to avoid plot congestion.

predictive use of a Marcus-type correlation problematic is the deficiency of the database of thermochemical data on chlorinated radicals. Although the heats of formation of chlorinated methyl radicals are established,[26] data on chlorinated ethyl radicals are far from being complete, and almost no data exist on larger chlorinated alkyl radicals.

II.2. Use of Isodesmic Reactions To Predict Properties of Reaction Transition States. *Approach.* Isodesmic reactions conserve the types of chemical bonds and their numbers. When energy changes (0 K enthalpies) of these reactions are obtained in quantum chemical calculations, it can be expected that computational errors specific to a particular bond type will, to a large extent, cancel on both sides of the chemical equation. Thus, enthalpies of a series of related chemical species can be evaluated on the basis of the known thermochemistry of one of these species and the enthalpies of appropriately chosen isodesmic reactions obtained in quantum chemical calculations. The same approach can be applied to the transition states (PES saddle points) of a series of cognate reactions. Barriers of a series of such reactions can be evaluated on the basis of quantum chemical calculations and the known barrier of one of these reactions. A necessary requirement for the success of such an approach is the availability of accurate knowledge of the barrier of the reference reaction belonging to the series in question. Of course, any such knowledge is always obtained through a prism of theory used to relate the barrier height to the physically measurable parameters, such as the temperature dependence of a rate constant. It can be expected, however, that when a barrier height value for a reference reaction is obtained from fitting parameters of a theory-based model to reproduce the experimental $k(T)$ dependence, the potential errors due to the imperfections of the theory will also cancel, at least partially, when the same theory is used to compute reaction rate constants using the barrier heights derived from isodesmic reactions.

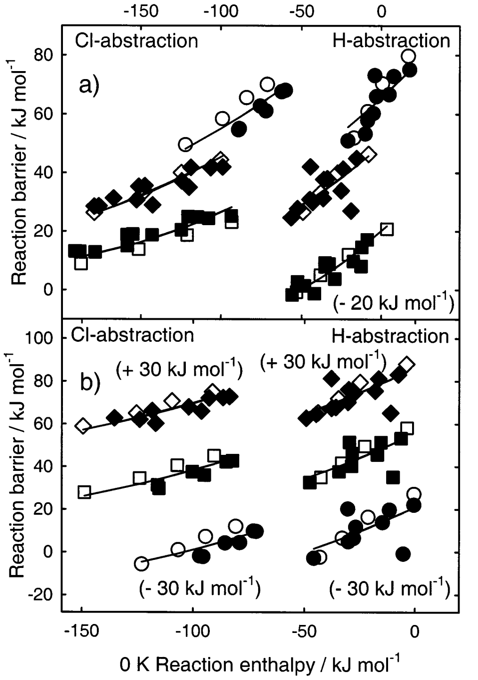

Figure 2. Correlation between the 0 K reaction enthalpies and energy barriers (ZPE included unless specified otherwise) for the reactions of H and Cl abstraction by an H atom from chlorinated and unchlorinated C$_1$ and C$_2$ alkanes. Different series of data correspond to different computational methods. In each series, different points correspond to different members of the C$_n$H$_x$Cl$_y$ class. Filled symbols display data for substituted ethanes, and open symbols, data for substituted methanes. Lines are fits with formula I (Marcus equation). Some of the data series are shifted upward or downward by 20 or 30 kJ mol^{-1} to avoid plot congestion, as indicated on the graph. (a) UMP2/6-311G(2d,2p) (circles); B3LYP/6-311G(d,p) (squares, ZPE not included); BH&HLYP/6-311G(d,p) (diamonds). (b) PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) (circles); QCISD(T)/6-311+G(2d,2p)//UMP2/6-311G(2d,2p) (squares); QCISD(T)/6-311+G(2d,2p)//BH&HLYP/6-311G(d,p) (diamonds). The scatter of the data around the fitted lines demonstrates the deterioration of the correlation when C$_2$ species are included.

Experimental Database and Isodesmic Reactions Used. For the reactions of H atoms with alkanes and chlorinated alkanes, the reactions of H atoms with methane and tetrachloromethane

$$H + CH_4 \rightarrow H_2 + CH_3 \qquad (1)$$

$$H + CCl_4 \rightarrow HCl + CCl_3 \qquad (2)$$

provide suitable choices of the reference reactions for the series of H abstraction and Cl abstraction reactions, respectively. Reaction 1, as well as the reverse reaction of the methyl radical with H$_2$, have been studied by many groups using a variety of experimental techniques. Reviews are available in refs 17, 18, and 27−29 and references therein. Approximate agreement has been reached between the results of different groups. However, in many of these studies, either indirect experimental methods were used or reaction 1 (or −1) was not completely isolated from the influence of other reactive processes. In three recent experimental studies, the kinetics of reactions 1[15,18] and −1[17] were studied by sensitive direct techniques (discharge flow/resonance fluorescence,[15] laser photolysis/shock tube/atomic resonance absorption spectrometry,[18] and laser photolysis/photoionization mass spectrometry[17]), where no other reactions influenced the kinetics of reactions 1 and −1. The results of refs 15, 17, 18 are in agreement. The combined temperature interval of these three studies covers the 646−1696 K range. Reaction 2 was recently studied by Bryukov et al.[15] using the highly sensitive discharge flow/resonance fluorescence technique. The rate constants were obtained in direct experiments as a function of temperature in the 297−904 K range.

The results of our recent direct experimental studies[15,16] of the reactions

$$\mathrm{H + CH_3Cl \rightarrow products} \qquad (586{-}839\ \mathrm{K}) \tag{3}$$

$$\mathrm{H + CH_2Cl_2 \rightarrow products} \qquad (498{-}787\ \mathrm{K}) \tag{4}$$

$$\mathrm{H + CHCl_3 \rightarrow products} \qquad (455{-}854\ \mathrm{K}) \tag{5}$$

$$\mathrm{H + C_2H_6 \rightarrow H_2 + C_2H_5} \qquad (467{-}826\ \mathrm{K}) \tag{6}$$

$$\mathrm{H + C_2H_5Cl \rightarrow products} \qquad (483{-}826\ \mathrm{K}) \tag{7}$$

$$\mathrm{H + 1{,}2\text{-}C_2H_4Cl_2 \rightarrow products} \qquad (483{-}826\ \mathrm{K}) \tag{8}$$

$$\mathrm{H + CH_3CCl_3 \rightarrow products} \qquad (358{-}850\ \mathrm{K}) \tag{9}$$

(temperature ranges are indicated in parentheses) and those of the investigation of reaction 6 by Jones et al.[19] (discharge flow/mass spectrometry technique, 385−544 K) provide the experimental *k*(*T*) dependences for reactions 3−9 with which the calculated results are compared for the purpose of validation of the computational approach. The results of an earlier study of reaction 3 by Westenberg and deHaas[30] are in agreement with those of ref 15 and thus are not used as a separate set of data.

In the current computational work, reactions 1 and 2 are used as reference, i.e., the properties of the corresponding transition states are derived from the experimental temperature dependences of the rate constants of these reactions. Then, isodesmic reactions of the types

$$\mathrm{H{\cdots}H{\cdots}R + CH_4 = H{\cdots}H{\cdots}CH_3 + RH} \tag{10}$$

$$\mathrm{H{\cdots}Cl{\cdots}R + CCl_4 = H{\cdots}Cl{\cdots}CCl_3 + RCl} \tag{11}$$

are used to evaluate the properties of the H···H···R and H···Cl···R transition states.

Quantum Chemical Methods Used. In the quantum chemical calculations, two methods are used for the optimization of the geometrical structures of the involved species. One is the UMP2/6-311G(2d,2p) method, which is rather demanding in terms of required computer resources when applied to molecules containing many chlorine atoms. Thus, a less computationally expensive BH&HLYP/6-311G(d,p) density functional method[22,23] (a version implemented in the Gaussian 98 program[24,25]) was also used. The choice of the BH&HLYP functional was based on the reported positive results of using this method for studies of the properties of transition states (see, for example, refs 31−36).

TABLE 1: Parameters of the Transition State Theory Models of Reference Reactions 1 and 2

reaction	QC method[a]	E_0/kJ mol^{-1} [b]	$F_{\mathrm{A,H}}$[c]	$F_{\mathrm{A,Cl}}$[c]
$\mathrm{H + CH_4 \rightarrow H_2 + CH_3}$	UMP2/6-311G(2d,2p)	50.65	0.49	
	BH&HLYP/6-311G(d,p)	50.84	0.52	
$\mathrm{H + CCl_4 \rightarrow HCl + CCl_3}$	UMP2/6-311G(2d,2p)	24.48		0.66
	BH&HLYP/6-311G(d,p)	22.76		0.44

[a] Quantum chemical method used for the geometry optimization and the calculation of vibrational frequencies. [b] Adjusted reaction energy barrier obtained in the fitting of the experimental data. [c] Preexponential correction factors for the H- and the Cl-abstraction channels ($F_{\mathrm{A,H}}$ and $F_{\mathrm{A,Cl}}$, respectively) applied to the calculated rate constants (at all temperatures) to achieve agreement with experiment.

With the UMP2/6-311G(2d,2p)-optimized geometries, energy values were calculated using two methods. One is the spin-projected[37] PMP4(SDTQ) method with the 6-311++G(3df,2p) basis set. This PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) combination (including the UMP2/6-311G(2d,2p) vibrational frequencies) was recently demonstrated by Louis et al.[38−40] to result in good agreement with experimental data for a series of reactions of abstraction of a hydrogen atom from halogenated hydrocarbons by an OH radical. In the second approach, the QCISD(T)/6-311++G(3df,2p) energy estimated via the formula

$$E[\mathrm{QCISD(T)/large}] \cong E[\mathrm{QCISD(T)/small}] + E[\mathrm{PMP2/large}] - E[\mathrm{PMP2/small}] \tag{II}$$

was used instead of the PMP4 values. Here, “large” and “small” represent the larger (6-311++G(3df,2p)) and the smaller (6-311+G(2d,2p)) basis sets, respectively. With the BH&HLYP/6-311G(d,p)-optimized geometries, two higher level single-point methods of energy calculation were used. In the first one, the QCISD(T)/6-311++G(3df,2pd) energies were estimated via formula II (using the same 6-311+G(2d,2p) “small” basis set). In the second single-point method, the lower level PMP2/6-311++G(3df,2pd) energies were used.

Calculation of the Rate Constants. Rate constant values were calculated using the classical transition state theory formula (see, for example, ref 41). Quantum tunneling correction was computed using the “barrier width” method.[15−17,42] The shape of the reaction potential enegy barrier was determined using the method of the reaction path following (intrinsic reaction coordinate, IRC)[43,44] in mass-weighted internal coordinates. The resultant barrier potential energy profiles were fitted with the unsymmetrical Eckart function[45] to determine the “width” parameter *l* that was used in the calculation of the tunneling correction. Details of the computational approach can be found in refs 15 and 16.

In the modeling process, first the rate constants of the two reference reactions 1 and 2 ($\mathrm{H + CH_4}$ and $\mathrm{H + CCl_4}$) were calculated using the known experimental reaction enthalpies and calculated geometries, barrier widths, and vibrational frequencies for all involved species. For each reference reaction, two parameters were adjusted to achieve agreement with the experimental data: a uniform correction factor F_{A} applied to the calculated rate constants and the reaction energy barrier, E_0. The value of F_{A} ($F_{\mathrm{A,H}}$ for H-abstraction and $F_{\mathrm{A,Cl}}$ for Cl-abstraction) has the meaning of the ratio of experimental-to-calculated preexponential, or “entropic” factors for reaction 1. The experimental data sets used in the fitting are composed from the results of refs 15, 17, and 18 for the $\mathrm{H + CH_4}$ reaction and from the results of our experimental study[15] for the $\mathrm{H + CCl_4}$ reaction, as described above.

Second, the energy barriers for the H abstraction and the Cl abstraction channels of reactions 3−9 were calculated from the values of E_0 of reactions 1 and 2 and the 0 K enthalpies of isodesmic reactions of the types 10 and 11 obtained using the

TABLE 2: Values of 0 K Enthalpies ($\Delta H°_0$) of the Isodesmic Reactions of the Types (10) and (11) Used To Evaluate the Energy Barrier Heights of the Individual Reaction Channels of Abstraction of H and Cl Atoms

transition state[a]	PMP4//UMP2[b]	QCISD(T)//UMP2[c]	QCISD(T)//BH&HLYP[d]	PMP2//BH&HLYP[e]
H-Abstraction Channels. $\Delta H°_0(H\cdots H\cdots R+CH_4=H\cdots H\cdots CH_3+RH)$/kJ mol^{-1}				
Individual Channels of Reactions 3−9				
$H\cdots H\cdots CH_2Cl$	10.74	10.64	10.47	11.91
$H\cdots H\cdots CHCl_2$	20.56	19.96	19.30	22.20
$H\cdots H\cdots CCl_3$	29.51	28.11	27.11	31.32
$H\cdots H\cdots C_2H_5$	13.31	13.10	13.01	13.72
$H\cdots H\cdots CH_2CH_2Cl$	7.41	7.18	7.18	7.76
$H\cdots H\cdots CHClCH_3$	20.66	20.19	19.93	22.19
$H\cdots H\cdots CHClCH_2Cl$	15.41	14.77	14.48	17.15
$H\cdots H\cdots CH_2CCl_3$	5.07	4.43	4.56	5.44
Individual Channels of Other H + Chloroethanes Reactions				
$H\cdots H\cdots CH_2CHCl_2$	6.93	6.49	6.47	7.25
$H\cdots H\cdots CCl_2CH_3$	26.17	26.90	26.30	29.92
$H\cdots H\cdots CHClCHCl_2$	22.29	21.58	21.25	23.42
$H\cdots H\cdots CCl_2CH_2Cl$	29.99	28.86	28.18	31.49
$H\cdots H\cdots CHClCCl_3$			15.08	17.74
$H\cdots H\cdots CCl_2CHCl_2$			26.35	30.63
$H\cdots H\cdots C_2Cl_5$			23.96	28.17
Cl-Abstraction Channels. $\Delta H°_0(H\cdots Cl\cdots R+CCl_4=H\cdots Cl\cdots CCl_3+RCl)$/kJ mol^{-1}				
Individual Channels of Reactions 3−9				
$H\cdots Cl\cdots CH_3$	−17.71	−17.99	−16.00	−16.78
$H\cdots Cl\cdots CH_2Cl$	−12.93	−12.81	−11.50	−12.27
$H\cdots Cl\cdots CHCl_2$	−6.74	−6.61	−5.93	−6.35
$H\cdots Cl\cdots C_2H_5$	−15.34	−15.54	−13.86	−14.92
$H\cdots Cl\cdots CH_2CH_2Cl$	−15.53	−15.69	−14.12	−15.27
$H\cdots Cl\cdots CCl_2CH_3$	−3.52	−3.50	−3.22	−3.54
Individual Channels of Other H + Chloroethanes Reactions				
$H\cdots Cl\cdots CHClCH_3$	−9.94	−9.89	−9.78	−9.01
$H\cdots Cl\cdots CH_2CHCl_2$	−10.11	−10.16	−9.89	−8.48
$H\cdots Cl\cdots CHClCH_2Cl$	−3.83	−3.59	−4.05	−2.82
$H\cdots Cl\cdots CH_2CCl_3$			−15.05	−14.00
$H\cdots Cl\cdots CCl_2CH_2Cl$			−3.86	−4.26
$H\cdots Cl\cdots CHClCHCl_2$			−8.79	−7.95
$H\cdots Cl\cdots CHClCCl_3$				−8.77
$H\cdots Cl\cdots CCl_2CHCl_2$				−2.36
$H\cdots Cl\cdots C_2Cl_5$				−2.32

[a] The H···H···R (or H···Cl···R) transition state for which isodesmic reaction 10 (or 11) is considered. [b] The PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method. [c] The QCISD(T)/6-311++G(3df,2p)(estimated)//UMP2/6-311G(2d,2p) method where the QCISD(T)/6-311++G(3df,2p) energy is estimated via formula II. [d] The QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) method where the QCISD(T)/6-311++G(3df,2pd) energy is estimated via formula II. [e] The PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) method.

above four quantum chemical methods (zero-point vibrational energy included). Third, the rate constants of the H- and the Cl-abstraction channels were calculated using the same transition state theory based approach used for reactions 1 and 2 and multiplied by the preexponential correction factors $F_{A,H}$ and $F_{A,Cl}$ obtained for the H-abstraction and the Cl-abstraction processes from modeling reactions 1 and 2. Rates of H- and Cl-abstraction channels were added to obtain the overall rate constants of reactions 3−9.

The first step, the adjustment of the barrier heights and determination of the $F_{A,H}$ and $F_{A,Cl}$ preexponential correction factors was performed twice, using both the UMP2/6-311G(2d,2p) and the BH&HLYP/6-311G(d,p) geometries and frequencies. The second and the third steps, i.e., calculation of the energy barriers and the rate constants for reactions 3−9, were performed four times, using the four quantum chemical methods described above. The use of the unsymmetrical Eckart formula for the tunneling correction requires the knowledge of the 0 K reaction enthalpy, even though the rate constants have only minor sensitivity to this parameter. Experimental values[26,46−55] of the heats of formation of the reactants and radical products were used for those reactions for which this information is available. For those reaction channels for which the experimental thermochemical data on the radical products R is not available, isodesmic reactions of the types

$$R + CH_4 = RH + CH_3 \tag{12}$$

$$R + CH_3Cl = RCl + CH_3 \tag{13}$$

were used. Reactions of types 12 and 13 were used to evaluate the enthalpies of the H- and Cl-abstraction channels, respectively. For species with internal rotations (torsions), the partition functions of these degrees of freedom were calculated using the Pitzer−Gwinn approximation.[56] The reduced moments of inertia of internal rotations were calculated using the formulas of refs 56 and 57. Torsional barriers V_0 were estimated from the values of the associated torsional frequencies ν via the formula $(h\nu)^2 = n^2BV_0$, where B is the rotational constant and n is the number of torsional minima. Energies, frequencies, and geometries of the lowest energy torsional conformations were used for all species with internal rotational degrees of freedom. In calculations of the rate constants, a reaction path degeneracy value of 2 (due to optical isomerism in the transition states[58−60]) was used for the reaction channels $H + C_2H_5Cl \rightarrow H_2 + CHClCH_3$ and $H + CH_2ClCH_2Cl \rightarrow H_2 + CHClCH_2Cl$.

The fitted values of the energy barrier heights for the reference reactions 1 and 2 and the derived $F_{A,H}$ and $F_{A,Cl}$ factors are

TABLE 3: Energy Barrier Heights (E_0) of the Individual Reaction Channels of Abstraction of H and Cl Atoms Obtained via the Formalism of Isodesmic Reactions

transition state[a]	PMP4//UMP2[b]	QCISD(T)//UMP2[c]	QCISD(T)//BH&HLYP[d]	PMP2//BH&HLYP[e]
H-abstraction Channels. E_0/kJ mol^{-1}				
Individual Channels of Reactions 3−9				
H···H···CH_2Cl	39.91	40.01	40.37	38.92
H···H···$CHCl_2$	30.09	30.69	31.54	28.63
H···H···CCl_3	21.14	22.54	23.72	19.52
H···H···C_2H_5	37.34	37.55	37.83	37.11
H···H···CH_2CH_2Cl	43.24	43.47	43.65	43.07
H···H···$CHClCH_3$	29.99	30.46	30.90	28.64
H···H···$CHClCH_2Cl$	35.24	35.88	36.36	33.68
H···H···CH_2CCl_3	45.58	46.22	46.28	45.40
Individual Channels of Other H + Chloroethanes Reactions				
H···H···CH_2CHCl_2	43.72	44.16	44.36	43.59
H···H···CCl_2CH_3	24.48	23.75	24.54	20.92
H···H···$CHClCHCl_2$	28.36	29.07	29.58	27.42
H···H···CCl_2CH_2Cl	20.66	21.79	22.66	19.34
H···H···$CHClCCl_3$			35.76	33.10
H···H···CCl_2CHCl_2			24.48	20.21
H···H···C_2Cl_5			26.87	22.66
Cl-abstraction Channels. E_0/kJ mol^{-1}				
Individual Channels of Reactions 3−9				
H···Cl···CH_3	42.19	42.47	38.76	39.54
H···Cl···CH_2Cl	37.41	37.29	34.26	35.03
H···Cl···$CHCl_2$	31.22	31.09	28.69	29.11
H···Cl···C_2H_5	39.82	40.02	36.62	37.68
H···Cl···CH_2CH_2Cl	40.01	40.17	36.88	38.03
H···Cl···CCl_2CH_3	28.00	27.98	25.98	26.30
Individual Channels of other H + Chloroethanes Reactions				
H···Cl···$CHClCH_3$	34.42	34.37	31.77	32.54
H···Cl···CH_2CHCl_2	34.60	34.65	31.24	32.65
H···Cl···$CHClCH_2Cl$	28.31	28.07	25.58	26.81
H···Cl···CH_2CCl_3			36.76	37.81
H···Cl···CCl_2CH_2Cl			26.62	27.02
H···Cl···$CHClCHCl_2$			30.71	31.55
H···Cl···$CHClCCl_3$				31.53
H···Cl···CCl_2CHCl_2				25.12
H···Cl···C_2Cl_5				25.08

[a] The H···H···R (or H···Cl···R) transition state for the particular reaction channel considered. [b] The PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method. [c] The QCISD(T)/6-311++G(3df,2p)(estimated)//UMP2/6-311G(2d,2p) method where the QCISD(T)/6-311++G(3df,2p) energy is estimated via formula II. [d] The QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) method where the QCISD(T)/6-311++G(3df,2pd) energy is estimated via formula II. [e] The PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) method.

listed in Table 1. The values of 0 K enthalpies of the isodesmic reactions and the resultant energy barrier heights of the individual channels of reactions 3−9 are presented in Tables 2 and 3, respectively. Parameters of the modified Arrhenius expressions resulting from the calculated temperature dependences of the rate constants obtained using the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) and the QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) methods are given in Tables 4 and 5. Detailed information on the results of quantum chemical and rate calculations is presented in the Supporting Information: optimized geometrical configurations (Table 1S); energy values obtained using different computational methods (Table 2S); vibrational frequencies, moments of inertia, and barrier widths associated with individual transition states (Table 3S); 0 K reaction enthalpies of individual reaction channels (Table 4S); and parameters of the rate expressions for individual reverse reaction channels (Table 5S).

Figures 3 and 4 demonstrate the results of calculations in comparison with the experimental data. As can be seen from the plots, the agreement with the experiment is very good for all reactions and all computational methods with the exception of the PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) results for the H + $CHCl_3$ reaction (reaction 5). All four computational approaches resulted in similar values of the predicted rate constants, thus demonstrating convergence of the technique with respect to the particular computational methods used. The only exception to this agreement between the methods is reaction 5 for which the PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) method shows poorer agreement with the experiment and rate constants differing from those of the other three methods by up to a factor of 2. The average absolute deviations of the calculated rate constants of reactions 3−9 from the experimental values are 19% for the two methods that use UMP2/6-311G(2d,2p) optimized geometries and vibrational frequencies with PMP4(SDTQ)/6-311++G(3df,2p) and estimated QCISD(T)/6-311++G(3df,2pd) energies, 17% for the QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) approach, and 24% for the PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) approach.

Predictive Calculations of the Rate Constants of Other H + Chloroethane Ractions. The agreement between the experimental rate constants of reactions 3−9 and those calculated via the method based on the use of isodesmic reactions for transition states demonstrates that this method is generally applicable to reactions of the H + chloroalkane type and that, most likely, high accuracy can be expected of the calculated rate constants. Therefore, the isodesmic reactions approach was used further to calculate the $k(T)$ dependences for the remaining 16 individual

TABLE 4: Temperature Dependences ($k = AT^n \exp(-E/T)$) of the Rate Constants of Individual Channels Obtained Using the Method of Isodesmic Reactions with the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) Energies

		200−400K			400−3000 K		
reactants	products[a]	A^b	n	E^c	A^b	n	E^c
Individual Channels of Reactions 3−9							
$H + CH_4$	$H_2 + CH_3$[d]	2.22×10^{-53}	14.007	225	2.00×10^{-18}	2.362	4567
$H + CH_3Cl$	**$H_2 + CH_2Cl$**	2.17×10^{-51}	13.215	−980	8.23×10^{-19}	2.416	3198
		2.58×10^{-51}			*9.78×10^{-19}*		
	$HCl + CH_3$	5.12×10^{-47}	11.821	445	2.06×10^{-17}	1.958	4124
		6.09×10^{-47}			*2.45×10^{-17}*		
$H + CH_2Cl_2$	**$H_2 + CHCl_2$**	4.97×10^{-40}	9.359	−647	8.46×10^{-19}	2.347	2137
		5.42×10^{-40}			*9.22×10^{-19}*		
	$HCl + CH_2Cl$	7.34×10^{-43}	10.514	301	6.07×10^{-17}	1.889	3545
		8.00×10^{-43}			*6.62×10^{-17}*		
$H + CHCl_3$	$H_2 + CCl_3$	5.35×10^{-30}	5.939	−256	1.06×10^{-18}	2.218	1252
	$HCl + CHCl_2$	4.07×10^{-36}	8.334	383	1.73×10^{-16}	1.813	2865
$H + CCl_4$	$HCl + CCl_3$[d]	2.88×10^{-29}	6.128	464	5.16×10^{-16}	1.734	2163
$H + C_2H_6$	$H_2 + C_2H_5$	3.00×10^{-45}	11.356	−370	9.48×10^{-18}	2.214	3093
		2.64×10^{-45}			*8.34×10^{-18}*		
$H + C_2H_5Cl$	$H_2 + CH_2CH_2Cl$	8.15×10^{-52}	13.443	−378	3.20×10^{-18}	2.27	3840
		8.55×10^{-52}			*3.36×10^{-18}*		
	$H_2 + CHClCH_3$	2.13×10^{-39}	9.211	−455	3.06×10^{-18}	2.208	2284
		2.23×10^{-39}			*3.22×10^{-18}*		
	$HCl + C_2H_5$	1.23×10^{-43}	10.695	596	5.70×10^{-17}	1.811	3910
		1.29×10^{-43}			*5.98×10^{-17}*		
$H + CH_2ClCH_2Cl$	**$H_2 + CHClCH_2Cl$**	1.59×10^{-44}	11.003	−517	3.05×10^{-18}	2.284	2837
		2.19×10^{-44}			*4.20×10^{-18}*		
	$HCl + CH_2CH_2Cl$	1.06×10^{-44}	11.153	428	1.03×10^{-16}	1.835	3922
		1.46×10^{-44}			*1.42×10^{-16}*		
$H + CH_3CCl_3$	$H_2 + CH_2CCl_3$	2.55×10^{-50}	12.933	111	2.96×10^{-18}	2.28	4168
		3.61×10^{-50}			*4.20×10^{-18}*		
	$HCl + CCl_2CH_3$	3.57×10^{-33}	7.357	368	2.92×10^{-16}	1.747	2529
		5.05×10^{-33}			*4.13×10^{-16}*		
Individual Channels of Other H + Chloroethanes Reactions							
$H + CH_3CHCl_2$	$H_2 + CH_2CHCl_2$	1.27×10^{-50}	13.05	−162	3.91×10^{-18}	2.252	3935
	$H_2 + CCl_2CH_3$	7.60×10^{-32}	6.575	−331	1.68×10^{-18}	2.181	1453
	$HCl + CHClCH_3$	4.30×10^{-40}	9.589	276	1.11×10^{-16}	1.806	3226
$H + CH_2ClCHCl_2$	$H_2 + CHClCHCl_2$	7.87×10^{-38}	8.691	−451	2.42×10^{-18}	2.257	2115
	$H_2 + CCl_2CH_2Cl$	1.17×10^{-29}	5.881	−195	2.27×10^{-18}	2.166	1321
	$HCl + CH_2CHCl_2$	3.98×10^{-40}	9.554	391	6.23×10^{-17}	1.851	3334
	$HCl + CHClCH_2Cl$	7.82×10^{-34}	7.535	360	2.01×10^{-16}	1.765	2600

[a] Products of the dominant channel (where such can be identified) are shown in bold font. For the reactions studied experimentally, dominant channels are identified in the experimental temperature ranges. [b] Values given in italics are for the preexponential factor adjusted to agree with the experimental $k(T)$ dependence (see subsection III.3). Units are cm^3 $molecule^{-1}$ s^{-1}. [c] In the units of Kelvin. [d] Reference reactions.

channels of other reactions of the H + chloroethane class for which no experimental data are available. The general computational approach used is identical to that used for reactions 3−9. Because the large numbers of Cl atoms involved impose limitations due to the required computational resources, only two methods (out of the four used for reactions 3−9) were used. In the first method, applied only to the reaction channels involving not more than three Cl atoms, the UMP2/6-311G(2d,2p) optimized geometries and frequencies with the PMP4(SDTQ)/6-311++G(3df,2p) energies were used. In the second method, the BH&HLYP/6-311G(d,p) optimized geometries and frequencies were used with the QCISD(T)/6-311++G(3df,2pd) single-point energies estimated via formula II. For the two reaction channels involving the largest number of Cl atoms, due to the limitations of the computer resources, the lower level PMP2/6-311++G(3df,2pd) single-point energies were used instead of the QCISD(T)/6-311++G(3df,2pd) ones. Isodesmic reactions of types 12 and 13 were used to evaluate the reaction enthalpies for the reactions for which no experimental thermochemical data on the radical products are available.

The values of 0 K enthalpies of the isodesmic reactions of the types 10 and 11 and of the energy barrier heights of the individual reaction channels are presented in Tables 2 and 3, respectively. Parameters of the modified Arrhenius expressions resulting from the calculated temperature dependences of the rate constants are given in Tables 4 and 5. Detailed data are presented in the Supporting Information.

III. Discussion

III.1. Method of Isodesmic Reactions for Transition States. Although the formalism of isodesmic reactions is widely used for evaluation of reaction enthalpies and heats of formation of chemical species, it has not seen an extensive application in assessing the properties of the transition states. The approach of isodesmic reactions used in this work is equivalent to a direct comparison of the absolute values of the energy barriers for a series of cognate reactions calculated at the same level of quantum chemical theory. This equivalence can be seen by formally adding an H atom to both sides of chemical eqs 10 and 11. Then it can be seen that the 0 K enthalpy (energy) change in, for example, isodesmic reaction 10 is equal to the difference between the 0 K enthalpies of the $H + RH = H\cdots H\cdots R$ and the $H + CH_4 = H\cdots H\cdots CH_3$ formal reactions, or the difference in the energy barriers of the $H + RH \rightarrow H_2 + R$ and the $H + CH_4 \rightarrow H_2 + CH_3$ reactions. In this latter form, that of the comparison between energy barriers of similar reactions, the isodesmic reaction formalism is sometimes applied

TABLE 5: Temperature Dependences ($k = AT^n \exp(-E/T)$) of the Rate Constants of Individual Channels Obtained Using the Method of Isodesmic Reactions with the QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) Energies

		200−400K			400−3000 K		
reactants	products[a]	A^b	n	E^c	A^b	n	E^c
Individual Channels of Reactions 3−9							
$H + CH_4$	$H_2 + CH_3$[d]	1.65×10^{-54}	14.374	54	1.57×10^{-18}	2.392	4533
$H + CH_3Cl$	**$H_2 + CH_2Cl$**	1.84×10^{-51}	13.242	−914	7.68×10^{-19}	2.419	3243
	$HCl + CH_3$	1.63×10^{-34}	7.648	1763	3.69×10^{-17}	1.872	3939
$H + CH_2Cl_2$	**$H_2 + CHCl_2$**	7.75×10^{-42}	9.933	−783	5.23×10^{-19}	2.395	2216
	$HCl + CH_2Cl$	2.37×10^{-31}	6.692	1581	1.24×10^{-16}	1.796	3431
$H + CHCl_3$	$H_2 + CCl_3$	8.99×10^{-33}	6.823	-428	5.09×10^{-19}	2.293	1410
		8.01×10^{-33}			*4.53×10^{-19}*		
	$HCl + CHCl_2$	4.01×10^{-28}	5.686	1302	3.11×10^{-16}	1.737	2810
		3.57×10^{-28}			*2.77×10^{-16}*		
$H + CCl_4$	$HCl + CCl_3$[d]	1.56×10^{-24}	4.555	1049	7.48×10^{-16}	1.677	2164
$H + C_2H_6$	$H_2 + C_2H_5$	4.42×10^{-46}	11.622	-452	6.63×10^{-18}	2.257	3099
$H + C_2H_5Cl$	$H_2 + CH_2CH_2Cl$	1.29×10^{-49}	12.732	29	3.71×10^{-18}	2.25	3931
	$H_2 + CHClCH_3$	4.52×10^{-40}	9.428	-428	2.13×10^{-18}	2.246	2358
	$HCl + C_2H_5$	2.52×10^{-30}	6.261	2072	1.20×10^{-16}	1.711	3791
$H + CH_2ClCH_2Cl$	**$H_2 + CHClCH_2Cl$**	2.46×10^{-46}	11.585	-671	1.73×10^{-18}	2.348	2886
	$HCl + CH_2CH_2Cl$	1.06×10^{-32}	7.154	1741	1.82×10^{-16}	1.754	3783
$H + CH_3CCl_3$	$H_2 + CH_2CCl_3$	1.95×10^{-50}	12.979	221	2.55×10^{-18}	2.292	4243
	$HCl + CCl_2CH_3$	3.50×10^{-26}	5.052	1244	5.61×10^{-16}	1.668	2551
Individual Channels of Other H + Chloroethanes Reactions							
$H + CH_3CHCl_2$	$H_2 + CH_2CHCl_2$	4.52×10^{-50}	12.874	29	3.68×10^{-18}	2.253	4017
	$H_2 + CCl_2CH_3$	1.26×10^{-33}	7.151	−353	1.14×10^{-18}	2.217	1624
	$HCl + CHClCH_3$	2.86×10^{-40}	9.590	276	7.40×10^{-17}	1.806	3226
$H + CH_2ClCHCl_2$	$H_2 + CHClCHCl_2$	9.44×10^{-40}	9.266	−760	8.56×10^{-19}	2.368	2049
	$H_2 + CCl_2CH_2Cl$	6.40×10^{-32}	6.575	-442	8.08×10^{-19}	2.274	1343
	$HCl + CH_2CHCl_2$	1.78×10^{-31}	6.671	1251	1.08×10^{-16}	1.768	3148
	$HCl + CHClCH_2Cl$	6.87×10^{-28}	5.565	974	3.17×10^{-16}	1.704	2488
$H + CH_2ClCCl_3$	$H_2 + CHClCCl_3$	9.56×10^{-46}	11.279	-577	7.48×10^{-19}	2.357	2852
	$HCl + CH_2CCl_3$	5.00×10^{-32}	6.857	1876	8.04×10^{-17}	1.800	3791
	$HCl + CCl_2CH_2Cl$	9.22×10^{-27}	5.245	1237	4.56×10^{-16}	1.696	2600
$H+CHCl_2CHCl_2$	$H_2 + CCl_2CHCl_2$	4.63×10^{-33}	6.965	−500	1.73×10^{-19}	2.484	1285
	$HCl + CHClCHCl_2$	6.95×10^{-29}	5.988	1444	4.30×10^{-16}	1.738	3062
$H + CHCl_2CCl_3$	$H_2 + C_2Cl_5$	2.89×10^{-36}	7.982	−478	4.62×10^{-19}	2.302	1784
	$HCl + CHClCCl_3$	5.84×10^{-30}	6.252	1441	1.97×10^{-16}	1.755	3147
	$HCl + CCl_2CHCl_2$	6.38×10^{-26}	4.971	1168	4.90×10^{-16}	1.691	2430
$H + C_2Cl_6$	$HCl + C_2Cl_5$	2.52×10^{-25}	4.880	1209	1.02×10^{-15}	1.692	2434

[a] Products of the dominant channel (where such can be identified) are shown in bold font. For the reactions studied experimentally, dominant channels are identified in the experimental temperature ranges. [b] Values given in italics are for the preexponential factor adjusted to agree with the experimental $k(T)$ dependence (see subsection III.3). Units are cm^3 $molecule^{-1}$ s^{-1}. [c] In the units of Kelvin. [d] Reference reactions.

for estimation of reaction barriers, and the term "isodesmic reaction" has been applied to such calculations in at least one instance.[61] In one example, Truong proposed an approach for the rapid estimation of thermal rate constants for large numbers of similar reactions.[62] Rates of a given reaction in a class are estimated relative to those of a "principal reaction" of the same class using computed differences in the energy barriers. In this approach,[62] further simplifications include an assumption of the invariability of the tunneling imaginary frequency and the use of a constant value for the ratio of the vibrational partition functions for the reaction in question and the principal reaction within the reaction class. Nevertheless, the author is unaware of any systematic study that would evaluate the performance of isodesmic reactions for calculating the properties of transition states. One reason for the lack of such studies is the difficulty of assessing the transition state properties from the experimental point of view. Energy barriers cannot be measured directly and are only obtained from computational modeling of experimental reaction rates. As already discussed above (subsection II.2), just as the uncertainties due to imperfections of quantum chemical theory are expected to largely cancel out when isodesmic reactions are used for energy calculations, those due to the intrinsic flaws of the rate theory can also be expected to, at least partially, counterbalance each other when the same method is used for the reference reaction and the reaction being studied.

It is interesting to note that the approach used in the current work for the evaluation of the preexponential, or "entropic" factors, can also be understood as being based on determining changes of a thermodynamic function (entropy) in isodesmic reactions. If the preexponential factors are considered as being proportional to $\exp(\Delta S^{\ddagger}/R)$, where $\Delta S^{\ddagger}$ is the entropy difference between the transition state and the reactants, then applying the preexponential correction factors F_A to calculated rate constants is equivalent to determining the experimental $\Delta S^{\ddagger}$ for the reference reaction ($\Delta S^{\ddagger}$(reference,experimental) $=$ $\Delta S^{\ddagger}$(reference,calculated) $+ R \ln(F_A)$) and then obtaining the $\Delta S^{\ddagger}$ values for other reactions via calculated entropies of isodesmic reactions.

III.2. Accuracy of the Method of Isodesmic Reactions. Figures 3 and 4 demonstrate a remarkable agreement between the calculated $k(T)$ dependences of reactions 3−9 and the experimental temperature dependences. One exception is reaction 5, $H + CHCl_3$, for which the lowest level quantum chemical method out of the four used, PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p), shows poorer agreement with the experiment. The average deviations of the calculated rate constants of reactions 3−9 from the experimental values are 17−24% for the four methods used in this work. Reaction-specific average deviations range from 4% to 72%, with the maximum values obtained using the PMP2/6-311++G(3df,2pd)//

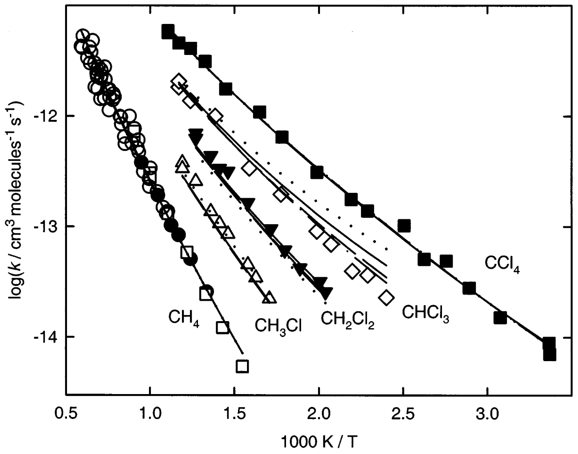

Figure 3. Results of modeling of reactions 3−5 (lines) with the method based on the use of isodesmic reactions for transition states and experimental data on the reference reactions 1 and 2, as described in the text. Symbols display experimental values of the rate constants. All experimental data are from ref 15 except for the H + CH_4 reaction, where the results of ref 18 (open circles) and ref 17 (open squares, rates of the $CH_3 + H_2$ reaction converted to the $k(H+CH_4)$ values) are also displayed. Lines represent the results of the computational modeling with different line styles corresponding to different levels of quantum chemical theory used: PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) (solid lines); QCISD(T)/6-311++G(3df,2p)(estimated)//UMP2/6-311G(2d,2p) (dashed lines); QCISD(T)/6-311++G(3df,2pd)-(estimated)//BH&HLYP/6-311G(d,p) (dashed-and-dotted lines); PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) (dotted lines). For the reference reactions 1 and 2, solid lines represent the $k(T)$ dependences resulting from the models fitted to the experimental data.

BH&HLYP/6-311G(d,p) method for reaction 5. Among the three higher level methods using the PMP4 and QCISD(T) energies, the deviations are smaller with the maximum reaction-specific average deviation of 36% obtained for reaction 5 using the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method.

Although comparison with the experimental data seems to indicate high accuracy of the computational approach, consideration of the rates of individual channels results in a less optimistic assessment of the expected accuracy of the technique. Table 6 shows the differences between the reaction barriers obtained with different quantum chemical methods used for isodesmic reaction calculations (columns with the ΔE_I heading). The differences (all relative to the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method), averaging in absolute values 1.30 kJ mol^{-1}, exceed 3 kJ mol^{-1} in some instances. An uncertainty of 3 kJ mol^{-1} in the energy barrier translates into a factor of 2 in the rate constant at 500 K. These differences in the energy barrier are reflected in the differences in the values of the H-to-Cl branching ratios for the different abstraction channels, as shown in Table 7, which lists these branching ratios for reactions 3−6 and 7−9. As can be seen from the data, the differences between the values obtained with different isodesmic reaction methods reach a factor of 2 in several cases and more than a factor of 3 in the worst case of reaction 5. Compared to these differences, the much better agreement achieved for the overall reaction rates (Figures 3 and 4), means that, for reactions 3−9, dominant reaction channels are described better. Also, for some of the reactions considered, changes from one method to another in the barrier of one channel are partially compensated by opposite changes in the barrier of the other channel. Both of these effects are, most likely, fortuitous and cannot be counted upon when these methods are used for predictive purposes.

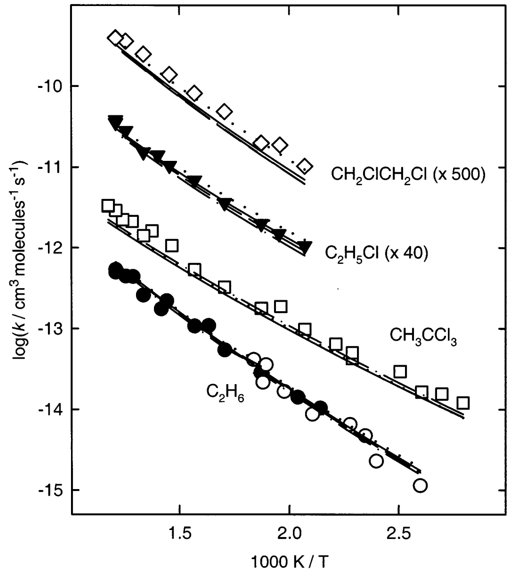

Figure 4. Results of modeling of reactions 6−9 (lines) with the method based on the use of isodesmic reactions for transition states and experimental data on the reference reactions 1 and 2, as described in the text. Symbols display experimental values of the rate constants. All experimental data are from ref 16 except for the H + C_2H_6 reaction, where the results of ref 19 (open circles) are also displayed. Lines represent the results of the computational modeling with different line styles corresponding to different levels of quantum chemical theory used: PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) (solid lines); QCISD(T)/6-311++G(3df,2p)(estimated)//UMP2/6-311G(2d,2p) (dashed lines); QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) (dashed-and-dotted lines); PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) (dotted lines). Rate constants of the reactions of H with C_2H_5Cl and CH_2ClCH_2Cl are multiplied by factors of 40 and 500, respectively, to avoid plot congestion.

Nevertheless, the approach based on the use of isodesmic reactions for the transition states results in significantly better agreement with experiment compared to what would result from a direct use of the results of quantum chemical calculations obtained at the same levels of theory. For the purpose of analysis, it is reasonable to compare such directly obtained barriers with those resulting from the isodesmic reactions approach at the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) level of quantum chemistry because this latter method yields good agreement with the experimental rate constant values. The differences between the values of E_0 obtained directly at each of the levels of quantum chemistry and the results of the isodesmic reactions approach (Table 6, columns with the ΔE_{II} headings) are large compared to the differences in the values of E_0 obtained via different isodesmic reaction-based methods, exceeding in some instances 12 kJ mol^{-1}. Even if only the three higher level methods are considered (without PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p)), the differences are still as large as 9 kJ mol^{-1}. One interesting exception worth noting is that the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) direct barrier calculations predict the barriers for the Cl atom abstraction channels remarkably well for reactions 2 and 9. (This can be meaningfully asserted because Cl abstraction is dominant for these reactions.) It should also be noted that direct use of vibrational frequencies obtained in the quantum chemical calculations results in an overestimation of the preexponential factors by approximately a factor of 2 (see Table 1, values of F_A). Thus, it can be concluded that the computational approach based on the use of isodesmic reactions for transition states provides a significantly better tool for evaluating the rate constants of the reactions of

TABLE 6: Differences between the Energy Barrier Heights (E_0) Obtained Using Different Computational Methods (with and without the Use of Isodesmic Reactions) and the Values of E_0 Obtained via Isodesmic Reactions at the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) Level

	PMP4//UMP2[b]		QCISD(T)//UMP2[c]		QCISD(T)//BH&HLYP[d]		PMP2//BH&HLYP[e]	
transition state[a]	ΔE_I[f]	ΔE_{II}[g]	ΔE_I[f]	ΔE_{II}[g]	ΔE_I[f]	ΔE_{II}[g]	ΔE_I[f]	ΔE_{II}[g]
H-Abstraction Channels								
Individual Channels of Reactions 1 and 3−9								
H···H···CH_3		*8.01*[h]		*2.41*[h]		*−0.99*[h]		*6.47*[h]
H···H···CH_2Cl	0.00	*6.51*	0.10	*8.53*	0.46	*5.66*	−0.99	*11.68*
H···H···$CHCl_2$	0.00	*6.51*	0.60	*9.03*	1.45	*6.66*	−1.45	*11.21*
H···H···CCl_3	0.00	*6.51*	1.39	*9.82*	2.58	*7.78*	−1.62	*11.04*
H···H···C_2H_5	0.00	*6.51*	0.21	*8.63*	0.49	*5.69*	−0.23	*12.44*
H···H···CH_2CH_2Cl	0.00	*6.51*	0.23	*8.65*	0.42	*5.62*	−0.16	*12.50*
H···H···$CHClCH_3$	0.00	*6.51*	0.47	*8.90*	0.92	*6.12*	-1.34	*11.32*
H···H···$CHClCH_2Cl$	0.00	*6.51*	0.64	*9.07*	1.12	*6.32*	-1.55	*11.11*
H···H···CH_2CCl_3	0.00	*6.51*	0.64	*9.06*	0.70	*5.90*	-0.18	*12.48*
Individual Channels of Other H + Chloroethanes Reactions								
H···H···CH_2CHCl_2	0.00	*6.51*	0.43	*8.86*	0.64	*5.84*	−0.14	*12.53*
H···H···CCl_2CH_3	0.00	*6.51*	−0.73	*7.69*	0.06	*5.26*	−3.56	*9.10*
H···H···$CHClCHCl_2$	0.00	*6.51*	0.70	*9.12*	1.22	*6.42*	−0.95	*11.72*
H···H···CCl_2CH_2Cl	0.00	*6.51*	1.14	*9.56*	2.00	*7.20*	−1.31	*11.35*
Cl-Abstraction Channels								
Individual Channels of Reactions 2−9								
H···Cl···CH_3	0.00	*−0.19*	0.28	*4.49*	−3.43	*1.54*	−2.65	*3.46*
H···Cl···CH_2Cl	0.00	*−0.19*	−0.12	*4.09*	−3.15	*1.82*	−2.38	*3.73*
H···Cl···$CHCl_2$	0.00	*−0.19*	−0.13	*4.08*	−2.53	*2.44*	−2.11	*3.99*
H···Cl···CCl_3		*−0.19*[h]		*4.21*[h]		*4.97*[h]		*6.11*[h]
H···Cl···C_2H_5	0.00	*−0.19*	0.20	*4.42*	−3.20	*1.77*	−2.14	*3.97*
H···Cl···CH_2CH_2Cl	0.00	*−0.19*	0.16	*4.37*	−3.13	*1.84*	−1.98	*4.13*
H···Cl···CCl_2CH_3	0.00	*−0.19*	−0.02	*4.19*	−2.02	*2.95*	−1.70	*4.40*
Individual Channels of Other H + Chloroethanes Reactions								
H···Cl···$CHClCH_3$	0.00	*−0.19*	−0.04	*4.17*	−2.65	*2.32*	−1.88	*4.23*
H···Cl···CH_2CHCl_2	0.00	*−0.19*	0.05	*4.26*	−3.36	*1.61*	−1.95	*4.16*
H···Cl···$CHClCH_2Cl$	0.00	*−0.19*	−0.24	*3.97*	−2.74	*2.23*	−1.50	*4.61*

[a] The H···H···R (or H···Cl···R) transition state for the particular reaction channel considered. [b] The PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method. [c] The QCISD(T)/6-311++G(3df,2p)(estimated)//UMP2/6-311G(2d,2p) method where the QCISD(T)/6-311++G(3df,2p) energy is estimated via formula II. [d] The QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) method where the QCISD(T)/6-311++G(3df,2pd) energy is estimated via formula II. [e] The PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) method. [f] ΔE_I is the difference between the E_0 value obtained via isodesmic reactions at two levels, the current one (see column heading) and the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) level. ZPE is included. [g] ΔE_{II} is the difference between the E_0 values obtained directly at the current (see column heading) level of quantum chemistry (not with the isodesmic reactions approach) and the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p)-level barrier resulting from the isodesmic reactions approach. ZPE is included. [h] For the reference reactions 1 and 2, the differences are given between the E_0 values obtained at the current (see column heading) level of quantum chemistry and those obtained from fitting the experimental data using geometries and vibrational frequencies obtained at the same level of theory (UMP2/6-311G(2d,2p) and BH&HLYP/6-311G(d,p)).

TABLE 7: Calculated Branching Ratios[a] of H- and Cl-Abstraction Channels of Reactions 3−5 and 7−9 at the Extremes of the Experimental Temperature Ranges

overall reaction		T/K	PMP4//UMP2[b]	QCISD(T)//UMP2[c]	QCISD(T)//BH&HLYP[d]	PMP2//BH&HLYP[e]
H + CH_3Cl	(3)	586	3.58	3.71	2.20	3.41
		839	2.63	2.70	1.89	2.58
H + CH_2Cl_2	(4)	491	4.18	3.55	2.04	2.49
		787	1.76	1.58	1.07	1.21
H + $CHCl_3$	(5)	417	3.39	2.31	1.37	4.37
		854	0.62	0.51	0.36	0.67
H + C_2H_5Cl	(7)	483	18.04 (1.10)[f]	16.99 (1.10)[f]	9.38 (0.64)[f]	20.32 (0.95)[f]
		826	5.50 (1.33)[f]	5.30 (1.32)[f]	3.65 (0.97)[f]	5.82 (1.22)[f]
H +CH_2ClCH_2Cl	(8)	483	4.47	4.03	2.40	5.76
		826	2.23	2.09	1.53	2.60
H + CH_3CCl_3	(9)	358	0.0026	0.0022	0.0017	0.0024
		850	0.054	0.049	0.042	0.049

[a] The values of the branching ratio in the table are the ratios of the rate constant of the H-abstraction to that of the Cl-abstraction channels. All rate constants are calculated using the approach of isodesmic reactions. [b] The PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method. [c] The QCISD(T)/6-311++G(3df,2p)(estimated)//UMP2/6-311G(2d,2p) method where the QCISD(T)/6-311++G(3df,2p) energy is estimated via formula II. [d] The QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) method where the QCISD(T)/6-311++G(3df,2pd) energy is estimated via formula II. [e] The PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) method. [f] Values for the abstraction of the α-hydrogen are given outside parentheses and for that of the β-hydrogen inside parentheses.

H atoms with chlorinated alkanes than the direct use of vibrational frequencies and energy barriers obtained at the same levels of quantum chemical theory.

The use of the BH&HLYP/6-311G(d,p) method for geometry optimization, as discussed above, was motivated by the desire to identify techniques that are less computationally expensive compared to those using the UMP2/6-311G(2d,2p)-level optimization but still provide comparable agreement with the experiment. The BH&HLYP/6-311G(d,p) optimized geometries differ significantly from those obtained at the UMP2/6-311G(2d,2p) level and, generally, result in "earlier" transition states. For example, the values of the H−H distance obtained for the $H\cdots H\cdots CCl_3$ transition state are 0.9135 and 0.9616 Å at the UMP2 and BH&HLYP levels, respectively. In a similar example, the H−Cl distance obtained for $H\cdots Cl\cdots CH_3$ in the UMP2 calculations is 1.5811 Å and that resulting from the BH&HLYP calculations is 1.661 Å. Despite such differences in the optimized structures, the isodesmic reaction approaches that use the QCISD(T)/6-311++G(3df,2pd)(estimated) energies with the UMP2/6-311G(2d,2p)-level and the BH&HLYP/6-311G(d,p)-level geometries result in similar agreement with experiment. The PMP2/6-311++G(3df,2pd)//BH&HLYP/6-311G(d,p) method was used in a further attempt to reduce computational costs while maintaining an acceptable level of accuracy. The agreement with the experimental data is somewhat worse for this method compared to the three higher level methods used. However, this lower level PMP2//BH&HLYP method may still be acceptable for some practical applications, considering that, when used within the framework of the isodesmic reactions approach, it gives better results than the direct use of the reaction barriers obtained from much more complicated and computationally expensive quantum chemical calculations. It is also interesting to note that the use of the even lower level PMP2/6-311+G(2d,2p) method for single-point energy computation with the BH&HLYP/6-311G(d,p)-optimized structures yielded differences in the barrier values (relative to the PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p) method) that are similar to those obtained using the PMP2 method with the larger 6-311++G(3df,2pd) basis set, with the average absolute difference of 1.60 kJ mol^{-1} and the maximum difference of 3.3 kJ mol^{-1}.

III.3. Recommendations for the Temperature Dependences of the Rate Constants of Individual Reaction Channels. Although the calculated overall rate constants of reactions 3−9 agree with the experimental data remarkably well (Figures 3 and 4), it still desirable to eliminate the observed minor disagreements so that the modeled $k(T)$ dependences can be used for practical purposes outside the experimental temperature ranges. For reactions 1, 2, and 6, there is no ambiguity in the assignment of channels. Therefore, the models created in refs 15 and 16 and fitted to reproduce the experimental $k(T)$ dependences can be used. For reactions 3−5 and 7−9, both channels of abstraction of H and Cl atoms are possible. All isodesmic reaction-based methods reproduce the activation energies of these overall reactions very well, with the exception of reaction 5 (Figures 3 and 4). Thus, better agreement with experiment can be achieved by changing the preexponential factors alone. For this purpose, the $F_{A,H}$ and the $F_{A,Cl}$ factors for reactions 3−5 and 7−9 were adjusted (for each reaction, both $F_{A,H}$ and $F_{A,Cl}$ were scaled by the same factor) to achieve agreement between the calculated and the experimental rate constants. The PMP4(SDTQ)/6-311++G(3df,2p)//UMP2/6-311G(2d,2p)-level method of isodesmic reactions was used for reactions 3, 4, and 7−9; the QCISD(T)/6-311++G(3df,2pd)(estimated)//BH&HLYP/6-311G(d,p) level was used for reaction 5. The resultant $k(T)$ dependences based on experiment and extrapolated through modeling are presented in Tables 4 and 5 (The adjusted preexponential factors are shown in italics.). It should be kept in mind when these results are used for practical purposes that the uncertainties in the rate parameters of the minor channels exceed those of the major channels; an uncertainty of ≈2−4 kJ mol^{-1} in the corresponding activation barriers can be expected, as discussed above (subsection III.2).

For the other 16 reactions of H atoms with chloroethanes considered in this work, data from Tables 4 and 5 can be used (with the reservations regarding the uncertainties expressed above). Also, the reaction models created in the current study were used to evaluate the rate constants of the reverse reactions. These data are presented in the Supporting Information. The uncertainties for the rate constants of the reverse reactions are larger because of the uncertainties in the heats of formation of the radical products. For many of the reaction channels, due to the absence of experimental data, the 0 K enthalpies were estimated here through the isodesmic reactions approach (see Table 4S in the Supporting Information).

IV. Summary of the Method and the Results

Reactions of H atoms with methane, ethane, and chlorinated methanes and ethanes were studied by computational methods. In the first part of the study, correlations between the energy barriers and reaction enthalpies were studied. Although a Marcus-type correlation was observed for the reactions of H with chlorinated methanes at relatively low levels of quantum chemical theory, use of higher levels resulted in a deterioration of the correlation. A much poorer correlation was observed for the reactions of H with chlorinated ethanes. It is concluded that such correlation does not provide a good predictive tool for evaluating temperature dependences of the reaction rate constants for the considered class of reactions, i.e., reactions of H atoms with chlorinated alkanes.

In the main part of the study, an approach to estimating reaction rate constants based on the use of isodesmic reactions for transition states is described and applied. In this approach, a reference reaction is selected for which highly accurate experimental data are available and thus the temperature dependence of the rate constant is well established. For this reaction, a transition state theory model is created on the basis of quantum chemical calculations. The model is adjusted to provide a match with the experimental data by varying two parameters: the barrier height $E_{0,REF}$ and the preexponential correction factor, F_A. Then transition state theory models of a series of cognate reactions are produced on the basis of same-level quantum chemical calculations. The energy barriers for these models are obtained from the value of $E_{0,REF}$ and the 0 K enthalpies $\Delta H_0{}^{\circ}{}_{ISO}$ of isodesmic reactions of the type

$$\mathrm{TS} + \mathrm{reactants(REF)} = \mathrm{TS(REF)} + \mathrm{reactants} + \Delta H_0{}^{\circ}{}_{ISO} \tag{14}$$

where TS, reactants, TS(REF), and reactants(REF) are the transition states and reactants of the particular reaction from the series and the reference reaction, respectively. $\Delta H_0{}^{\circ}{}_{ISO}$ values are obtained in quantum chemical calculations. The energy barriers for the reactions from the series are then calculated as

$$E_0 = E_{0,REF} - \Delta H_0{}^{\circ}{}_{ISO} \tag{15}$$

The rate constants of the reactions from the series are calculated using the thus created models and corrected via multiplying by the preexponential correction factor F_A. The energy evaluation part of the approach is equivalent to using the difference between the reaction barriers obtained at the same level of theory for a series of similar reactions.

The described approach of isodesmic reactions for transition states was applied to 30 channels of reactions of H atoms with methane, ethane, and chlorinated methanes and ethanes. Reactions of H atoms with CH_4 and CCl_4 (clear cases of H and Cl abstraction, respectively) were used as reference reactions. Rate constants of all other reactions from the series were calculated using the isodesmic reactions approach. For the seven reactions for which directly obtained experimental data are available, the resultant calculated temperature dependences of the overall reaction rate constants demonstrate a remarkable agreement with experiment. Average deviations between calculations and experiment are 17−24%, depending on the quantum chemical method used. However, deviations for individual reactions are larger and the variations between the reaction barriers of individual channels obtained with different quantum chemical methods, in some instances, exceed 3 kJ mol^{-1}. Nevertheless, the accuracy of the approach of isodesmic reactions for transition states, when applied to the reactions studied in the current work, is significantly better than that of the more conventional method when quantum chemically generated barriers and properties of transition states are used directly to compute reaction rate constants.

Rate constants of all 30 reaction members of the H + chloromethane and H + chloroethane classes were calculated as functions of temperature using the described approach. Individual channels of H and Cl abstraction were quantitatively characterized. Rate constants of the corresponding reverse reactions were also obtained.

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Supporting Information Available: Detailed results of the quantum chemical and rate constants calculations: optimized geometrical configurations (Table 1S); energy values obtained using different computational methods (Table 2S); vibrational frequencies, moments of inertia, and barrier widths associated with individual transition states (Table 3S); 0 K reaction enthalpies of individual reaction channels (Table 4S); parameters of the rate expressions for individual reverse reaction channels (Table 5S) (32 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Certain commercial instruments and materials are identified in this article to adequately specify the procedures. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the instruments or materials are necessarily the best available for this purpose.

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