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An open molecular science cloud approach to the H + CH_2 low temperature reactivity

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Abstract – As a test bed for the implementation of an Open Molecular Science Cloud (OMSC) approach to low temperature chemical reactivity, we investigated the temperature dependence of the rate coefficient of the title reaction. We used for that purpose extended quasi-classical trajectory calculations implemented on the cloud and focused on the efficiency of the H extraction process so as to validate the rate coefficient values commonly adopted by some popular kinetic databases also at low temperatures. The calculations clearly indicated that the computed low temperature (around 10 K) rate coefficient of the H + CH_2 H extraction process is not temperature independent (as quoted in some popular kinetic databases) and that it reproduces, within a factor of two, the positive trend suggested by the experiments of Fulle and Hipper in their J. Chem. Phys. 1997, 106, 8691-8698 paper.

Keywords: OMSC; rate coefficient; H extraction; kinetic database

Riassunto – Come banco di prova per l'implementazione di un approccio Open Molecular Science Cloud (OMSC) alla reattività chimica a bassa temperatura, abbiamo studiato la dipendenza dalla temperatura del coefficiente di velocità della reazione in oggetto. Abbiamo utilizzato a tale scopo calcoli di traiettorie quasi-classiche estesi implementati sul cloud e focalizzati sull'efficienza del processo di estrazione di H in modo da validare i valori di coefficienti di velocità comunemente adottati da alcuni noti database cinetici anche a basse temperature. I calcoli hanno indicato chiaramente che il coefficiente di velocità a bassa temperatura calcolato (circa 10 K) del processo di estrazione di H di H+CH_2 non è indipendente dalla temperatura (come riportato in alcuni noti database di cinetica) e che riproduce, entro un fattore due, l'andamento positivo suggerito dagli esperimenti di Fulle e Hipper nel loro articolo su J. Chem. Phys. 1997, 106, 8691-8698.

Parole chiave: OMSC; rate coefficient; H extraction; kinetic database

Introduction

In order to activate a European Open Science Cloud [1] (EOSC) approach to the sharing of validated Molecular Science (MS) data for modelling the efficiency of chemical processes at different temperature (T) ranges in accuracy sensitive applications for astro-chemistry, combustion, environment, etc. use has been made in the past of infrastructures and services established by the MS community members within COMPCHEM VO[2], CMMST VRC[3], D23 [4] and D37 [5] COST Actions, ECTN [6], EGEE III [7] and EGI Inspire [8] projects, etc. At present our activities are being directed towards contributing to the creation of the MS contents of the EOSC portal. EOSC is in fact an initiative aimed at developing a trusted, open environment for the scientific communities for storing, sharing and re-using scientific data and results leveraging the supercomputing capacity, the fast connectivity and high capacity of present cloud solutions provided by the European Data Infrastructure (see Figure 1).

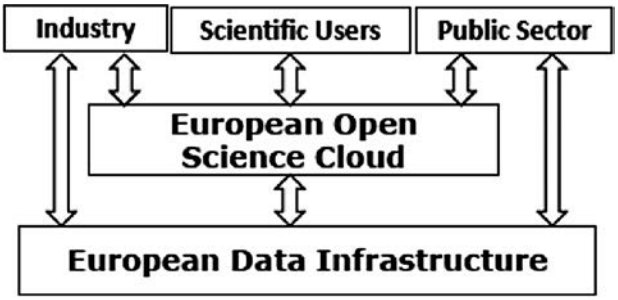

Fig. 1. The basic scheme of the European Open Science Cloud.

As a matter of fact, EOSC aims at developing cloud based services for Open Science by creating a specific pan-European governance structure that generalizes the openness of data produced, develops interoperability and data sharing across disciplines and infrastructures and enlarges the user base to researchers and innovators from all disciplines. Accordingly, the EOSCpilot project [9], in addition to establishing a governance framework, has supported the development of a number of demonstrators in Environmental and Earth Sciences, High Energy Physics, Social Sciences, Life Sciences and Physics.

The basic articulation of the activities common to all disciplines is:

- a. Produce/Discover/Access/Download available MS data set(s)
- b. Running/Checking/Terminating/Validating: MS data set(s)
- c. Annotating/Curating/Preserving: specific MS data set(s)
- d. Evaluating and Rewarding the Quality of Provided Services

The OMSC approach

In recent years, the attention to Open Science and its cloud services has increased among the members of the MS community (even if MS is not included in the list of disciplines supported by EOSCpilot). In particular, the members of the MS community have been actively involved in designing and developing the Molecular Open Science Enabled Cloud Services (MOSEX) [10] infrastructure for:

a) *producing/discovering and downloading* MS data for the open collaborative and fully re-usable databases and repositories. For this purpose CHEMCONNECT [11], ioCheM-BD [12] and QCArchive [13] open databases of FAIR (Findable, Accessible, Inter-operable and Re-usable) validated data enhancing TOP (Transparency and OPenness) MS knowledge are used by promoting good scientific practices of accountability, traceability and reproducibility;

b) *running/checking/correcting (where possible) or discarding and validating* data of service (a) through iterative cycles collaboratively undertaken by the members of the community for the validation of MS data by comparing results obtained by different users when adopting different computational tools;

c) *annotating/curating/preserving* data of service (b) for a more efficient re-use according to the standards adopted by the EOSC-Pillar initiative. The development of appropriate tools for their efficient re-use will be of invaluable help in order to further enhance research and applications by public institutions and private companies;

d) *evaluating the quality of services* (a), (b) and (c) provided by the members of the MS community using QoS (quality of service) techniques while the users will be profiled using QoU (quality of users) techniques;

e) *offsetting debits with credits of the adopted Prosumer (Producer+Consumer) model* (at present experimented only for the electronic assessment EChemtest® product) in which the community members are at the same time users (making debits for used services) and producers (gaining credits for produced services) of cloud services and some Market spinners take care of offering auxiliary paid services to external users (http://ectn.eu/committees/virtual-education-community/echemtest/).

The specific case of rate coefficients of gas phase chemical reactions

Through the collaborative efforts of the members of the MS community several computational tools needed for the calculation of rate coefficients project will provide their services in the area "gas phase chemical reactions". In this case the blocks involved in the operational diagram are (see Figure 2):

α) the construction of the potential energy surface governing the process out of the cloud implemented electronic structure calculations (lhs panel);

β) the evaluation of the rate coefficient of the reactive process out of the cloud implemented integration of the dynamical equations of the involved atomic nuclei (central panel);

γ) the Data Handling cloud services mentioned in the previous section.

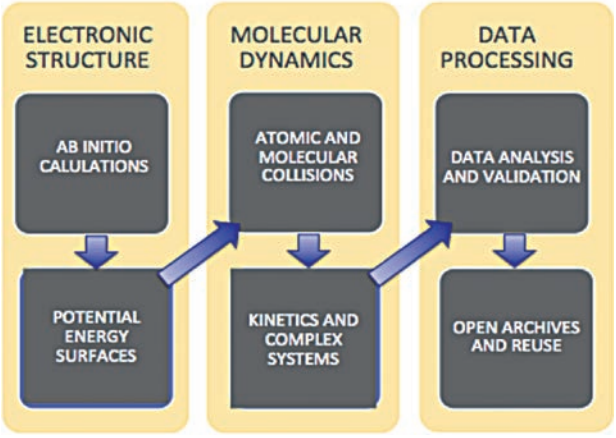

Fig. 2.The basic scheme of the European Open Science Cloud.

The different blocks of Figure 2 are:

Block α is the most typical MS theoretical and computational area and several computational tools of different quality (depending on the complexity of the molecular systems involved) are available for the purpose of carrying out ab initio electronic structure calculations and the subsequent formulation of the resulting potential energy surface as a suitable functional form in the cloud environment;

Block β is either a classical trajectory or a quantum mechanics (or a mixed quantum classical one) dynamical treatment of the nuclei equations performed for the different initial collision and internal energy values necessary for evaluating thermal rate coefficients in the cloud environment;

Block γ is the MOSEX implementation following the analysis and validation of related data and the database and repository storage for open collaborative re-use.

The accurate evaluation H + CH_2 → H_2 + CH rate coefficient

The H + CH_2 reaction plays an important role in astro-chemistry studies because H, CH_2, H_2 and CH are among the most abundant species in the inter-stellar medium. Accordingly, accurate estimates of its rate coefficients need to be provided in order to ground the computational modelling of some astro-chemistry phenomena on accurate estimates of the dependence of related efficiency parameters on the temperature T. In particular, for the modelling of the properties of the inter-stellar medium, temperature values as low as 10 K need to be considered.

The only measured values of the thermal rate coefficient of the title reaction in the T range 298-3000 K are those of ref. [14] with those at T = 300 K differing almost one order of magnitude among them. Experimental data for a reasonably extended temperature interval (13-744 K) are also available [15] for the inverse reaction CH + H_2.

Rate coefficient values of the title reaction quoted in kinetic databases like KIDA [16], UDfA [17] and OSU [18] are taken as temperature independent for a wide range of temperatures. On the contrary, the formula inferred by Fulle and Hippler [19] to rationalize the temperature and pressure dependence of the outcome of their experiment and by Hebrard [20] to rationalize the properties of the atmosphere of Titan for the rate coefficient ($2.2x10^{-10}(T/300)^{0.32}$), exhibits a positive temperature dependence.

Calculations of the thermal rate coefficient for the

$$H(^2S) + CH_2(X^3B_1) \rightarrow H_2(X^1\Sigma^+_g) + CH(^2\Pi) \quad (1)$$

abstraction process were performed by adopting the already implemented experimental steps of the above mentioned MOSEX procedure. The MHG [21] Potential Energy Surface (PES) exoergic by 4.1 kcal/mol, with no barrier to reaction and having a well of 115.4 kcal/mol in the strong interaction region (corresponding to the methyl radical stable geometry) was used. Quasi-classical trajectory (QCT) calculations were performed using a cloud version of Venus96 [22]. The code was modified to incorporate the MGH PES, numerically evaluate the PES derivatives and use a model quantum mechanical formulation of the angular momentum and

rotational energy. The time step adopted to perform the time integration of the trajectories was 0.01 fs. An initial atom diatom distance of 13.7 Å and a maximum impact parameter value of 8.7 Å were adopted. The full thermal rate coefficient values k(T) were calculated from 5 to 1000 K. Computed k(T) values are plotted in Figure 3 as a function of T.

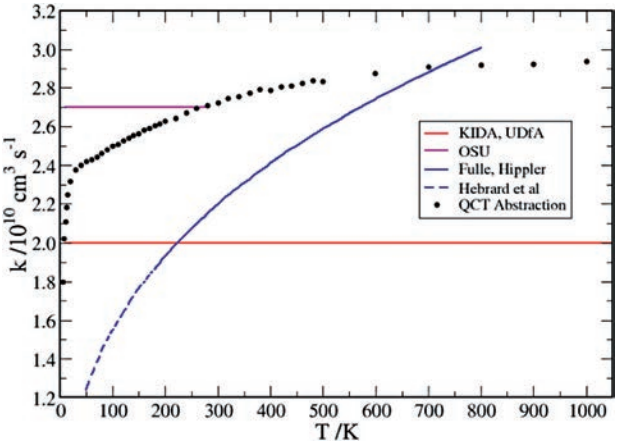

Fig. 3. Full thermal abstraction rate coefficient values plotted as a function of T.

The plots show a mild increase of k(T) with temperature. For comparison also values measured by Fulle, Hippler and Hebrad et al are shown together with the constant values quoted in the KIDA, UDfA and OSU libraries.

Conclusions

The use of the preliminary cloud version of MOSEX is found to work properly for computing the rate coefficients of the title system. The outcomes of the reported calculations clearly show the inaccuracy of the rate coefficient values quoted by the popular astro-chemistry KIDA, UDfA and OSU libraries and clearly indicate a positive temperature dependence in the temperature range of interest for related simulations. The computed k(T) values will be made available to the MS community on the being assembled repositories of the MOSEX project.

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