

EFFECT OF MOLECULAR STRUCTURE ON FRAGMENTATION OF ISOLATED ORGANIC MOLECULES IN SOLID RARE GAS MATRICES

A.V. Kobzarenko, F.F. Sukhov, A.Yu. Orlov, G.V. Kovalev, I.A. Baranova and V.I. Feldman

Department of Chemistry, Moscow State University, 119991 Moscow, Russia

Elucidation of high-energy reaction pathways in the condensed phase is an important issue for basic understanding of the radiation stability of complex organic molecules. As was shown previously, organic radical cations (RC) may undergo fragmentation or rearrangement in solid matrices due to excess energy [1]. The probability of this process depends on both ionization potential (IP) of the molecule and molecular structure. In the present work we have studied the role of "hot" ionic reaction channels for RC of some bifunctional compounds and alkynes.

The effect of excess energy was simulated by matrix isolation method as described in detail earlier [1, 2]. The formation of fragmentation products was monitored by EPR and FTIR spectroscopy. In the present work it was shown that the RC of bifunctional compounds ($\text{CH}_3\text{OCH}_2\text{COCH}_3$, $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COCH}_3$, $n = 0\div 2$) dissociated efficiently producing $\cdot\text{CH}_3$ radicals upon irradiation in solid argon matrix at $T \leq 16$ K. The probability of fragmentation decreases with decrease of excess energy by switching from Ar to Xe. It is worth noting that acetone RC does not show fragmentation under these conditions [1]. Thus, bifunctional molecules were found to be less stable to "hot" ionic fragmentation in low-temperature solids in comparison with simple prototype carbonyl compounds. In the case of alkynes of the R-C \equiv CH type, a noticeable yield of fragmentation products was observed when R = -C(CH₃)₃, but it was negligible for R = -CH₃. It means that the presence of triple bond stabilizes the molecular skeleton of linear alkynes toward "hot" fragmentation, similarly as it was shown for alkenes [2]. The mechanisms of "hot" reactions and excess energy relaxation are discussed.

This work was supported by the Russian Foundation for Basic Research (project 09-03-00848a).

References

- [1] V.I. Feldman et al., *Phys. Chem. Chem. Phys.*, **5**, 1769 (2003)
- [2] V.I. Feldman et al., *Radiat. Phys. Chem.*, **75**, 106 (2006)