

The calculation of thermal rate constants for gas phase reactions: A semiclassical flux–flux autocorrelation function (SCFFAF) approach

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A semiclassical approach to the calculation of thermal rate constants, based on the flux–flux autocorrelation function method, is presented with its applications. The autocorrelation function is generated along classical trajectories using a classical interpretation of the Boltzmannized flux operator. The activation energies for considered reactions are calculated using the G2/MP2 procedure. The forces are generated using a new parametrization of the PM3 NDDO Hamiltonian optimized for accurate gradients. Thermal rate constants for hydrogen abstraction from ethane and haloethanes by hydroxyl radical serve as a first test of this approach. Calculated results are in good agreement with cumulative rate constants for all systems considered over a range of temperature including room temperature. The approach is able to distinguish between α and β abstraction with a result for fluoroethane at room temperature that is consistent with the available experiment and trends that are in line with those expected. © 2001 American Institute of Physics. [DOI: 10.1063/1.1344890]

I. INTRODUCTION

Rate constants are perhaps the most fundamental quantity in chemistry and the calculation of gas-phase thermal rate constants, in particular, is of interest for theoretical and experimental investigations of combustion and atmospheric chemistry.^{1,2} Of special importance is the interaction of hydroxyl radical with airborne molecules as a primary degradation mechanism for many organic pollutants. Hydrocarbons and halogenated hydrocarbons are released into the troposphere from combustion fuels and from other industrial and domestic uses. Common characteristics of the systems of interest for atmospheric degradation and combustions are that molecules are comprised of many atoms, between 10 and 100 or more, and that the geometry of the reaction coordinate may be somewhat complicated. Any theoretical method to treat such systems must be able to accommodate a large number of degrees of freedom while being computationally tractable. This semiclassical flux–flux autocorrelation function (SCFFAF) approach attached to an *an initio* parametrization of a simplified Hamiltonian (NDDO) addresses both of these concerns.

Due to the computational demands of fully quantum mechanical methods for the determination of thermal rate constants, a number of semiclassical techniques have been developed. We do not intend a comprehensive survey of this literature, however we discuss a few methods that generate thermal rate constants from classical trajectories. Keck³ calculated thermal rate constants by integrating over classically generated trajectories at a dividing surface. The thermal rate constant is then expressed as

$$k(T) = \int_{s, \vec{v} \cdot \vec{n} > 0} \vec{v} \cdot \vec{n} \rho \, d\sigma, \quad (1)$$

a surface integral of the outgoing flux $\vec{v} \cdot \vec{n}$ over the density

of states at the dividing surface ρ . This procedure finds an upper bound to the thermal rate constant. Anderson⁴ introduced a multiplicative correction which was used to account for the effect of trajectories that recross the dividing surface and hence increased the calculated rate constants.

Another semiclassical procedure for the calculation of thermal rate constants is variational transition state theory (VTST). In this method, the thermal rate constant is expressed as

$$k(T, s) = \kappa(T) \frac{k_B T}{h} \frac{Q^{\text{GT}}(T, s)}{\Phi^R(T)} \exp\left(-\frac{V_{\text{MEP}}(s)}{k_B T}\right), \quad (2)$$

where $\kappa(T)$ is an effective transmission coefficient encompassing classical and quantal effects, k_B is the Boltzmann constant, h is Planck's constant, s is the reaction coordinate, $Q^{\text{GT}}(T, s)$ is the partition function for vibration and rotation of the generalized transition state, $\Phi^R(T)$ is the reactant partition function, and $V_{\text{MEP}}(s)$ is the Born–Oppenheimer potential at s . The dividing surface is determined by minimizing the thermal rate constant along the minimum energy path thereby obtaining the position of the dynamical bottleneck. This procedure is termed canonical VTST.^{5–7} Computation of the transmission coefficient is a two stage procedure, in which one separates a classical reaction coordinate from quantized transverse mode in stage 1 and then adds in multidimensional quantum mechanical contributions semiclassically in stage 2. These latter contributions are sometimes referred to as tunneling corrections.

Recently, there has been a resurgence of interest in a quantum mechanical approach called the flux–flux autocorrelation function (FFAF) method.^{8–11} The general outline of the theory is well-established, so only a summary is presented here. The details of the various quantum mechanical calculations differ with respect to implementation and the

system that is being investigated. A substantial advantage is found in using the Boltmannized FFAF as well as using the FFAF as opposed to the flux-side autocorrelation function that can also be related to the thermal rate constant.

The thermal rate constant can be calculated from the time integral of the FFAF according to

$$k(T) = Q_r(T)^{-1} \int_0^\infty C_{\text{ff}}(t) dt, \quad (3)$$

where $Q_r(T)$ is the reactant partition function per unit volume and the FFAF is defined by

$$C_{\text{ff}}(t) = \text{tr} [e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar}], \quad (4)$$

with $\beta = 1/(k_B T)$, \hat{H} is the system Hamiltonian, and \hat{F} is the flux operator. We propose a semiclassical procedure for the computation of the FFAF, and using Eq. (3), we arrive at the SCFFAF thermal rate constants.

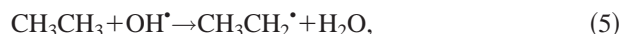
The size of the systems that we wish to consider precludes the use of *ab initio* electronic structure calculations at each atomic configuration visited by the system dynamics. It is convenient to reparametrize a semiempirical Hamiltonian, particularly the NDDO Hamiltonian, to yield an approximate system Hamiltonian parametrized from the *ab initio* results. This approach has been used for dual level direct dynamics based on VTST and is referred to as the specific reaction (or range) parameter (NDDO-SRP) fit to model potential energy surfaces in chemical reactions.^{12,13} A similar procedure has been developed for condensed phase reactions and is termed AM1 system specific parameters (AM1-SSP).¹⁴ In the SCFFAF procedure that we have implemented, we have adjusted the original PM3 NDDO parameters with the intent of reproducing high level calculations of the gradients which drive the dynamics calculation. This procedure is distinct from those cited above in which energetics or thermodynamics properties have been included in the optimization procedure. We refer to the NDDO parameter, which we have so generated, as general reaction parameters (GRPs). We use an interpolation procedure based on a Taylor expansion of gradients around a number of points calculated on the MEP for the system considered. A number of other interpolation procedures are available in the literature,¹⁵ however the procedure used herein appears to achieve acceptable results.

The computation of accurate activation energies is essential for the calculation of thermal rate constants. For this computationally intensive task we have employed the G2/MP2 procedure.¹⁶ There are a number of other approaches to this sort of extrapolation for basis set limits and correlation energy. A more recently available approach is the G3 procedure¹⁷ which modifies the G2 procedure for greater efficiency and accuracy. Other authors have proposed generalizations of these procedures to allow for the generation of potential energy surfaces. In particular, a multicoefficient G3 method¹⁸ has been developed and applied to geometry optimization.¹⁹

A sophisticated variant of VTST has been applied to the abstraction of hydrogen by hydroxyl radical from ethane, fluoroethane, and chloroethane. Sekuřak *et al.*¹³ employed a number of techniques for the generation of the PES including

fitting from points calculated using the G2 extrapolation procedure.¹⁶ A set of reaction parameters was also generated using a genetic algorithm to find a new set of PM3 NDDO parameters for the underlying semiempirical Hamiltonian. Two types of tunneling corrections were also calculated to enable the authors to calculate the thermal rate constants over a range of temperature near and above room temperature.

The present study, the first undertaken using the SCFFAF approach, focuses on the abstraction of hydrogen by hydroxyl radical from ethane, fluoroethane, and chloroethane. The reactions for which thermal rate constants are calculated are



where X is either F or Cl. Hydrogen abstraction from a haloethane occurs either from the carbon bonded to the halogen [Eq. (6a), α abstraction] or from the other carbon [Eq. (6b), β abstraction]. Our newly developed SCFFAF approach follows from the quantum mechanical FFAF method while using classical dynamics for the propagation of all degrees of freedom in the region of the transition state.

II. METHOD

Historically, thermal rate constants have been fitted to the Arrhenius relation. Here it is clear that the accurate determination of the activation energy is paramount for the accurate calculation of the thermal rate constants,

$$k(T) = A \exp\left(-\frac{E_A}{k_B T}\right), \quad (7)$$

where E_A is the activation energy. This is an empirical relation and it can occur that the preexponential factor A is a function of the temperature leading to so-called non-Arrhenius behavior in the thermal rate constant.

Since the accuracy of the thermal rate constant is extremely sensitive to the determined activation energy, we have chosen to employ an extrapolation technique for its determination. We have used the G2/MP2 procedure for the determination of the activation barriers by comparing calculations of the reactant energies with the energies of the various transition states. For ethane, there exists a single transition state structure, whereas for each of the haloethanes there are three transition state structures to be considered. One of the haloethane transition states corresponds to α abstraction while there are two distinct transition states for β abstraction. Table I summarizes the activation energies for each of the seven transition state geometries associated with the various hydrogen atom abstraction reactions we have considered.

As described in the introduction, the FFAF method has gained a good deal of attention recently for a fully quantum mechanical calculation of thermal rate constants. It is convenient to work with the Boltmannized flux operator

$$\hat{F}(\beta) = e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2}, \quad (8)$$

TABLE I. Activation energies for the seven transition states considered.

System	Orientation	Barrier (kcal/mol)	Sekuřak <i>et al.</i> ^a
Ethane	All	2.7	2.9
Chloroethane	α abstraction	1.0	1.1
	β abstraction I	3.3	3.4
	β abstraction II	2.5	2.8
Fluoroethane	α abstraction	1.6	2.1
	β abstraction I	4.3	4.3
	β abstraction II	3.0	3.3

^aReference 13.

$$\hat{F} = \frac{i}{\hbar} [\hat{H}, \hat{\Theta}(s)].$$

The flux operator is the commutator of the system Hamiltonian with the Heaviside step function along the reaction coordinate s defined as

$$\Theta(s) = \begin{cases} 1, & s > 0, \\ 0, & s < 0. \end{cases} \quad (9)$$

In all the cases that we consider in this study, the reaction coordinate is defined by the distance between the abstracted hydrogen and the carbon from which it is abstracted. This choice allows for a similar description of all the transition states considered and within the context of the FFAF method, variations in the choice of dividing surface have not led to changes in the calculated rate constants.

The Hamiltonian can be written in Cartesian coordinates as

$$\hat{H}(\{\mathbf{p}, \mathbf{q}\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + \hat{V}(\{\mathbf{q}\}). \quad (10)$$

N is the number of atoms in the system, and p_i , q_i , and m_i , are the momentum, coordinate, and mass associated with the i th degree of freedom, respectively. Interpreting the flux operator presented in Eq. (8) within the usual quantum mechanical framework and observing that the potential commutes with the step function, we obtain an expression for the flux operator,

$$\hat{F} = \frac{1}{2} \sum_{i=1}^{3N} \left(\frac{\vec{p}_i}{m_i} \cdot \nabla_{iS} \delta(s) + \delta(s) \nabla_{iS} \cdot \frac{\vec{p}_i}{m_i} \right), \quad (11)$$

which is used for the generation of the FFAF in our semiclassical method. The delta function is interpreted using the definition of the derivative as

$$\delta(s) = \frac{\Theta(s+h) - \Theta(s-h)}{2h}, \quad (12)$$

where h is the width of the dividing surface which is defined for the convenience of the calculation. It should be noted that this formulation of the delta function allows freedom in the thickness of the dividing surface without significant change in the calculated integral of the FFAF and hence the thermal rate constants.

The FFAF method can benefit from absorbing boundary conditions to limit the region of space in which wave packets must be propagated, and to limit the amount of the PES in

the vicinity of the transition state structure that must be computed to generate the thermal rate constants. Problems related to the recrossing of the dividing surface are not encountered in the FFAF method in that the crossing and recrossing of the dividing surface are included in the FFAF with their proper sign. Furthermore, use of the Boltzmannized flux operator simplifies the generation of the FFAF by providing algorithmic advantages, particularly in the use of the Lanczos matrix reduction. However, because of the computational complexity of the method, it is not useful for application to systems with more than a few atoms without substantial simplification.

A. Semiclassical implementation of FFAF

There are a number of possible implementations of the FFAF equations in the previous section that could be considered. The implementation that provides the results for this article treats all the degrees of freedom in the abstraction of hydrogen from ethane and haloethanes by hydroxyl radical explicitly through the solution of Hamilton's equations for their motions. The Boltzmannized flux operator is used in the construction of the FFAF, which is constructed along the classical trajectories calculated. In lieu of absorbing boundary conditions, trajectories are simply terminated when they propagate sufficiently far away from the dividing surface. The forces under which the atoms move are generated along the reaction path. Here we use the minimum energy path (MEP), by the use of our parametrization of the NDDO Hamiltonian. Forces for trajectories that deviate from the MEP are generated from a Taylor expansion of the potential along the MEP. The PES for the reaction under consideration is never explicitly generated. The NDDO Hamiltonian is reparametrized to reproduce gradients at the positions of the transition state and the reactant and product van der Waals structures. The vibrational partition function of the reactants is generated from vibrational frequencies calculated using the B3LYP functional in a density functional theory (DFT) calculation.²⁰ Moments of inertia are determined for the reactants and the transition state to incorporate the rotational partition function in the thermal rate constant calculation.

The SCFFAF procedure must provide the information necessary for calculating the thermal rate constants as defined in Eq. (3). The interpretation of the trace in Eq. (4) is simplified in the consideration of the FFAF from each classical trajectory as it becomes the product of the flux at the initial time with the flux at some later time t . The flux defined by Eq. (11) is interpreted using the momentum in each relevant degree of freedom when the reaction coordinate is defined by

$$s = |\vec{r}_C - \vec{r}_H|, \quad (13)$$

where H is the abstracted hydrogen and C is the carbon from which the hydrogen is abstracted.

This implementation of the SCFFAF procedure involves the generation of a set of initial conditions in which the positions of the atoms are initially chosen to be at the location of the activated complex. Momenta are chosen, weighted to approximately account for vibrational zero-point energies, randomly for each of the degrees of freedom of the

TABLE II. The percent difference of the varied PM3 atomic parameters.

Parameter	Atom	PM3	PM3-GRP	% difference
U_{ss}	H	-13.073 321	-13.202 997	-0.991 912
G_{ss}	H	14.794 208	14.878 398	0.569 077
β_s	H	-5.626 512	-5.727 858	-1.801 223
U_{ss}	C	-47.270 320	-47.280 822	-0.022 217
U_{pp}	C	-36.266 918	-35.999 012	0.738 707
G_{ss}	C	11.200 708	12.484 437	11.461 138
G_{sp}	C	10.265 027	10.262 732	-0.022 362
G_{pp}	C	10.796 292	11.304 365	4.705 994
G_{p2}	C	9.042 566	8.805 893	-2.617 325
H_{sp}	C	2.290 980	2.379 499	3.863 799
β_s	C	-11.910 015	-11.882 620	0.230 019
β_p	C	-9.802 755	-9.791 892	0.110 819
U_{ss}	O	-86.993 002	-95.431 336	-9.700 012
U_{pp}	O	-71.879 580	-71.875 280	0.005 976
G_{ss}	O	15.755 760	17.198 173	9.154 832
G_{sp}	O	10.621 160	12.242 819	15.268 194
G_{pp}	O	13.654 016	13.864 919	1.544 624
G_{p2}	O	12.406 095	11.786 533	-4.994 007
H_{sp}	O	0.593 883	0.692 335	16.577 682
β_s	O	-45.202 651	-46.160 997	-2.120 105
β_p	O	-24.752 515	-25.258 174	-2.042 859

atoms at the activated complex, and the total kinetic energy is constrained to be below some threshold that is a randomly chosen fraction of a kinetic energy maximum. The kinetic energy maximum is chosen to maximize the calculated thermal rate constants. The time evolution of the system is then generated by solving Hamilton's equations²¹ for all degrees of freedom as a set of simultaneous differential equations,

$$\frac{\partial H}{\partial q_i} = -\dot{p}_i, \quad \frac{\partial H}{\partial p_i} = \dot{q}_i. \quad (14)$$

These equations are solved in Cartesian coordinates, hence the derivative of the Hamiltonian with respect to positions reduces to the derivative of the potential and the derivative of the Hamiltonian with respect to momentum reduces to the derivative of the kinetic energy,

$$\dot{p}_i = -\frac{\partial V}{\partial q_i}, \quad \dot{q}_i = \frac{p_i}{m_i}. \quad (15)$$

The solution of these equations requires the knowledge of the positional derivative of the potential at an arbitrary configuration of the atoms involved in the reaction. For this purpose, a number of configurations, usually about 100, are generated along the MEP for the reaction considered. At each of these points along the MEP, gradients and Hessians are calculated using the GRP parametrization of the NDDO Hamiltonian so that the potential is expanded in a Taylor series,

$$V(\vec{q}) = V(\vec{q}_0) + \sum_j \frac{\partial V}{\partial q_j} \Big|_{\vec{q}=\vec{q}_0} (q_j - q_{j0}) + \frac{1}{2} \sum_{j,k} \frac{\partial^2 V}{\partial q_j \partial q_k} \Big|_{\vec{q}=\vec{q}_0} (q_j - q_{j0})(q_k - q_{k0}), \quad (16)$$

where \vec{q}_0 are coordinates along the MEP. Taking the derivative with respect to positions of Eq. (15),

TABLE III. The characteristic bond lengths of the transition state.

\AA	MBPT(2)		PM3	
	6-31G(d,p)	6-311++G(d,p)	Original	Optimized
r_{C-H}	1.107	1.177	1.230	1.226
r_{H-O}	1.321	1.364	1.337	1.336

$$\frac{\partial V}{\partial q_i}(\vec{q}) = \frac{\partial V}{\partial q_i} \Big|_{\vec{q}=\vec{q}_0} + \sum_j \frac{\partial^2 V}{\partial q_i \partial q_j} \Big|_{\vec{q}=\vec{q}_0} (q_j - q_{j0}). \quad (17)$$

The gradient is calculated by determining the nearest MEP points to the current coordinates at any time along the given trajectory and using the NDDO Hamiltonian. The values are linearly interpolated between the two closest configurations with respect to the distance along the reaction coordinate.

B. NDDO potential

The semiempirical PM3 NDDO Hamiltonian²²⁻²⁴ was reparametrized to reproduce, to the extent possible within the chosen parameter space, MBPT(2)/6-311++G(d,p) structures at three stationary points on the MEP described in the hydrogen abstraction reaction of ethane with hydroxyl radical. This parameter "optimization" was carried out using GAFORTRAN 1.6.4,²⁵ a global, genetic algorithm²⁶ (GA)-based, optimization program. The NDDO parameters varied were all one- and two-electron atomic integrals (see Table II) with the bounds of the variation set to $\pm 20\%$ of each parameter's initial value. The error function to be optimized by the GA is defined as follows:

- any of the individual parameter sets (forming the "population" of the GA) for which the computed activation barrier was less than zero or the computed heat of reaction was greater than zero were rejected outright;
- the parameter set would also be rejected if the atomic parameters failed to make sense (e.g., the work needed to remove a valence *s*-electron must remain greater than that needed to remove a valence *p*-electron, etc.);
- the error function is then defined to be the root-mean-square of the percent differences between the computed NDDO gradient and a chosen acceptable error of 0.03 au for each of the following MBPT(2) stationary points: the reactant-side van der Waals complex, the product-side van der Waals complex, and the transition state structure, with the percent difference of the transition state structure being preferentially weighted by a factor of 3.

TABLE IV. The gradient norms of the three MBPT(2)/6-311++G(d,p) structures computed using the two NDDO approaches.

System	Original PM3	Optimized
TS	45.1	13.7
R-VDW	45.9	13.5
P-VDW	49.1	35.8

The error function is then minimized using the GA. The specifications used in conjunction with running the GA were a uniformly distributed starting generation of 100 individuals, 30 bits per parameter, a uniform crossover probability with a crossover ratio of 0.5, and a mutation probability of 0.005. The optimization was considered converged when the returned value of the error function had stabilized and the individual errors were acceptably small.

For this work the MEP was determined at about forty equally spaced points on each side of the barrier top, yielding some eighty plus points in all including the barrier top. The classical barrier top was located using the eigenvector following (EF) algorithm²⁷⁻²⁹ available in MOPAC 5.07mn.³⁰ The MEP connecting reactants to products through the first-order saddle point, located using the EF technique, was determined using the intrinsic reaction coordinate following algorithm available in the standard version of MOPAC.³¹

The potential does not include dissipation and Hamilton's equations are energy conserving hence the total energy of any given trajectory is a constant of the motion. The Boltzmann factor for the Boltzmannized flux is taken to be the initial energy of each trajectory. The FFAF is accumulated along each trajectory and at equal time intervals and the total FFAF is the sum of the accumulated FFAF for all the trajectories considered. For the results presented in the next section we have used 1000 randomly generated trajectories, each of which originates at the position of the activated complex. The semiclassically calculated FFAF is then integrated over the time of the propagation. The trajectories are propagated until they reach the boundary, in which case the trajectory is terminated, or until final time is obtained. In all cases, the FFAF is seen to diminish to zero at late times so that no contribution to the thermal rate constants is neglected. The rotation of the activated complex is included in the calculation by the inclusion of the rotational partition function for the transition state, as free rotations are not included in the dynamics modeling. The vibrations of the reactants are calculated using DFT with the B3LYP functional.

The G2/MP2 calculations have been carried out on a SGI Origin 2000 with a R12000 processor. The NDDO parametrization, the generation of the MEP, and the SCFFAF dynamics have been calculated using IBM-compatible personal computer with Pentium II chips.

III. RESULTS

In Tables III and IV we present how the optimized parameters performed versus the original PM3 parametrization for ethane. Note that while the semiempirical characteristic TS bond lengths (Table III) are approximately the same (both Hamiltonians describe a later TS than those yielded by the second-order calculations), the forces computed for the MBPT(2)/6-311++G(*d,p*) structure (Table IV) are significantly different, with the optimized Hamiltonian yielding a gradient norm for the TS less than one third that of the original parametrization. The curvature (Hessian) of the second-order TS structure described by the original parametrization has three large negative eigenvalues, while that of the optimized Hamiltonian has only one, thus the signature of the Hessian is correct for the optimized semiempirical method; though both NDDO methods yield repulsive modes describing the hydrogen atom transfer with too acute (approximately 50%) a curvature.

The SCFFAF procedure has been applied to hydrogen abstraction from ethane, chloroethane, and fluoroethane by hydroxyl radical over a range of temperatures for which experimental results exist. There is a wealth of experimental data on the ethane system,³² as well as a recent application of interpolated VTST with interpolated corrections (IVTST-IC) with various types of tunneling corrections, as well as direct dynamics within a dual-level dynamics framework. The activation energy that we calculated from the G2/MP2 prescription differs slightly from that calculated by Sekuřak *et al.* with our result, 2.7 kcal mol⁻¹, being 0.2 kcal mol⁻¹ lower. Sekuřak *et al.* applied three different approaches to this problem. The first calculates the PES using G2/MP2 interpolations and employs the small curvature tunneling correction to IVTST-IC (SCBS I). The second is a dual-level direct dynamics approach in which G2/MP2 energetics and specific reaction parameters (taken from the ethane abstraction) in the PM3 Hamiltonian drive the calculation. Again, small curvature tunneling corrections are used (SCBS II). Finally, the specific reaction parameters are used in the direct dynamics calculation, as in SCBS II, with the microcanonical multidimensional tunneling correction (SCBS III). Figure 1 presents the thermal rate constants for abstraction from ethane. Over the range of temperature that we have consid-

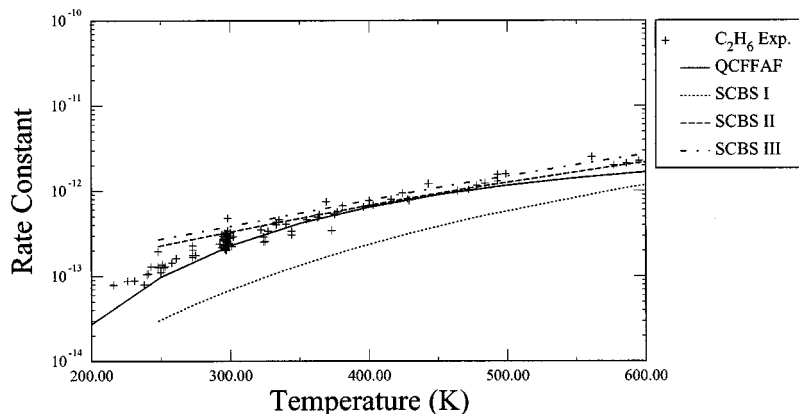


FIG. 1. Comparison of present work with experiment (Ref. 32) and other theory (Ref. 13) for abstraction from ethane, the thermal rate constant units are cm³ molecule⁻¹ sec⁻¹. See text for definition of SCBS results.

TABLE V. Percent abstraction from alpha and beta carbons in chloroethane.

Temperature	% Alpha abstraction	% Beta abstraction
300	93.9	6.1
350	91.6	8.4
400	89.4	10.6
450	87.3	12.7
500	85.4	14.6

ered, 200–600 K, we find excellent agreement between SCFFAF results and experiment. The SCBS I method underestimates the rate constants throughout the range, while SCBS II and SCBS III agree well with experiment.

In the case of hydrogen abstraction from chloroethane, the SCFFAF procedure is able to distinguish between (relative rate of) α and β abstraction, and the resulting percentages for each type as a function of temperature is presented in Table V. As would be expected from the relative activation energies, α abstraction is dominant at all the temperatures that we have considered. With rising temperature, β abstraction becomes a more significant portion of the total rate constant and, as there are three β hydrogens and only two α hydrogens, would be expected to be dominant in the high temperature limits (60%/40%). Figure 2 presents a comparison of the cumulative rate constants. Again the SCFFAF results are in excellent agreement with the experiment³³ throughout the considered temperature range, 300–500 K. As is the case for ethane, the SCBS I results are much lower than the experimental data. SCBS II and SCBS III are within about a factor of 3 throughout the range, while they underestimate and overestimate the rate constants, respectively. We employ the same NDDO parametrization for the haloethanes as for ethane.

Hydrogen abstraction from fluoroethane presents the opportunity to evaluate the accuracy of the SCFFAF procedure for the prediction of α and β abstraction as an experimental result is available. Singleton *et al.*³⁴ found an α abstraction percentage of $85\% \pm 3\%$ at 297 K (see Table VI). Although the SCFFAF result (90.6%) is slightly outside the error bars of the experiment, it shows a dominance of the α abstraction that is close to what has been observed. Figure 3 presents the cumulative thermal rate constants for this abstraction. The SCFFAF results are within a factor of 2 for this case, yet

TABLE VI. Percent abstraction from alpha and beta carbons in fluoroethane*(Exp) (Ref. 34) $85\%/15\% \pm 3\%$ α/β .

Temperature	% Alpha abstraction	% Beta abstraction
243	94.2	5.8
273	92.2	7.8
296*	90.6	9.4
324	88.7	11.3
373	85.4	14.6

they are consistently larger than the measured rate constants.³⁵ Again, the SCBS I method greatly underestimates the rate constants. The SCBS II method performs better than SCBS I yielding results that are lower than the measured rate constants by about a factor of 3. Again, the SCBS III method overestimates the rate constants by a similar factor.

For the three systems that we have considered, the SCFFAF procedure consistently performed as well as, if not better than, the IVTST-IC calculations recently reported. The comparison to experimental results is quite good for thermal rate constants across a range of temperatures and for chemically distinct systems. The ratio of α to β abstraction is able to be calculated by the SCFFAF procedure and for the single available experimental data point is seen to be in line with experiment, though not in complete agreement. From these results, it appears that this semiclassical implementation of the FFAF formalism is sufficient for the calculation of thermal rate constants for hydrogen abstraction from ethane and haloethanes by hydroxyl radical.

IV. CONCLUSIONS

The FFAF method for the calculation of thermal rate constants is extended through a semiclassical procedure to be applicable to systems comprised of many atoms. The SCFFAF procedure realized here relies on a multilevel description of the dynamics of chemical reactions. As is seen from the Arrhenius relation, the accurate determination of the activation energy is extremely important for a realistic description of the thermal rate constants. In accordance with this principle, the activation energies of the reactions considered have been determined with the G2/MP2 extrapolation procedure. This determination is done independently from

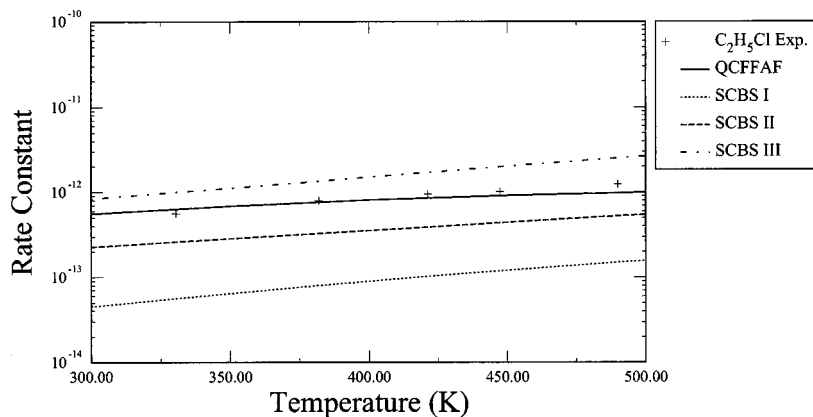


FIG. 2. Same as Fig. 1 for hydrogen abstraction from chloroethane, experimental results from Ref. 33.

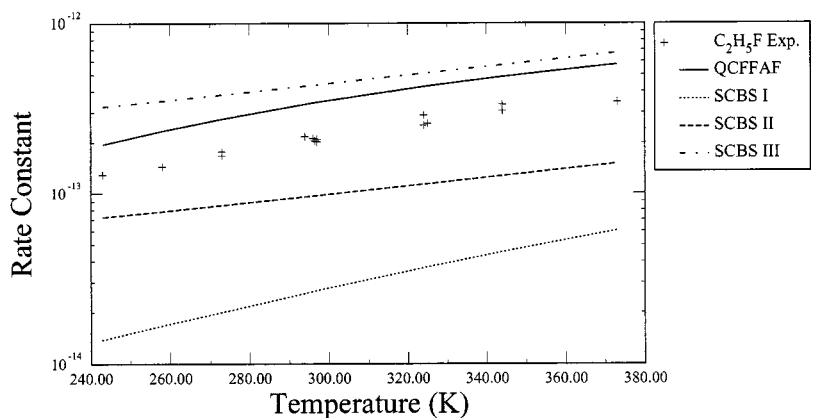


FIG. 3. Same as Fig. 1 for hydrogen abstraction from fluoroethane, experimental results from Ref. 35.

the calculation of the FFAF. The FFAF is generated along classical trajectories from a expression for the flux operator that is interpreted in terms of classical quantities. The Boltzmannized flux operator is used to include statistical thermodynamic contributions from each of the classical trajectories. The forces that govern the evolution of the classical trajectories are calculated from a reparametrized NDDO Hamiltonian and interpolated from a series of points along the MEP. All degrees of freedom are propagated in the dynamics calculations and no tunneling corrections have been employed. The vibrational contribution to the reactant partition function is calculated from frequencies taken from DFT using the B3LYP functional. Possible contributions from electronically excited states have not been considered in this treatment, as they have previously been found to be unimportant.¹³

The results of the application of this SCFFAF procedure has served as a first test of this new method and has yielded results in good agreement with experiment for hydrogen abstraction from ethane and haloethanes by hydroxyl radical. The results have been consistently as good as, if not superior to, a recent IVTST-IC calculation. SCFFAF results for the ratio of α to β abstraction are consistent with available experimental results and the trend with temperature is as would be expected.

The present SCFFAF procedure is capable of extension to more complicated reactions. It would be possible to include estimated or experimentally determined activation energies to replace the computationally intensive G2/MP2 procedure, which is the rate-limiting step in this procedure. The generation of FFAF in this framework could be routinely accomplished for as many as a few hundred atoms opening many systems of interest in combustion and atmospheric chemistry to theoretical investigation.

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