CROATICA CHEMICA ACTA
CCACAA **79** (1) 125–128 (2006)

ISSN-0011-1643
CCA-3073
Original Scientific Paper

Gas Phase Ligation of U^+. Comparison of Pyrene, Phenanthridine and Phenanthrene as Ligands*

Saša Kazazić, Snježana P. Kazazić, Leo Klasinc, Marko Rožman, and Dunja Srzić**

Laboratory for Chemical Kinetics and Atmospheric Chemistry, Ruđer Bošković Institute, P.O. Box 180,
HR-10002 Zagreb, Croatia

RECEIVED OCTOBER 17, 2005; REVISED JANUARY 9, 2006; ACCEPTED JANUARY 13, 2006

Keywords
ligation reaction
gas phase kinetics
uranium monocation
pyrene
phenanthridine
phenanthrene
FT ICR MS

Ligation of U^+ with phenanthrene in an FT ICR MS instrument is compared with previous results on U^+ with pyrene and phenanthridine. All investigated processes compete with U^+ oxidation by water and oxygen traces in the instrument. The comparison indicates that oxidation preferentially involves dehydrogenated ligation products.

INTRODUCTION

Investigations of gas phase ligation of metal monocations by polycyclic aromatic hydrocarbons (PAH) and their heteroanalogs provided interesting results concerning both metals and ligands.[1–16] Thus, the ligation number varies from zero to five and proceeds either as a corresponding number of consecutive simple additions or by more or less extensive rearrangement and fragmentation of the ligand during attachment. An interesting and rather complicated example was the ligation of U^+ by phenanthridine (9-azaphenanthrene, Ap), which along with competing oxidation (from water and oxygen traces in the instrument) and fragmentation of the ligand (loss of HCN) yielded the main reaction line of five ligand attachments but only the first involving a loss of two hydrogen atoms (probably as H_2). On the other hand, ligation with pyrene (Py) overwhelmingly proceeds as simple addition and UPy^+ (440), UPy_2^+ (642) and UPy_3^+ (844) would be the main products without interference of the competing oxidations (*vide supra*). Thus, analogous chains with one or two, but not with three Py ligated exist for UO^+ (254) and UO_2^+ (270), *i.e.*, $UOPy^+$, UO_2Py^+, $UOPy_2^+$, $UO_2Py_2^+$. And finally, because a parallel chain of Py addition by loss of H_2 in each step also exists, $(UPy - 2)^+$, $(UOPy - 2)^+$, $(UO_2Py - 2)^+$ in the first, $(UPy_2 - 4)^+$, $(UOPy_2 - 4)^+$, $(UO_2Py_2 - 4)^+$ in the second and $(UPy_3 - 6)^+$ with, surprisingly, some $(UOPy_3 - 8)^+$ in the last step are also observed. All these products indicate that U^+ has a coordination number of ≥ 6, whereby each Py occupies two of them. As the reaction time proceeds, the UO_2-species show an increase in mass by 2 units, indicating formation of $U(OH)_2$-analogs instead. So, after 5 s the main (end) products are *m*/*z* 677 (probably $UPy_2(OH)_2^+$) with some *m*/*z* 671 (probably $UO_2Py_2^+$) and the UPy_3-products disappear. Since most of our results on various met-

---

* Dedicated to the memory of the late Professor Marko Branica.

** Author to whom correspondence should be addressed. (E-mail: klasinc@irb.hr)

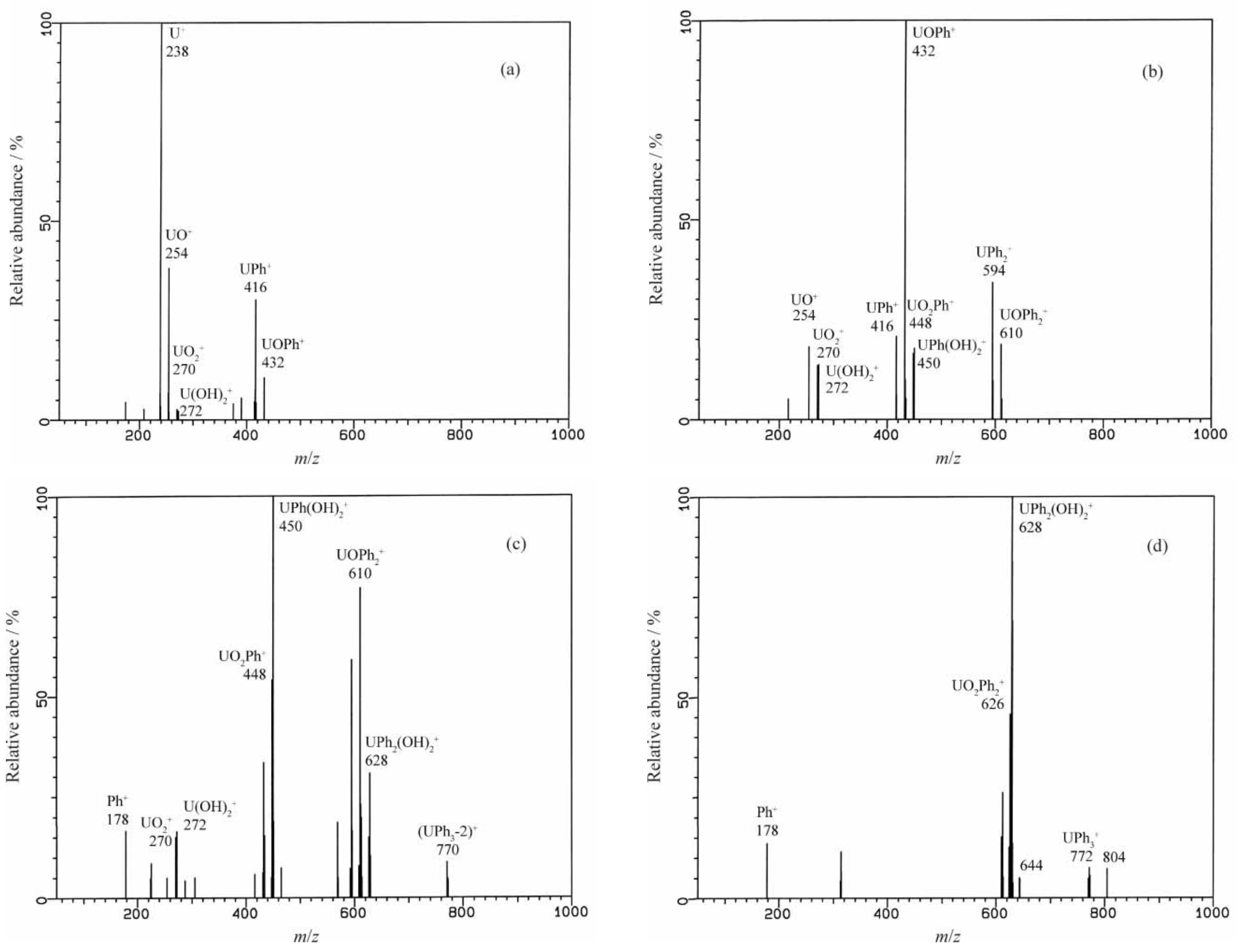


Figure 1. LDI-FT mass spectra of the reaction products of U^+ with phenanthrene (Ph) after: (a) 100 ms (b) 1 s (c) 2 s and (d) 8 s reaction time.

als were with Py as ligand and phenanthrene is structurally and chemically related to both Ap and Py, we report here the results of ligation of U^+ with this ligand and compare them with the above results. Formation of $U(OH)_2$-analogs during such a study is also of interest for comparison with the results of Branica *et al.*[17–20] on uranyl peroxo species in aqueous media and with earlier findings.[13]

EXPERIMENTAL

Single shots of a pulsed Nd:YAG Quanta Ray DCR-11 laser (Spectra-Physics, Mountain View, CA, USA) operating at the 1064 nm fundamental wavelength were used to produce U^+ ions from a small piece of pure metal. Phenanthrene (Ph) was previously administered by evaporating an alcoholic solution in the vicinity of the metal probe.

All experiments were performed on a FT/MS 2001-DD Fourier-transform mass spectrometer (Finnigan, Madison, Wisconsin, USA) with a 3 T superconducting magnet and a Nicolet 1280 data station. Following ion formation, the gas phase reaction of U^+ with Ph was investigated at delay times of 10^{-4} to 10 s.

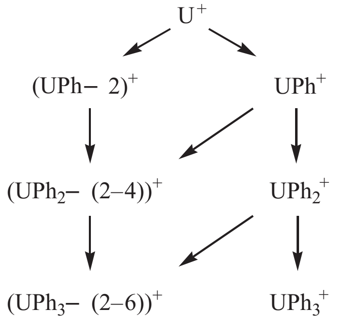
RESULTS AND DISCUSSION

Mass spectra of U^+ ligation with gas phase Ph at times of 100 ms, 1 s, 2 s and 8 s after the reaction start are shown in Figures 1a-d. Despite competing oxidations, the reaction scheme (Figure 2) looks rather straightforward. The U^+ (238) reacts at about the same pace with Ph, yielding UPh^+ (416) as it transforms into UO^+ (254). At this time (100 ms, Figure 1a), a certain amount of their oxidized products $UOPh^+$ (432), UO_2^+ (270) and $U(OH)_2^+$ (272) are observed as well. The ligation of U with Ph is much slower than with Py and Ap. Only UPh^+ shows some loss of hydrogen (20 %) on formation.

After 1 s delay time (Figure 1b), the U^+ has disappeared with some UO^+, UO_2^+ and $U(OH)_2^+$ still present, $UOPh^+$ is the most abundant and its oxidized products UO_2Ph^+ and $UPh(OH)_2^+$ have already started to form. Formation of the next ligation products without additional loss of hydrogen UPh_2^+ (594) and its oxidation to $UOPh_2^+$ (610) are also observable, as well as still some presence of the precursor UPh^+ (416).

After 2 s (Figure 1c), the highest Ph coordination is achieved in UPh_3^+ (772), but interestingly the minor product (UPh$_3$ – 2)$^+$ has arrived at this endpoint much faster. The reason why the main ligation line U$^+$ → UPh$^+$ → UPh$_2^+$ → UPh$_3^+$ is losing intensity underway is evidently that Ph ligations which took place with the loss of H$_2$ resulted in products which are more prone to addition of H$_2$O and oxidation towards UO$^+$ and UO$_2^+$-species. The UO$_2$-species at this point clearly show to be quite unreactive. Thus, the main final product, which ought to be UPh$_3^+$ (772), is actually UO$_2$Ph$_2^+$ (626) and UPh$_2$(OH)$_2^+$ (628) (Figure 1d) with the surprising possibility of addition of O$_2$ (*m*/*z* 804), H$_2$O or O (*m*/*z* 644). On the other hand, appearance of Ph$^+$ (*m*/*z* 178) at later stages of the experiment (Figure 1c and 1d) indicates its formation through a partial break-up of higher ligated complexes (*e.g.*, UPh$_3^+$) during the reaction mixture excitation to record the spectrum (*vide infra*).

The main characteristic of the present ligation study of U$^+$ with Ph is that only a negligible amount of the expected final product UPh$_n^+$, n = 3 is formed. This is evidently due to two reasons: i) the ligation is unusually slow, which enables the competing oxidation reactions with ubiquitous impurities to take control, and ii) the »minor« ligation path, including loss of H$_2$, produces a species particularly prone to oxidation. Thus, the substrate is continuously being depleted and the main final product is an unwanted byproduct. We know from Ap ligation that H$_2$ is lost only in the first step and that consecutive ligation products (up to (UAp$_5$ – 2)$^+$) are remarkably stable with respect to oxidation. Also Py, which may either lose H$_2$ in every ligation step or ligate all three times by simple addition to UPy$_3^+$, is much less prone to concurrent oxidations.[13] Therefore, the »impurity free« ligation would look as follows:



One can now wonder where the H$_2$ comes from. Ap, which like Ph loses H$_2$ only in the first step, cannot do it at the 9,10-positions and probably does it from the corresponding 4,5-positions of phenanthrene. Py does not have such chemically equivalent positions. Thus, if Ph like Py actually loses H$_2$ in every ligation step but the product is rapidly transformed, then only equivalent positions in both ligands are the 9,10-positions of Ph. A dehydrogenated such species, *i.e.*, 9,10-dehydrophenanthrene, is certainly much more reactive than the one resulting from H$_2$ loss at the corresponding site in Py. Therefore, the whole chain of H$_2$-losses with the Py ligand survives and can be traced to the end products whereas in the Ph case it is only observed as a single event. The results of all three ligation experiments demonstrate the importance and stability of the here unwillingly formed U(OH)$_2$L$_n^+$ or UL$_n$(H$_2$O$_2$)$^+$ species, which were, however, as uranyl peroxo complexes claimed to be important in aqueous media.[17–20]

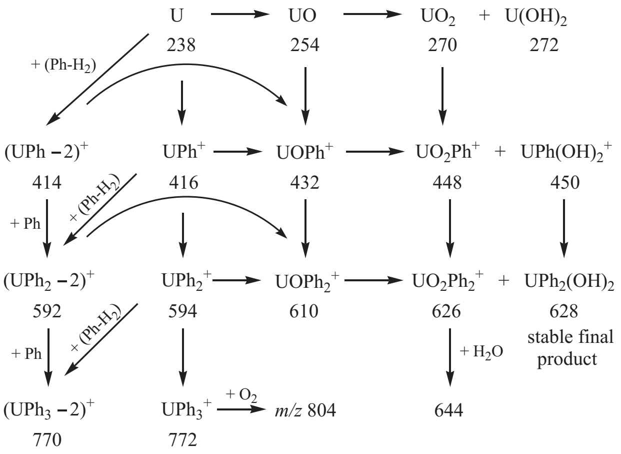


Figure 2. Reaction scheme for U$^+$ ligation with phenanthrene (Ph) and concurrent oxidation by impurities based on the observed peaks.

REFERENCES

1. B. S. Freiser, *J. Mass Spectrom.* **31** (1996) 703–715.
2. H. Schwarz, *Angew. Chem., Int. Ed. Engl.* **42** (2003) 4442–4454.
3. M. Diefenbach, C. Trage, and H. Schwarz, *Helv. Chim. Acta* **86** (2003) 1008–1025.
4. H. Higashide, T. Kaya, M. Kobayashi, H. Shinohara, and H. Sato, *Chem. Phys. Lett.* **171** (1990) 297–302.
5. W. W. Yin, A. G. Marshall, J. Marcalo, and A. P. Dematos, *J. Am. Chem. Soc.* **116** (1994) 8666–8672.
6. H.-F. Wu and J. S. Brodbelt, *Inorg. Chem.* **34** (1995) 615–621.
7. D. Srzić, S. Kazazić, and L. Klasinc, *Rapid Commun. Mass Spectrom.* **10** (1996) 688–690.
8. D. Srzić, S. Kazazić, L. Klasinc, and H. Budzikiewicz, *Rapid Commun. Mass Spectrom.* **11** (1997) 1131–1133.
9. H. Budzikiewicz, T. Cvitaš, S. Kazazić, L. Klasinc, and D. Srzić, *Rapid Commun. Mass Spectrom.* **13** (1999) 1109–1111.
10. T. Cvitaš, S. Kazazić, S. P. Kazazić, N. Kezele, L. Klasinc, D. Srzić, and H. Budzikiewicz, *Croat. Chem. Acta* (a) **74** (2001) 725-733; (b) **75** (2002) A31–A32.
11. D. Srzić, S. Kazazić, and L. Klasinc, *Croat. Chem. Acta* **69** (1996) 1449–1454.
12. D. Srzić, S. Kazazić, B. Kralj, L. Klasinc, J. Marsel, H. Güsten, and S. P. McGlynn, *Int. J. Mass Spectrom.* **230** (2003) 135– 140.
13. D. Srzić, S. Kazazić, L. Klasinc, H. Güsten, and S. P. McGlynn, *Croat. Chem. Acta* **70** (1997) 223–228.
14. S. Kazazić, L. Klasinc, M. Rožman, D. Srzić, and J. von Knop, *Croat. Chem. Acta* **77** (2004) 321–324.

15. S. Kazazić, S. P. Kazazić, L. Klasinc, S. P. McGlynn, and D. Srzić, *Rapid Commun. Mass Spectrom.* **18** (2004) 2354–2356.
16. X.-P. Xing, Z.-X. Tian, H.-T. Liu, and Z.-C. Tang, *Rapid Commun. Mass Spectrom.* **17** (2003) 1743–1748; see also: G. K. Koyanagi and D. K. Bohme, *Proceedings of the 50th ASMS Conference on Mass Spectrometry and Allied Topics,* Orlando, Florida, June 2–6, 2002.
17. R. Đogić, L. Šipoš, and M. Branica, *Limnol. Oceanogr.* **31** (1986) 1122–1131.
18. R. Đogić, G. Kniewald, and M. Branica, *Uranium in the marine environment. A geochemical approach to its hydrologic and sedimentary cycle,* in: J. C. Guary, P. Gueguenlat, and R. J. Pentreath (Eds.), *Radionuclides: a tool for oceanography,* Elsevier, London, 1988, 171–182.
19. R. Đogić and M. Branica, *Electroanalysis* **4** (1992) 151–159.
20. R. Đogić, B. Raspor, and M. Branica, *Croat. Chem. Acta* **66** (1993) 363–372.

SAŽETAK

Ligacija U^+ u plinskoj fazi. Usporedba pirena, fenantridina i fenantrena kao liganada

Saša Kazazić, Snježana P. Kazazić, Leo Klasinc, Marko Rožman i Dunja Srzić

Ligacija U^+ fenantrenom u FT ICR spektrometru masa uspoređuje se s ranijim rezultatima na U^+ s pirenom i fenantridinom. Svi istraženi procesi su u kompeticiji s oksidacijom U^+ tragovima vode i kisika u instrumentu. Usporedba pokazuje da oksidacija preferira dehidrogenirane produkte ligacije.