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On the Accuracy of an Analytical Potential Energy Surface for the $CH_4 + Cl$ Reaction and the Quasi-Classical Trajectory Calculations for Thermal Rate Constants

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The $CH_4 + Cl$ reaction was studied by means of quasi-classical trajectory calculations using an analytical potential energy surface previously developed by Truhlar and two of the present authors. Our conclusion is that this analytical potential energy surface is accurate, and previous studies that questioned its quality were biased by the neglect of quantum effects.

Introduction

The $CH_4 + Cl$ reaction has been widely studied[1] because of its importance in atmospheric chemistry, since it can eliminate harmful chlorine atoms by reacting with methane whose importance for the greenhouse effect is well-established. Thus, many experimental studies have been devoted to the detailed analysis of the kinetics and dynamics of this reaction. Moreover, because of its small size, it has also been the subject of numerous theoretical studies. High-level ab initio calculations as well as accurate dynamical calculations are affordable for this reaction (see ref 2 and references therein).

In 2000, Truhlar and two of the present authors proposed an analytical potential energy surface (PES) to describe the $CH_4 + Cl$ reaction.[2] The PES was tested using canonical unified statistical theory with semiclassical multidimensional tunneling (CUS/MT), and it reproduces the behavior of the experimental measurements of thermal rate constants, kinetic isotope effects, and enhancement of the reaction rate by vibrational excitation.

However, in a recent work by García et al.,[3] quasi-classical trajectory (QCT) calculations based on this PES questioned its validity. Their QCT rate constants are significantly higher than our CUS/MT results, especially at low temperatures. In particular, the QCT values are about 200 times our CUS/MT values, and they are almost temperature-independent in the low-temperature range (i.e., the activation energy is close to zero). Given that tunneling is neglected by QCT methods, it would be more appropriate to compare QCT results to CUS results (without tunneling corrections). Thus, the QCT constants are almost 3 orders of magnitude higher than the CUS rate constants.

These results are surprising, and they question not only the PES we developed, but also statistical theories of reactions themselves. One can expect transition-state theory to overestimate the exact rate constant, because it neglects recrossing, so that the expected behavior would be the opposite to what is found. CUS methods may overestimate recrossing, but since the CUS recrossing factor has values between 1 and 0.5, it cannot be responsible for a QCT/CUS ratio larger than 2.

Moreover, it can be seen that the spin−orbit coupling of the Cl atom was not taken properly into account in ref 3, where the nonrelativistic QCT rate was divided by 3; the CUS results, however, do correctly include the two low-lying electronic states of Cl. Its effect on the rate constant is to divide the nonrelativistic rate constants by a temperature-dependent factor of about 2.0 at 200 K and about 2.3 at 1000 K. Therefore, the ref 3 results should be slightly lower than the CUS results.

Hence, it would be surprising if the independent harmonic normal-mode approximation employed in the CUS calculations, the vibration−rotation coupling, or the neglect of total angular momentum of transition-state theory were responsible for the remaining factor of 500. To elucidate the reasons for the discrepancies, we repeated the calculations of ref 3 on our PES.[2] Thus, the goals of the present work were to analyze the accuracy of the results of ref 3 and to test the validity of the PES of ref 2.

Results

To avoid introducing differences that could give rise to misleading conclusions, we repeated the calculations of ref 3 using the same settings: The rotational and translational energies were thermally sampled, vibrations were assumed to be in their ground state, and the maximum impact parameter was set to 8 Å. We performed QCT calculations at 200, 300, 500, 600, and 1000 K, also using the VENUS 96 code.[4] Our QCT results are shown in Figure 1 as filled squares, and they are essentially the same as those of ref 3. For comparison, the CUS and CUS/MT results are also shown as dotted and solid lines, respectively.

As we mentioned above, the QCT calculations do not include the effect of spin−orbit coupling on the Cl atom. This can be dealt with by multiplying the QCT rate constants by a multiple-surface coefficient[5]

$$f = \frac{2}{4 + 2\exp(-\Delta E/k_b T)} \qquad (1)$$

with k_b being Boltzmann's constant and ΔE the difference between the two low-lying electronic states of the chlorine atom, $Cl(^2P_{1/2})$ and $Cl(^3P_{1/2})$, 882 cm^{-1}.[6] This correction diminishes the QCT rates by a factor of about 2, as mentioned above.

We found it surprising that García et al.[3] used an a priori very large maximum impact parameter, 8 Å. However, it was

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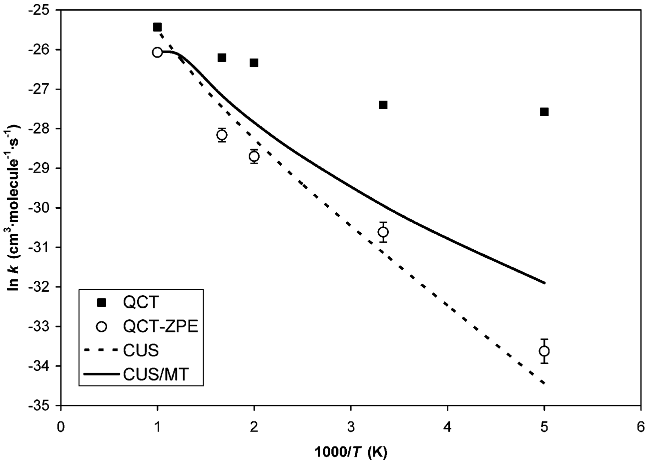

Figure 1. Arrhenius plot of the rate constants from QCT (solid squares), ZPE-corrected QCT (open circles), CUS (dashed line), and CUS/MT (solid line) calculations. The statistical uncertainty of the ZPE-corrected QCT calculations is shown by error bars.

even more surprising to find reactive trajectories with impact parameters over 7.9 Å. These trajectories were the key to understanding the reasons for the discrepancy between QCT and CUS rate constants.

Our PES has a van der Waals well in the entrance channel that is about 3 kcal/mol deep (note that this well is not an artifact of the PES, and ab initio calculations[7] also predict a well like this, although only 1 kcal/mol below the reactants). We found that, for some trajectories, as the Cl atom approaches the CH_4 molecule, even if it approaches it with a large impact parameter, the energy of the system decreases as a consequence of the van der Waals forces, eventually falling into the well. Thus, the Cl atom orbits around the methane molecule for a long period of time (more than 600 fs in some of our trajectories). During this time, there is an energy transfer from the CH_4 vibrational energy to the Cl, which eventually has the appropriate orientation and energy enough to collide with an H atom and break the C−H bond. The reaction thus takes place even though the collision occurred with low energy and large impact parameter. We found a large number of reactive trajectories for which the reaction takes place after a long orbiting time.

Most of these trajectories, however, are unacceptable in a nonclassical world. The reason is that the transfer of a large amount of vibrational energy to translational energy is a consequence of the fact that in a classical world the energy has no lower bound. Thus, in a classical world, the vibrational energy of the CH_4 molecule can lie below the vibrational zero-point energy (ZPE), and after a long orbiting time, the chances are that a large amount of vibrational CH_4 energy has been transferred to Cl translational energy. Therefore, the reaction that takes place is the collision between a hot Cl and a CH_4 molecule with a vibrational energy below its ZPE. These reactive trajectories need to be removed from our calculations, since they are an artifact of the QCT calculations and are not allowed in the quantized real world. Thus, to perform a better comparison between the QCT and CUS rate constants, we have to introduce a correction to the QCT calculations to avoid the ZPE leakage along the trajectories. This issue is commonplace in QCT calculations,[8,9] and many strategies have been proposed to correct the problem (see, for instance, refs 10 and 11, and references therein).

Here, we employed a so-called passive method[11] and discarded all the reactive trajectories that fulfill the following conditions:

1. The initial total energy is lower than the classical energy of the saddle point of the reaction plus its harmonic ZPE, since in a quantum-mechanical world, it could never overcome the barrier to reaction.

2. The vibrational energy of the products is lower than their ZPEs, within an error bar of 10% of the ZPE (derived from the error associated with the internal energy calculation).

The QCT results obtained after discarding these reactive trajectories are shown in Figure 1 as open circles. In general, they agree with the CUS results. Therefore, we can conclude that the analytical PES is accurate and that the ZPE problem of QCT calculations is particularly severe for this reaction on this PES. The fact that García et al. did not correct the ZPE problem is the reason underlying their erroneous conclusions on the lack of accuracy of the PES and the CUS calculations that led them to propose a different surface. Note that the new surface they proposed has no wells on the entrance channel; this may be the reason the ZPE problem is not so important for their QCT calculations on that surface.

The results plotted in Figure 1, especially the low-temperature rate constants, lack numerical precision (the uncertainties are shown by error bars) because of the inappropriate selection of initial conditions. The large value of the maximum impact parameter and the thermal distribution of collision energies lead to very few occurrences of reactive trajectories. Thus, at 200 K, we computed 2 000 000 trajectories and found only 8 reactive trajectories. To reproduce the CUS rate constant, we would need to find 1 reactive trajectory for every 550 000 nonreactive trajectories. To obtain precise values of the rate constant (less than 5% statistical error), it would therefore be necessary to compute a huge number of trajectories. Since a precise value of the QCT rate constant was not the goal of the present work, we did not carry out such a demanding calculation. A better choice of initial conditions would make this goal much more affordable (shorter maximum impact parameter, performing trajectory calculations at fixed collision energies and then averaging the energy-dependent rate constants, etc.), but we used the same initial conditions as García et al. so as to compare our results to theirs.

One can indicate several reasons for the discrepancies between the CUS results and the ZPE-corrected QCT results, in particular, that the low-temperature QCT values are about twice the CUS results, while at high temperatures, the behavior is the opposite, the CUS results being about twice the QCT. First, it could be due to some recrossing, which one assumes to be more important at high temperatures and would lead to an overestimate of the CUS rate constants. Second, anharmonicity, which usually makes harmonic CUS rate constants too high, could also have an important effect. Third, vibrational excitation, which is taken into account in the CUS calculations but is neglected in the QCT ones (since the CH_4 vibrational modes were set to their ground states), could also have a major influence especially at high temperatures.[1] Fourth, another possible cause may be the way of estimating the ZPE correction of the products, which might be too approximate. For instance, Varandas[12] proposed a method to correct the ZPE problem, named QCT-IEQMT, and found that for the $H + O_2$ reaction at low energies the QCT-IEQMT values are smaller than the corresponding ZPE-corrected QCT values, while for high energies, they may even become larger. If these results were extrapolated to our calculations, the QCT-IEQMT method would agree better with the CUS rate constants than the ZPE-corrected QCT ones. Fifth, the aforementioned statistical errors due to the very low percentage of reactive trajectories could also have some effect, especially at low temperatures. It is possible that all or some of these factors may be involved, but as was mentioned above, a precise value of the QCT rate constants was not the goal of the present work.

Conclusions

The present work shows that, contrary to the conclusions of García et al.,[3]

1. The PES we developed[2] for the $CH_4 + Cl$ reaction is accurate and appropriate for QCT calculations whenever ZPE effects are taken into account.

2. The lack of agreement between the results of García et al. and the CUS values is not due to deficiencies of the PES, but to the fact that the ZPE corrections to the QCT calculations are very important for this reaction on this analytical PES.

3. To obtain precise values of the thermal rate constants, it is advisable not to use the same settings that García et al. used, since the number of trajectories required would be enormous.

Obviously, only a full-dimensional quantum study of this polyatomic system would clarify the doubts about our analytical PES. However, the excellent agreement between our CUS/MT results[13,14] and the very sophisticated quantum-mechanical values[15,16] for the $CH_4 + O$ and $CH_4 + H$ reactions using analytical PESs developed in our group[13,14] with similar functional forms and calibration procedures permit a certain optimism.

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