

Peculiarities of the formation of long-lived molecular negative ions from mono-, bis-, and tris-(trimethylsilyl)cyclopentadienyltitanium trichlorides

V. K. Mavrodiev,* I. I. Furley, M. S. Miftakhov, and G. A. Tolstikov

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Octyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

The main feature distinguishing the formation of molecular negative ions (MNI) due to resonance electron capturing by the molecules $C_5H_5TiCl_3$ (1), $Me_3SiC_5H_4TiCl_3$ (2), $(Me_3Si)_2C_5H_3TiCl_3$ (3), and $(Me_3Si)_3C_5H_2TiCl_3$ (4) from the earlier studied analogous transformations of substituted bis-cyclopentadienyltitanium dichlorides consists in additional MNI peaks arising on the electron energy scale when a hydrogen atom is replaced by a Me_3Si group.

It can be seen from the effective output curves of the compounds 1-4 (Fig. 1) that the number of additional peaks on the electron energy scale corresponds to the number of trimethylsilyl groups. The average lifetimes (t_a) of these ions relative to the electrons autosplitting are equal to -290 (1), 390, 83 (2), 465, 370, and 59 (3), 477, 463, 400, and 63 μs (4), the first resonance t_a value increasing with the number of Me_3Si groups in the Cp-cycle, thus indicating the MNI stabilization by this group is likely caused by the existence of a vacant d-orbital, providing delocalization of an excess electron. Note that for $C_5Me_5TiCl_3$ the MNI peak at the electron energy value equal to 0.05 eV is observed solely. For the remaining apparently electron-excited Feschbach resonances the t_a values do not change noticeably except the last resonance for each compound. Considering t_a to be a qualitative measure of an excess energy of MNI excitement this result is indicative of the proximity of MNI excitement excess energies in these resonances, though the energies of captured electrons are different.

Such a situation is possible, if a considerable part of the excess energy is spent on irradiation or transformation of intramolecular coordination of ligands.

The last resonance for compounds 2-4 is characterized by a noticeably lower t_a value and its fall within the resonance. Such a regularity is most often characteristic of fragmentary ions formation, and it seems plausible that in the given resonance the MNI are stabilized owing to the rupture of an intramolecular Si-Cl bond

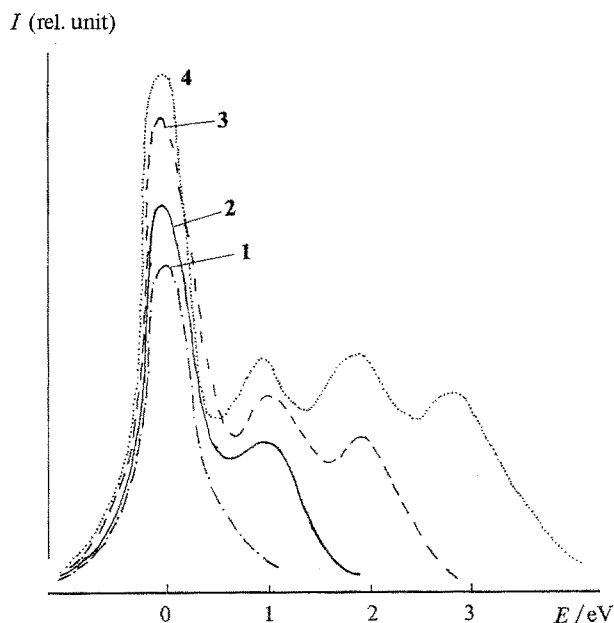


Fig. 1. Effective output curves for molecular negative ions of compounds 1, 2, 3, and 4.

resulting from the interaction of the Si atom vacant d-orbitals and the Cl atom p-orbitals. Such an interaction is sterically possible for only one Me_3Si group in the Cp-cycle.

References

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