INVITED ARTICLE

From quantum chemistry to dissociation kinetics: what we need to know

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(Received 25 February 2014; accepted 15 May 2014)

The relationship between rate constants for dissociation and the reverse association reactions and their potential energy surfaces is illustrated. The reaction systems \( e^- + SF_6 \leftrightarrow SF_6^- \rightarrow SF_5^- \rightarrow F, H + CH_3 \leftrightarrow CH_4, 2 CF_2 \leftrightarrow C_2F_4, H + O_2 \rightarrow HO_2, HO + O \leftrightarrow HO_2 \leftrightarrow H + O_2, \) and \( C + HO \rightarrow CHO \) are chosen as representative examples. The necessity to know precise thermochemical data is emphasised. The interplay between attractive and anisotropic components of the potentials influences the rate constants. Spin–orbit and electronic–rotational coupling in reactions between electronic open-shell radicals so far generally has been neglected, but is shown to have a marked influence on low temperature rate constants.

Keywords: reaction kinetics

1. Introduction

Dissociation and the reverse association reactions play an important role in combustion, atmospheric and interstellar chemistry, as well as in many other gas-phase reaction systems. While the energy levels of the reacting species generally are well known from high-resolution molecular spectroscopy and quantum chemical calculations, the dissociation and association rates are much less precisely measured and rate theories are generally far from being satisfactory. By presenting a few examples, this essay describes the state of the art and highlights areas where priority needs for determining rate parameters can be identified.

Electron attachment to \( SF_6 \) and the reverse detachment from \( SF_6^- \) in competition to the dissociation of \( SF_6^- \) is chosen as the first example. This system is of considerable fundamental and practical importance and it has been studied in detail over some time. Many characteristic features of plasma chemical kinetics are encountered here and progress in the understanding can be documented particularly well. Thermal dissociation of methane is of similar importance in hydrocarbon pyrolysis and oxidation and hence in combustion chemistry. This system has been chosen because theoretical studies of its elementary processes – collisional energy transfer between the excited molecule and its surrounding bath gas as well as intramolecular bond breaking and bond formation – are reaching a mature state without the necessity for empirical adjustment of parameters. The thermal dissociation of perfluoroethene and the reverse dimerisation of difluorocarbene are described for comparison, again illustrating the present understanding, but in addition emphasising the basic differences between hydrocarbon and fluorocarbon dissociation and association kinetics. Finally, the ‘simple’ reaction system \( H + O_2 \leftrightarrow HO_2 \leftrightarrow HO + O \) is analysed with respect to various aspects of dissociation and association dynamics. The open-electronic shell character of the reactants renders a quantitative analysis of the dynamics particularly difficult. The effects to be expected are illustrated by a comparison with the \( C + HO \) association process for which the consequences of spin–orbit coupling have already been analysed. The interplay between attractive and anisotropic components of the potential energy surface, as in the \( CH_4 \) and \( C_2F_4 \) systems, is illustrated also for the \( HO_2 \) system with respect to its influence on the dissociation and association dynamics.

In summary, this report describes which properties of potential energy surfaces and which details of the reaction dynamics on these potentials need to be known with priority in order to arrive at least at a semiquantitative understanding of dissociation and the reverse association processes.

2. Kinetics of the \( e^- + SF_6 \leftrightarrow SF_6^- \rightarrow SF_5^- + F \) reaction system

The inert, non-toxic, and insulating molecule \( SF_6 \) is used in many technical applications. For example in the plasma etching of silicon chips the reaction \( SF_6 + e^- \rightarrow SF_5^- + F \) acts as a source for fluorine atoms which may remove unprotected silicon in a reaction \( 4 F + Si \rightarrow SiF_4 \). By acting as an ‘electron sponge’, \( SF_6 \) efficiently reduces the concentration of mobile electrons from ionised gases. Because of this ability, \( SF_6 \) may be used to shape switching arcs in circuit breakers of power plants and here finds wide practical

Received 25 February 2014; accepted 15 May 2014

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†The Molecular Physics Lecture presented at the 23rd Colloquium on High Resolution Molecular Spectroscopy, Budapest, August 2013.
The cross sections for dissociative electron attachment to SF₆ have a peculiar shape such as illustrated in Figure 3. At low energies, the decrease reflects the decrease of the capture cross section with increasing electron energy \( E_d \). Here, the temperature-dependent high energy tail of the
Figure 2. Specific rate constants for electron detachment ($k_{\text{det}}$, $\text{SF}_6^− \rightarrow \text{SF}_6 + e^−$) and dissociation ($k_{\text{dis}}$, $\text{SF}_6^− \rightarrow \text{SF}_5^− + F$) of $\text{SF}_6^*$ (modelling from Ref. [10]; the energies $E$ should be decreased by 0.17 eV after re-evaluation [6] of $E_a$).

Figure 3. Dissociative electron attachment cross sections of $\text{SF}_6$ as a function of electron energy $E_{\text{el}}$ and gas temperature $T_{\text{gas}}$ (experimental points from Ref. [11]; modelling from Ref. [10], dashed curves: total cross sections).

Figure 4. Branching fractions $R = [\text{SF}_5^−]/([\text{SF}_5^−] + [\text{SF}_6^−])$ for dissociative electron attachment to $\text{SF}_6$ (filled experimental points after 4 ms of reaction time, open experimental points after 14 ms, from Ref. [4]; low-pressure decrease of $R$: collisional stabilisation of primary $\text{SF}_6^−∗$, high-pressure increase of $R$: collisional thermal dissociation of $\text{SF}_6^−$ after primary collisional stabilisation of primary $\text{SF}_6^−∗$).

Boltzmann distribution of thermal $\text{SF}_6$ molecules (together with the electron energy) produces some $\text{SF}_6^−∗$ which is capable of dissociation. With increasing electron energy, $E_{\text{el}}$ finally exceeds the dissociation energy of $\text{SF}_6^−∗$. Then the sum of $E_{\text{el}}$ and the thermal energy of $\text{SF}_6$ leads to increasing ion fragmentation, before finally the drop of the capture cross section leads to the marked decrease of the dissociative cross section at large $E_{\text{el}}$. What looks like a ‘resonance in the cross section’ near $E_{\text{el}} = 500$ meV has nothing to do with a resonance, but is the result of a competition of several rate processes and their convolution over energy distributions.

Similar to the dissociative cross sections, also the product branching fractions $R = [\text{SF}_5^−]/([\text{SF}_5^−] + [\text{SF}_6^−])$ have a peculiar shape such as shown in Figure 4. The decline of $R$ at lower pressures in Figure 4 corresponds to collisional quenching of the excited $\text{SF}_6^−∗$ produced by the primary electron attachment, while the increase of $R$ at higher pressures (for $T = 620$ K) is brought about by the thermal reactivation of $\text{SF}_6^−$ after primary collisional quenching. Kinetic modelling allows one to understand the details of the shown $R(T, P)$ (see Ref. [3]).

From quantum chemistry to dissociation kinetics: what we need to know in this case, first, obviously is the proper thermochemistry. Then, the non-Born–Oppenheimer electron attachment (and detachment) dynamics needs to be understood which is far from being the case today. Instead, empirical models still are necessary to bridge unknown territory (see Ref. [10]). Finally, the dissociation dynamics and collisional deactivation of highly excited molecular ions needs to be quantified. The latter has much in common with the analogous processes for neutral molecules.
although the potential energy surfaces and the properties of collisional energy transfer are different. Nevertheless, such processes for ionic and neutral species should be treated on a common level. The following sections present examples for neutral reaction systems.

3. Dissociation/recombination studies in the CH₄ ↔ CH₃ + H and C₂F₄ ↔ 2 CF₂ reaction systems

The temperature and pressure dependence of methane dissociation CH₄ ( + M) → CH₃ + H ( + M) and the reverse combination of CH₃ with H to form CH₄ have been investigated in remarkable detail and are particularly suitable for a demonstration of the present situation. Examples [13, 14] of experimental pressure dependences (or dependences on the bath gas concentrations [M]) at fixed temperatures are shown in Figures 5–7. The so-called ‘falloff curves’, log k vs. log [M], reach from low-pressure (k ∝ [M]) to high-pressure behaviour (k independent of [M]).

Figures 5–7 illustrate experimental data and modelling results (full curves). The high-pressure limiting behaviour corresponds to a capture of H by CH₃ (for combination) on the potential energy surface of CH₄ (see Refs [15–17] and, for more details, see [18–20]). The low-pressure behaviour reflects the properties of collisional energy transfer on CH₄–M potential energy surfaces (see Refs [21,22]). As the two potentials now are known, one may perform a complete modelling of the reaction dynamics on these surfaces and study how close the experiment and theory come. At the same time, one may ask which details of the potentials matter most and which would be the minimum knowledge required for a meaningful comparison of experiment and theory.

We first consider the high-pressure limit of the CH₄ reaction system governed by the CH₄ potential only. Two properties of the potential turn out to be of primary importance: the minimum-energy path (MEP) potential and the anisotropy of the potential. In the CH₄ case, a Morse-type MEP potential fairly well reproduces the ab initio results (see Ref. [20]). Using the MEP potential only and treating the orbital motion of H around CH₃ leads to a capture rate constant (analogous to the Langevin rate constant in electron capture, see above) such as described by phase-space theory (PST) or loose activated complex theory. However, the presence of an anisotropy of the potential reduces the capture rate by introducing ‘dynamical hindrance’ (or ‘tightening of the activated complexes’). One way to account for this effect is the use of a model potential. For example, a potential of the form

\[ V(r, \theta) = D[\exp[-2\beta(r - r_e)] - 2\exp[-\beta(r - r_e)]] + C \exp[-\beta(r - r_e)]\sin^2(\theta - \pi/2) \quad (3.1) \]

was considered in Ref. [14] (with a fitted Morse parameter \( \beta \), the dissociation energy \( D \), the H–CH₃ distance \( r \), the angle \( \theta \) between the H–CH₃ line and the CH₃ plane, and an anisotropy amplitude factor \( C \)). Alternatively [23], one may employ a different decay parameter \( \alpha \) in the second
term of Equation (3.1), e.g. here replace $\beta$ by $2\alpha$ and determine $C$ from the corresponding deformation vibrations at $r = r_c$. Ab initio potentials obviously differ from this simple form. Therefore, two possibilities to characterise an average overall anisotropy have been tested. First, the high-pressure capture rate constant was calculated by classical trajectory calculations both on the ab initio potential and on the model potential, which allowed for a fit of the ratio $C/D$ (as done in Ref. [14]). Second, transitional-mode frequencies along the MEP of the $ab$ initio potential were determined and trajectory calculations were performed on the corresponding deformation vibrations of such potentials, one is in the position to model the MEP potential and an average overall anisotropy parameter $\beta$ need to be known with first priority, while further details of the potential are less important for kinetic quantities like dissociation/association rates. The reduction of the capture rate constant by the anisotropy of the potential is well illustrated in Figure 8, PST overestimating the rate by about a factor of 2. We note that the analysis of the $ab$ initio potential of Ref. [16] in Ref. [14] led to an effective Morse parameter $\beta \approx 2 \text{Å}^{-1}$, while the analysis of the anisotropy of the $ab$ initio potential in Ref. [19] gave $\alpha \approx 0.7–0.8 \text{Å}^{-1}$ (being close to the value of 1 Å$^{-1}$ suggested long ago in Ref. [23]). With a ratio $\alpha/\beta \approx 0.4$ this close to the ‘normal’ ratio of 0.5 derived from a series of typical dissociation and recombination reactions in Ref. [24].

The low-pressure limiting rate constant requires solution of the master equation for intermolecular collisional energy transfer [21, 22, 25–27]. Assuming very efficient energy exchange, ‘strong collision rate constants’ are obtained as upper limits, only containing an overall collision number. The assumption that the latter can be identified with the Lennard-Jones collision number has been confirmed by classical trajectory calculations (see, e.g. Refs [21, 22] for CH$_4$ collisions with inert colliders M). On the other hand, more efficient colliders like M = H$_2$O are characterised by larger collision numbers $Z$ (see, e.g. Refs [22, 28]). When collisional energy is less efficient, the rate constant is reduced by a ‘collision efficiency’ $\beta_c$, being related to the average energy transferred per collision $<\Delta E>$. The contribution of vibrational and rotational energy transfer to $<\Delta E>$ has been investigated in detail [21, 25]. Again minor details do not matter too much, but an almost temperature independent $<\Delta E>$ in practice generally has to be used as a fit parameter (a temperature independence of $<\Delta E>$ corresponds to [25] an increase of the average energy transferred per down collision $<\Delta E_{down}> \propto T^{1/2}$). The necessity to use this fit parameter obviously presents a limitation to the prediction of low-pressure rate constants. For the methane system, this problem has been overcome. Here, the trajectory calculations of Ref. [21] on the $ab$ initio potential for the CH$_4$–M interaction led to $<\Delta E>$ values in agreement with values derived by evaluating experimental low-pressure rate constants [28].

With the information on the dissociation/association and collisional energy transfer dynamics obtained from calculations on $ab$ initio potentials and simplified versions of such potentials, one is in the position to model full falloff curves of the dissociation/association reactions [14, 26]. The results of such modelling are included in Figures 5–7. Obviously kinetics averages out finer details of the
potentials and of the dynamics and only few key properties need to be known. These are the parameters \( D, \beta, \) and \( C \) (or \( \alpha/\beta \)) on the side of the intramolecular potential of Equation (3.1), and \( Z \) and \( \langle \Delta E \rangle \) on the side of the collisional energy transfer.

The interplay between the attractive and anisotropic parts of the potential in dissociation/association dynamics has been demonstrated extensively with the statistical adiabatic channel model (SACM) \([23]\) in combination with classical trajectory calculations (CT) \([29]\). In the original version \([23]\) of the SACM, the anisotropy of the potential was expressed by the quantum states of deformation motions, changing from bending vibrations into free rotations along the MEP of dissociation. We illustrate this feature of an anisotropic potential for the \( \text{C}_2\text{F}_4 \rightarrow 2\text{CF}_2 \) dissociation. Figure 9 shows the results of quantum-chemical calculations \([30]\) of vibrational frequencies of five torsional modes as a function of the C–C bond length \( r \). One observes an exponential decay, confirming suggestions from the original SACM \([23]\) and presenting the mentioned alternative to the anisotropy of the model potential of Equation (3.1). Inserting the corresponding ratio of the decay parameter \( \alpha \approx 1.2 \, \text{Å}^{-1} \) and the effective Morse parameter \( \beta \approx 5.2 \, \text{Å}^{-1} \), i.e. \( \alpha/\beta \approx 0.23 \), into the modelling relationships from SACM/CT calculations \([29]\), leads to high-pressure rate constants which are in close agreement with experimental data \([30]\) (see Figure 10). As the calculation is based on \textit{ab initio} potential data and does not involve additional empirical fit parameters, one concludes that the leading properties of the potential have been characterised realistically and are validated by the experimental results. In particular, the unusually small value of the ratio \( \alpha/\beta \) (being much smaller than the normal value of this ratio such as observed for the \( \text{CH}_4 \) system described above) is identified to be responsible for the small value of the high-pressure association rate constant and its markedly positive temperature coefficient (see Figure 10).

4. The association reaction \( \text{H} + \text{O}_2 \leftrightarrow \text{HO}_2^* \) followed by \( \text{HO}_2^* + \text{M} \rightarrow \text{HO}_2 + \text{M} \)

The recombination reaction \( \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \) plays a key role in the oxidation of hydrogen and hydrocarbons and, thus, is one of the most important reactions of combustion chemistry. Comparing its potential energy surface with that of \( \text{H} + \text{CH}_3 \rightarrow \text{CH}_4 \), one observes marked differences, mainly in the MEP potential such as illustrated in Figure 11. While the \( \text{CH}_4 \)- and \( \text{C}_2\text{F}_4 \)-systems were characterised by simple Morse-type MEP potentials, now there is something like a ‘shoulder’ in the potential which may be the remnant of an avoided crossing of electronic states. This has profound consequences for the capture dynamics. Employing the \textit{ab initio} potential from Ref. \([31]\), adiabatic channel potential curves were constructed in Ref. \([32]\). Figure 12 shows examples of such curves, along which the quantum
numbers of the HO_2 modes and the quantum number of the H + O_2 orbital motion of the dynamics adiabatically are kept constant. One notices ‘transition state switching’ from large H–O_2 distances for low energy to H–O_2 distances near 4.5 \alpha_0 (= 2.4 Å) for higher energies. The consequences for the capture dynamics are considerable. Figure 13 shows thermal capture rate constants, in the upper curve for PST (neglecting the anisotropy of the potential) with clear evidence for transition state (TS) switching, from an outer TS at low temperatures to an inner TS at temperatures above about 50 K. Taking into account the anisotropy of the potential, the capture rate constant \( k_{\text{cap}} \) decreases to the lower curve, but still showing the consequences of TS switching.

In the H + O_2 system, we first encounter the ‘open-shell dilemma’ of radical–radical reactions. All reaction partners are in open-electronic shells: H(2S_{1/2}), O_2(3\Sigma_{1g}), and HO_2(2A^{\prime\prime}, 4A^{\prime\prime}). The question arises which of the fine-structure states contribute to the reaction. Simply assuming that only the lowest states with a thermal population \( f_{\text{el}}(T) \) are relevant, conventionally one assumes that the high-pressure recombination rate constant \( k_{\text{rec,\infty}} \) here is given by

\[
k_{\text{rec,\infty}} \approx f_{\text{el}}(T)k_{\text{cap}}
\]

with \( f_{\text{el}}(T) = 1/3 \) (at ‘not too low temperatures’ and assuming that only doublets contribute). We come back to this point in the next section. Comparing this calculated \( k_{\text{rec,\infty}} \) with experimental falloff curves from Ref. [28], one obtains very good agreement (see Figure 14). The agreement even reaches over into the liquid phase, where H + O_2 → HO_2 plays an important role in the radiation chemistry of water [33]. For the full falloff curves [28], one needs information on collisional energy transfer again such as described above for the CH_4 + M system. One should mention that M = H_2O is a particularly efficient collider. It was suggested in Ref. [28] to identify the corresponding collision number \( Z \) with an HO_2–H_2O dipole–dipole capture rate constant instead of a Lennard-Jones collision number.

5. Open-electronic shell effects in radical–radical reactions

The question arises whether Equation (4.1) applies in general, i.e. whether a capture-controlled bimolecular reaction of open-electronic shell radicals proceeds on a single-potential energy surface, connecting the lowest electronic fine-structure states of the reactants with the electronic ground
state of the intermediate adduct, and whether Equation (4.1) accounts for this. The fine-structure states at large distances generally are degenerate or nearly degenerate. When the reactants approach each other, then there may be a multitude of electronic states of the adduct, before the latter states sufficiently separate at close approach. Figure 15 illustrates such a situation [34] for the association process C + HO → CHO. During the capture kinetics, there will be efficient non-Born–Oppenheimer mixing of the shown states. In order to quantify this mixing, the potential has to be determined including long-range electrostatic, dispersion, induction, and exchange interactions; in addition spin–orbit and electronic–rotational coupling has to be taken into account. The reaction C + HO → CHO is the single example where the corresponding non-Born–Oppenheimer coupling dynamics has been implemented into an adiabatic channel treatment accounting for electronic–rotational (rotronic) couplings [35]. The results of this generalised SACM treatment using asymptotic potentials here were compared with detailed calculations based on Equation (4.1), see also Ref. [36]. Figure 16 compares the resulting association rate constants $k_{\text{ass}}$. Over the range 15–200 K, the non-Born–Oppenheimer rate constant markedly exceeds the single-potential rate constant based on Equation (4.1) ($k_{\text{rec, } \infty}$ and $k_{\text{ass}}$ are equivalent). Apparently, rotronic coupling within the multitude of electronic states arising from the degenerate separated reactants generates a large amount of state mixing. This then leads to contributions from higher fine-structure states to capture into the electronic ground state of the adduct.

Other radical–radical reactions should be treated in a similar way. There is particular interest in the reaction HO + O → HO2 → H + O2. Low temperature experimental rate constants are shown in Figure 17. The experimental rate differ considerably below about 150 K. One would hope that theory helps to settle the situation. It looks that full quantum time-independent calculations of cross sections and classical trajectory calculations from Ref. [37] favour the lower experimental values. However, these theoretical results were based on Equation (4.1) and did not account for rotronic couplings like those treated for C + HO in Ref. [35]. Figure 17 may suggest that the latter effects raise the...
rate constants to the upper values shown [38]. First steps towards a non-Born–Oppenheimer treatment of the reaction \( \text{HO} + \text{O} \rightarrow \text{H} + \text{O}_2 \) have been done in Ref. [39], but more work is required. Extending the temperature range of Figure 17 up to 5000 K, where data for the reverse reaction \( \text{H} + \text{O}_2 \leftrightarrow \text{HO}_2 \rightarrow \text{HO} + \text{O} \) are available, one reaches conditions where a single-potential Born–Oppenheimer treatment becomes sufficient. Figure 18 compares the detailed results from Ref. [40] with experiments. Here, from 300 to 5000 K, experiment and theory agree satisfactorily without that reaction parameters have to be empirically fitted. However, this agreement was only obtained after the enthalpy of formation of the OH radical finally could be established in Ref. [41]. Without proper thermochemistry such agreement could not have been reached.

6. Conclusions

From quantum-chemistry to dissociation dynamics: of course, a complete and accurate knowledge of the potential energy surface(s) of the reaction would be desirable to have and quantum-scattering calculations on the potential(s) should be made. However, this may involve enormous effort whose finer results would finally be lost by thermal averaging. Therefore, the simpler approaches described here may provide sufficient insight for the time being and a combination of the semiquantitative theoretical results with experimental data may lead to the presently most realistic values of the rate constants.

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