

Radiation chemistry in astrochemical models: From the laboratory to the ISM

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Abstract. Most interstellar and planetary environments are suffused by a continuous flux of several types of ionizing radiation, including cosmic rays, stellar winds, x-rays, and gamma-rays from radionuclide decay. There is now a large body of experimental work showing that these kinds of radiation can trigger significant physicochemical changes in ices, including the dissociation of species (radiolysis), sputtering of surface species, and ice heating. Even so, modeling the chemical effects that result from interactions between ionizing radiation and interstellar dust grain ice mantles has proven challenging due to the complexity and variety of the underlying physical processes. To address this shortcoming, we have developed a method whereby such effects could easily be included in standard rate-equations-based astrochemical models. Here, we describe how such models, thus improved, can fruitfully be used to simulate experiments in order to better understand bulk chemistry at low temperatures.

Keywords. astrochemistry, atomic processes, diffusion, comets: general, ISM: cosmic rays, ISM: molecules

1. Introduction

As the launch date for the James Webb Space Telescope (JWST) draws nearer, so does a new astrochemical “ice age.” Unfortunately, however, the current treatment of chemistry on and in dust-grain ice mantles used in astrochemical codes remains, in many cases, either simplistic or uncertain. For example, two major shortcomings of most current models are, (1) the very limited treatment of cosmic ray/dust interactions, despite the fact that the resulting physicochemical effects are known to be significant (Rothard *et al.* 2017), and (2) uncertainty regarding how chemistry in the bulk of dust-grain ice mantles is treated, specifically, whether or to what degree bulk-chemistry is driven by diffusion, and if so, what is the underlying mechanism, e.g. swapping or diffusion along interstitial sites. If models do include bulk chemistry, rate coefficients are calculated from diffusion barriers that are highly speculative and usually assumed to be $\sim 70\%$ of the desorption energy (Garrod 2013). This diffusive assumption means that, at low temperatures, the often large bulk diffusion barriers lead to slow reaction rates, even for radicals, thereby causing the calculated abundances of such species to become unphysically large.

2. Model description and Results

We have attempted to address these two shortcomings in astrochemical modeling through simulations, not of ill-constrained interstellar systems, but rather, of well-constrained laboratory astrophysics experiments on ion-irradiated ices (Shingledecker *et al.* 2019). Doing so gives us an unprecedented insight into how well (or poorly) our models are actually reproducing real ice chemistry. As described in Shingledecker *et al.*, we carried out simulations of both pure O₂ and pure H₂O ice, irradiated by 100 and 200 keV H⁺, respectively. For each ice system, the following three sets of models were run:

Model A: Here, radicals within the ice were assumed to react non-diffusively. For the reaction A + B, where either reactant is a radical, rate coefficients were calculated using $k_{\text{fast}} = [(\nu_0^A + \nu_0^B)/N_{\text{bulk}}] \exp(-E_a^{AB}/T_{\text{ice}})$, where ν_0 is the characteristic vibrational frequency for the reactants, N_{bulk} is the total number of bulk species, and E_a^{AB} is the activation energy for the reaction. This formula is therefore similar to the standard Langmuir-Hinshelwood expression, but lacks the term accounting for diffusion.

Model B: Our fiducial model, in which all bulk species are assumed to react via thermal diffusion;

Model C: Similar to Model B, but with the additional assumption that H, H₂, and O tunnel under bulk diffusion barriers.

For the pure O₂ ice we compared calculated O₃ abundances with those measured by Baragiola *et al.* (1999) at 5 K. A similar method was used in the pure water system with H₂O₂, where abundances at 16 and 77 K having been measured by Gomis *et al.* (2004). In all cases, we found Model A to give the best agreement with experiments. In the H₂O ice, moreover, only Model A predicted the previously measured decrease in H₂O₂ concentration at ~80 K, compared with values at lower temperatures (Gomis *et al.* 2004).

3. Conclusions

These data serve to establish three main points. Firstly, we have shown that even comparatively simple astrochemical models, suitably modified, are capable of simulating the kind of radiation chemistry driven by cosmic rays and other energetic particles. Secondly, though, our data clearly show that bulk chemistry is best modeled using a non-diffusive approach for at least reactive species such as radicals. In so doing, not only do we achieve a satisfying agreement between our models and experiments, we also both eliminate the need to rely on the dubious values for barriers against bulk diffusion currently employed, and keep the abundances of radicals - which collectively should not comprise more than ~1% of the ice (Greenberg & Yenchu 1973) - at more realistic levels. Thirdly, this work highlights the utility of simulating well-constrained laboratory astrophysics experiments which, as shown here, can help prepare models for the coming astrochemical “ice age.”

References

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