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Heterogeneous radiolysis of urea. Implications in astrobiology and prebiotic chemistry

Abstract: Urea is an organic molecule present in most living organisms. Historically, it was the first organic molecule synthesized in the laboratory. In prebiotic chemistry, urea readily forms in different laboratory simulations using different energy sources. Furthermore, the role of solid surfaces, particularly minerals, might have been crucial to increase the complexity of the organic matter which may have led to the subsequent emergence of life on Earth.

In this work, the radiolysis of urea in presence of a clay is studied to determine to what extent the mineral surfaces influence the decomposition of organics. The results indicate that urea is relatively stable to ionizing radiation in aqueous solutions and up to 20 kGy no decomposition is observed. Moreover, the presence of sodium montmorillonite, by a mechanism until now unknown, affects the radiolytic behavior and urea remains in the heterogeneous solution without a change in concentration even at very high doses (140 kGy). These results indicate that solids could have protected some organics, like urea, from degradation enabling them to remain in the environment on the primitive Earth.

Keywords: Urea, gamma radiation, chemical evolution, montmorillonite

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1 Introduction

Urea is an organic molecule with a molecular formula CON_2H_4 . This compound was one of the first organic molecules obtained by synthesis in the laboratory [1]. Urea is currently present in the urine and dung of many animals because of the degradation of nucleic acids and proteins. For instance, in the majority of animals, pyrimidines are degraded to ammonia and urea, and the amino moiety of the amino acids, ingested in the form of proteins, is converted into urea; the liver of mammals is also able to synthesize it [2]. Urea is also present in fungi, as well as in the larvae of invertebrates and seeds of numerous legumes and cereals.

From the point of view of prebiotic chemistry, urea is easily formed in different experiments. For example, sparking mixtures of H_2 , H_2O , NH_3 or N_2 or CO or CH_4 and CO_2 produces urea [3,4]. In addition, the irradiation with protons [5], beta rays [6], and X rays [7] yield urea from a mixtures of gases (methane, ammonia, and water). It is also easily synthesized from the irradiation of hydrogen cyanide (HCN) in a liquid or solid state [8]. Additionally, it has been suggested that the participation of urea in different reactions could have favored the synthesis of more complex organic compounds. Regardless of this, Robertson and Miller [9] suggested that the reaction of cyanoacetaldehyde (formed by the hydrolysis of the cyanoacetylene) with urea gives the formation of cytosine, a pyrimidine base. In this latest experiment, the concentration of urea is very high, and some authors [10] have noted that these conditions are not naturally occurring.

The chemical evolution had been understood by studying the reactions that might occur in a single phase, for example in the atmosphere. Even though, in the 1950s a new idea proposed by Bernal [11] suggested that surfaces (specifically clay minerals) might have served, at the interface composed of the hydrosphere and the lithosphere, as sites for concentration and catalysis of different reactions. They also could have served as places of shelter,

where the molecules might not be degraded by the same sources that formed them. Solid surfaces perhaps could also have contributed to the self-organization of monomers. Therefore, in this work we have looked deeper in the study of the effect played by solids in the radiolysis of urea.

2 Experimental procedure

All chemicals used were of the highest purity available. The glassware was cleaned with a sulfo-nitric solution according to the procedures recommended in Radiation Chemistry [12].

The testing of some minerals (*i.e.*, olivine and sodium montmorillonite) was performed to study the adsorption of urea. The clay was obtained from the Clay Minerals Repository of the Clay Mineral Society (Missouri, U.S.A.)

2.1 Adsorption experiments

The urea solutions (5 mL, 10^{-4} mol L⁻¹) were mixed with 0.5 g of the mineral (sodium montmorillonite or olivine), the samples were stirred in a vortex and kept in agitation for 15, 30, 60 and 120 minutes. The experimental procedure with minerals was performed at different pH values: the natural pH of the urea solution (pH = 6.7), then the pH was adjusted by the addition of drops of HCl (pH = 2) or NaOH (pH = 12).

2.2 Irradiation experiments

Irradiations were carried out in a gamma source of cobalt-60, Gammabeam 651-PT (Instituto de Ciencias Nucleares, UNAM) at different irradiation doses (10-140 kGy), with a dose rate of 170 Gy min⁻¹. Dose was determined by a ferrous sulfate-cupric sulfate dosimeter [12].

Two sets of samples were prepared: aqueous solutions of urea without clay (homogeneous systems) and with it (heterogeneous systems). The first set of samples consisted on 5 mL of deaerated urea (10^{-4} mol L⁻¹) that were put in glass syringes for irradiation. For heterogeneous samples, the clay (0.5 g) was evacuated during 4 h in 5 mL glass tubes with a stopcock. Five milliliters of the deaerated urea solution (10^{-4} mol L⁻¹) were added to the clay in an atmosphere bag filled with argon. The supernatant was separated by centrifugation, for 15 min at 15,000 rpm, in a Beckman Allegra centrifuge. The percentage of urea not adsorbed on the mineral was determined by spectrophotometry.

2.3 Analysis

Urea was quantified by spectrophotometry using the DAM method, which is based in the reaction of urea with diacetyl monoxime (DAM) in the presence of a catalytic solution (FeCl₃·6H₂O: thiosemicarbazide: H₂SO₄ and H₃PO₄), forming a red complex with a maximum of absorption in the visible spectra at 526 nm. To accurately quantify the concentrations of urea in the sample, calibration curves were built using this method. The calibration curves were made by triplicate. The same procedure was followed in homogeneous and heterogeneous samples (after centrifugation) to determine the percentage of remnant urea.

2.4 Modeling

The molecular structure of urea was optimized by Ground State, Hartree-Fock 3-21G(0) basis set (solvated in water). Here, preliminary results of the potential coordination of the urea to the inorganic local groups of the montmorillonite are presented. This insight aims to understand how the molecular structure of the urea changes when interacting with the mineral parts. The total energy, dipole moments and Mulliken charges were obtained with Gaussian 03 package (Gaussview) [13].

3 Results and discussion

The results show that urea can be accurately quantified by the DAM method. Fig. 1 shows the calibration curve used to make the determination. Experiments of the adsorption of urea into sodium montmorillonite and olivine showed that the adsorption in our system was nil. These results did not change by modifying the concentration of urea, which was diminished by an order of magnitude (from 1×10^{-3} to 1×10^{-4} mol L⁻¹), or by increasing the contact time. In our previous experiments we detected that a pH change toward an acidic environment favors the adsorption of certain organic molecules on the surface of the clay [14]. However, in this case, we did not notice any change in the dynamics of the molecule adsorption by changing the pH (Fig. 2). These results strongly contrast with those reported previously by other authors [15,16], who reported urea adsorption on the clay; this difference can probably be attributed to the experimental conditions and the determination method. The DAM method is very sensitive at low urea concentrations such as ours (10^{-4} mol L⁻¹). Other studies claim that urea is readily

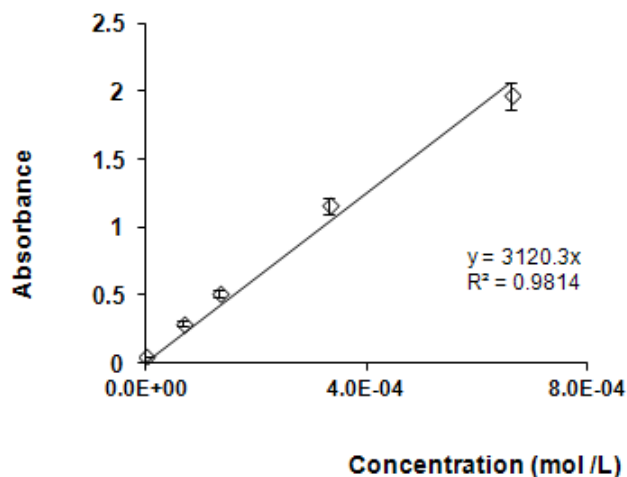


Figure 1: Calibration curve for urea with the DAM method.

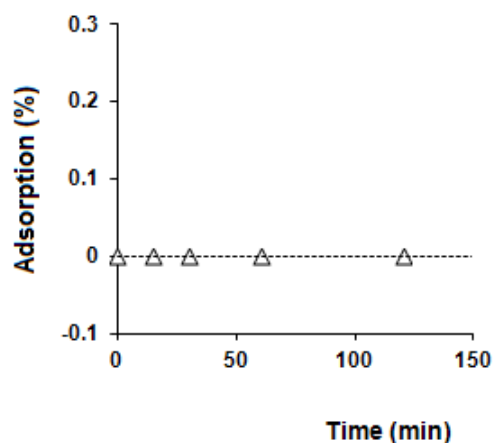


Figure 2: Adsorption curve of the urea onto sodium montmorillonite (10^{-4} mol L^{-1} , pH=2). There is no adsorption of the organic molecule into the clay.

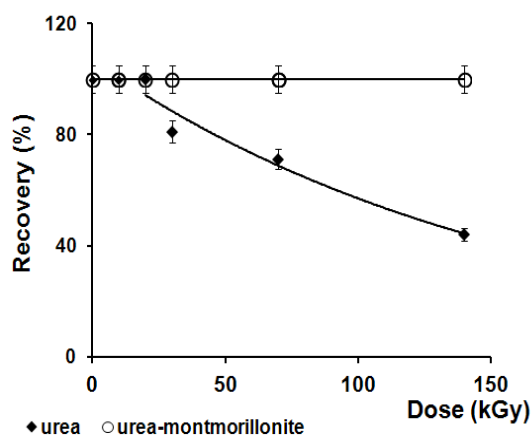


Figure 3: Urea decomposition as a function of dose. Legend: aqueous solutions of urea 10^{-4} mol L^{-1} (◆), urea (10^{-4} mol L^{-1}) and sodium montmorillonite in heterogeneous samples (○).

absorbed by soils [17]. Nevertheless, soils are naturally complex, and the diversity of minerals present in a soil sample can be crucial in the differential adsorption of urea.

The decomposition of the aqueous solution of urea as a function of the irradiation dose is shown in Fig. 3. The aqueous solution of urea presented a relative stability under irradiation, and it was observed that at doses below 50 kGy the decomposition was low, but above that dose strength the decomposition increased rapidly. These decomposition results are consistent with previously published studies, where radiolysis of aqueous solutions of urea (0.05 mol L^{-1}) was carried out [18]. The solutions of urea show a good response to ionizing radiation, and this behavior must be studied in depth due to the potential use of the molecule as a retrospective dosimeter. Since, dosimetry needs a joined-up approach and new methods development [19], the use of organics like urea is very promising.

In the experiments in heterogeneous systems, the presence of montmorillonite modified the behavior of urea, and the decomposition was very low. It has been previously demonstrated that at those irradiation doses montmorillonite does not suffer an alteration in its lattice [20]. In these experiments, the clay protects the organic molecule from the action of radiation, through a yet unidentified mechanism. Nonetheless, our preliminary theoretical results (total energy, dipole moments and Mulliken charges) are in agreement with the experimental studies, which show an important decrease in the energy when urea interacts with silicate and sodium groups (Table 1 and Fig. 4). A more detailed analysis will be performed since the urea molecular structure is modified in terms of the parameters related to the dipole moment when interacting with the sodium ion. Current experiments of irradiation with other solid surfaces (olivine, pyroxene and attapulgite) show the same results and no decomposition of urea was detected.

4 Conclusions

In the context of prebiotic chemistry, the synthesis of compounds that could serve as raw material for further reactions is very important. The synthesis of compounds of biological importance is just as important as their stability in the prebiotic scenario, as well as the existence of protection mechanisms that helped the already formed molecules to protect against decomposition. This work indicates that clay minerals might contribute to shelter

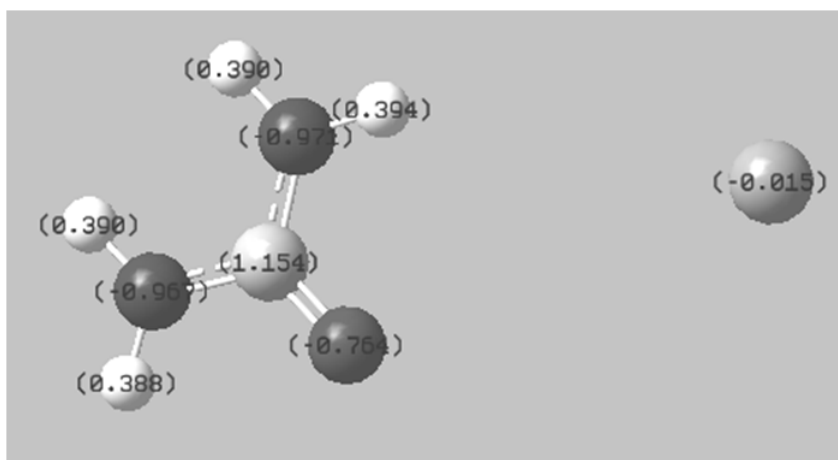


Figure 4: Local molecular charges in urea change when interacting with the clay (Mulliken charges).

Table 1: Simulated molecular features change of urea through non-covalent interactions with the silicate and cation from the clay.

Molecule	Energy (Hartrees)	Dipole moment (Debye D)	Convergence
Urea	-222.75	5.96	Yes
Silicate	-289.69	0.00	Yes
Na+	-160.40	0.00	Yes
Urea to Silicate	-512.45	5.94	No
Urea to Na+	-383.60	4.36	No
Na+ to Silicate	-450.50	3.75	No

certain organic molecules, in this case urea, from decomposition. Results indicate that although urea is not adsorbed on sodium montmorillonite, the presence of the solid affects the stability of the organic molecule, probably by lowering the total energy of the system. The type of reactions that involve a solid could be very important as protection mechanisms or catalysis of reactions from the point of view of chemical evolution. The results showed the protective role of the clay against ionizing radiation. This is a distinct advantage, since the molecules that were formed by ultraviolet light, ionizing radiation, or electric discharges had to survive in order to interact with each other to form more complex molecules.

Clay minerals might have played an important role in the early stages of the Earth. They are considered the most likely inorganic materials to have promoted organic reactions at the interface of the hydrosphere and lithosphere. The relevance of clay minerals in the emergence of the origin of life is due to their ancient origin, their wide distribution and especially their physico-chemical properties. Clays are known to have a high affinity for organic compounds. Bernal [11]

suggested that: a) clays act as concentrators of biological precursor molecules; b) in the clays, polymerization to macromolecules was possible; c) clays might protect these molecules from high-energy radiation, as in the case with urea exposed to gamma radiation in our experiments.

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