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Anion formation in gas-phase potassium–uridine collisions

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We dedicate this contribution to Professor Tilmann Märk, not only a distinguished scientist but also a loyal colleague and trusted friend, on the occasion of his 70th birthday.

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ABSTRACT

In this study we report negative ion fragmentation patterns obtained from time-of-flight (TOF) mass spectrometry in potassium–uridine collisions at 30, 70 and 100 eV. The dominant fragments from uridine are also the most abundant from the individual units in potassium collisions with uracil, tetrahydrofuran (THF) and D-ribose. We observe no dehydrogenated parent anion formation. Special emphasis is given to the dissociation mechanisms lending support to the breaking of the N-glycosidic bond as an initial step in the fragmentation of the transient negative ion (TNI). Within their role as sugar unit surrogates, THF and D-ribose (DR) provide useful information for the study of uridine, and presumably other nucleosides from the point of view of DNA/RNA subunits integrity in the biological environment.

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1. Introduction

The interest in studying electron interactions with increasingly complex sub-units of the DNA/RNA molecule follows from an initial breakthrough set of studies that relates electron-induced molecular reactions in DNA/RNA constituents to the creation of single and double strand breaks, as well as loss of helicity [1]. Owing to the need for greater knowledge of how the DNA molecule behaves in its natural environment, two different research pathways can be followed from: (1) increasing the complexity of the target molecule, i.e. starting with the nucleobases but progressively increase their complexity (e.g. nucleosides and there on); (2) the presence of free electrons in the physiological environment is somewhat of an insufficient model of how electron-induced reactions occur in the biological medium. As such, studies of interactions with bound or quasi-bound electrons with a particular molecular target can provide valuable insight to the underlying molecular mechanisms. By studying electron transfer processes to uridine, we attempt to address both of these approaches.

As far as free electron interactions are concerned, theoretical [2] and experimental [3] studies on nucleosides have been reported in the gas-phase. Furthermore, it is also worth mentioning the extensive work on dissociative electron attachment (DEA) to uridine's constituents, i.e. uracil [4–6] and the sugar unit surrogates [7–11]. In contrast, studies pertaining to electron transfer to these molecules are somewhat scarce, with literature only available for pyrimidine-like bases [12–15] and sugar unit surrogates [16,17].

In this study, we report negative ion time-of-flight mass spectra from collisions of neutral potassium atoms with uridine. The negative ions result from a transfer of an electron from the neutral potassium to the uridine (dU) molecule, as:

$$K + dU \Rightarrow K^+ + (dU^*)^- \quad (1)$$

where K represents the potassium atom and dU the uridine molecule. After electron transfer, the resulting transient negative

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ion (TNI) will eventually decay through several possible pathways. It is critical to note that the presence of the potassium cation after electron transfer can greatly affect not only the initial state of the resulting TNI, but also the pathways through which the decay of the TNI proceeds. Briefly, electron transfer in atom–molecule collisions is based on the premise that, at a given distance between the potassium and the target molecule (designated by R_c), there is a probability for the valence electron of the potassium atom to be transferred to the molecule due to a coupling between the covalent and ionic states of the [K + dU] and [K^+ + $(dU^*)^-$] systems. The anion yields as a function of the collision energy that result from this electron transfer will provide valuable information about the occupied states and the collision dynamics. Such information, apart from the obvious fundamental importance in understanding the nascent mechanisms behind DNA/RNA damage by incident radiation, is also critical from a more applied point-of-view. In particular, recent advances in Monte Carlo-based simulations (e.g. PENELOPE and Low Energy Particle Track Simulations [18]) of radiation transport and energy deposition in tissue-equivalent materials [18] have shown the relevance of electron transfer processes. These simulations are an important complement in dosimetry for clinical applications, and owing to their empirical nature, require data regarding several underlying molecular processes that result from the interaction of the primary radiation and the secondary species formed along its track.

2. Experimental details

The experimental setup used to obtain the TOF mass spectra has already been described elsewhere (see e.g. [14]). Briefly, the neutral hyperthermal potassium beam is obtained when positively charged potassium atoms accelerated to a particular energy value pass through a chamber where they resonantly charge exchange with neutral thermal potassium atoms. A pair of deflecting plates is used to both monitor the K^+ beam and deflect the ionic potassium atoms that did not charge exchange. The target molecule is brought to the gas-phase by means of a lamp-heated molecular oven to yield an effusive molecular beam. The potassium and molecular beams collide within a collision region, where a pulsed electric potential of −400 V repels the resulting negative ions into a modified Wiley–Mclaren-type mass spectrometer, where the negative ions are TOF mass analysed. Owing to the large mass of the target molecule (244 u), the present spectra were obtained with a pulsed beam technique, with a 2 μs width in a 80 μs duty-cycle. This method allows for a much better determination of adjacent mass peaks, which proved to be important in the 39–45 mass range. This method has the disadvantage of providing a significantly lower yield than the obtained using a continuous beam method. For each mass spectrum, a corresponding background spectrum was also acquired and subtracted, in order to account for the residual gas.

A critical experimental issue regarding this study lies in guaranteeing that uridine molecules remain intact after being brought into the gas-phase. Indeed, this issue was a subject of discussion in a recent DEA study on both uridine [19] and thymidine [3], where it was shown that at temperatures of ∼420 K, only a marginal amount of molecules appear to be fragmented by the heating process. Likewise, additional care was taken in order to prevent such decomposition. Indeed, TOF mass spectra (not shown) were obtained at higher temperatures (∼433 K) and major differences in the relative intensity of fragment anions (as well as appearance of new fragments) were observed. As such, the operating temperature of ∼405 K was determined to provide a good compromise between signal intensity and avoiding thermal decomposition.

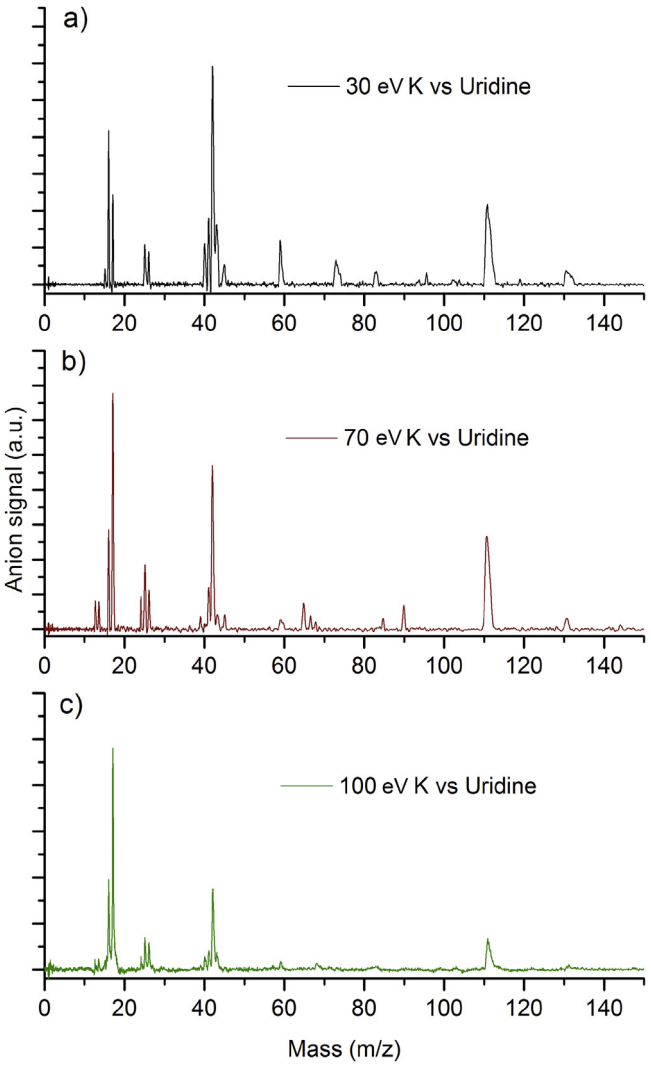

Fig. 1. TOF mass spectrum of potassium–uridine collisions at: (a) 30 eV; (b) 70 eV; (c) 100 eV collision energy in the laboratory frame.

3. Results and discussion

The negative ion TOF mass spectra obtained for 30, 70 and 100 eV potassium energies in the lab frame are presented in Fig. 1(a–c). The branching ratios (BR) for the main anionic products are presented in Fig. 2, and peak assignments are shown in Table 1.

A simple glean of the spectra shows a roughly similar fragmentation pattern for all collision energies. This study presents a quite rich fragmentation pattern, with the main fragments being O^-, OH^-, CNO^- and $(U\text{-}H)^-$, amounting to ∼60% of the total anion yield. It is interesting to note that these fragments are also dominant anionic species in potassium collisions with the corresponding isolated sub-units, e.g. uracil [14], D-ribose [17] and THF [16] (see Table 1). Of relevance the fact that in potassium–uridine collisions, we neither detect the dehydrogenated parent anion formation, nor any anionic fragment that contains the N-glycosidic bond intact. This is a strong indication of the fragile nature of this bond upon electron transfer, which was also reported within the context of electron attachment experiments [3].

Finally, it is interesting to note that the fragment anions formed in potassium collisions with uridine sub-units (uracil [14], D-ribose [17] and THF [16]), i.e. O^-, OH^- and $((DR\text{-}H_2O)^-)$ will come from the extra electron captured by the furanosic ring, while CNO^- and $(U\text{-}H)^-$ can easily be attributed to the extra electron remaining at

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