

Electronic structure of 10-alkyl(aryl)phenoxarsines and the mechanism of their reactions with methyl iodide

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The structure of 10-alkyl(aryl)phenoxarsines has been investigated by the semiempirical quantum-chemical PM3 method. The As^{III} atom has a positive charge and simultaneously exhibits nucleophilic properties in the reaction with methyl iodide. The reactions of 10-alkyl(aryl)phenoxarsines with methyl iodide are probably controlled by charge distribution.

Key words: quantum-chemical calculations; PM3 method; 10-alkyl(aryl)phenoxarsine; methyl iodide; nucleophilic substitution.

It has been shown^{1,2} that the As atom is the nucleophilic center in reactions of 10-alkyl(aryl)phenoxarsines in an acetone medium. At the same time, the character of the excessive charge on the As atom remains unclear. The purpose of this work is the quantum-chemical estimation of charges on the As atom in 10-alkyl(aryl)phenoxarsines molecules and elucidation of the mechanism of their reactions with methyl iodide.

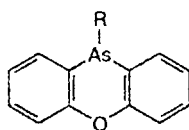
Calculation procedure

Calculations were carried out by the semiempirical quantum-chemical PM3 method. The structures of the organoarsenic compounds studied are presented in Refs. 1 and 2. The geometry was optimized by the PM3 method³ using the Berni algorithm with an accuracy to the gradient of 10^{-8} a.u. and self-consistency in energy to 10^{-5} a.u. The molecules studied had closed electron shells (multiplicity 1); therefore, the calculations were performed by the restricted Hartree–Fock method.

The cations studied contained an additional CH₃ group at the As atom, and the charge of the system +1 and multiplicity 1 were specified. These compounds were calculated similarly to the starting molecules. Quantum-chemical calculations were performed using the Gaussian 94 Rev. E.1 program package.⁴

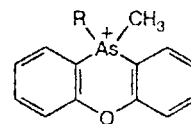
Results and Discussion

According to the calculated data, in 10-alkyl(aryl)phenoxarsine molecules the angles between the bonds of As and C atoms of the benzene rings and substituent R are within 93.4°–101.5°, which indicates sp³-hybridization and, hence, a small contribution of s-AO.⁵ Despite the fact that the As atom is nucleophilic in the reaction with methyl iodide, it has a positive charge most likely due to the +I-effect, since its electronegativ-



ity is lower than that of the C atom (2 and 2.5, respectively⁶). An increase in nucleophilicity of the substituent in the series Et < Pr < Prⁱ < Bu^s results in a decrease in the positive charge on the As atom only from 0.571 to 0.554. The calculated values of charges in CH₃I are –0.10 on the I atom and –0.07 on the C atom.

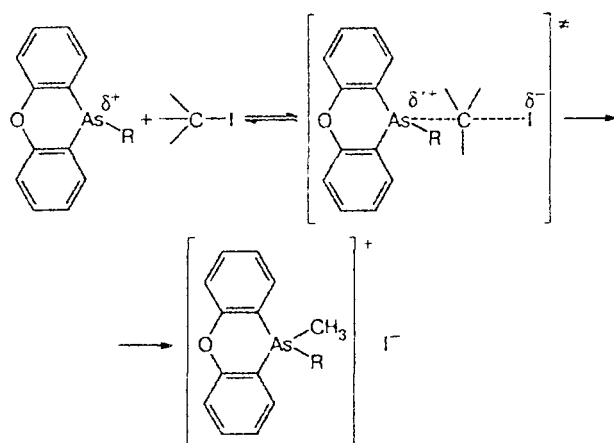
The reactions of 10-alkyl(aryl)phenoxarsines with methyl iodide^{1,2} involve the formation of cations due to the addition of CH₃⁺. The quantum-chemical calculations of these cations showed an increase in the positive charge on the As atom by ~3 times (from 0.6 to 1.6). The addition of CH₃⁺ also leads to the appearance of steric hindrances resulting in an increase in the degree of participation of s-AO in sp³-hybridization and an increase in the angles between the bonds of the As atom with C atoms of the benzene rings and substituent R by 10°, on the average, with the corresponding decrease by 0.01 nm in the bond lengths forming these angles.



We also calculated the populations and energies of frontier molecular orbitals (MO) of the starting compounds and their cations. The authors of Ref. 7 believe that the lower the energy *E* of the lower unoccupied molecular orbital (LUMO), the easier the occurrence of reactions with nucleophilic reagents. The values obtained indicate a considerable decrease in *E*_{LUMO} due to the reaction (from –0.2 eV in the starting molecules to –5.0 eV in the cations), which likely results in the almost synchronous formation of the cation and its interaction with the iodide anion.

As the results of our calculations show, the reactions of 10-alkyl(aryl)phenoxarsines with methyl iodide proceed despite the fact that the As atom possesses a sufficiently high excessive positive charge (+0.6), being simultaneously the nucleophilic center. Most likely, this

Scheme 1



is due to a higher position of the E_{HOMO} level in 10-alkyl(aryl)phenoxarsines (-8.7 eV) as compared to that of methyl iodide (-9.47 eV) and, therefore, due to the easy participation of the unshared electron pair on the sp^3 -AO of the As atom in the formation of the bond with CH_3^+ according to the donor-acceptor mechanism. This assumption is also favored by the fact that the electron population of the C atom (4.07) of methyl iodide is considerably lower than that of the As atom (4.4).

To confirm additionally the nucleophilic properties of the As atom with an excessive positive charge, we calculated the total energies E_{total} ⁸ of arsenic trichloride and its protonated cation by the PM3 method. The difference between them, which characterizes the proton affinity of the AsCl_3 molecule, is -553 kJ mol⁻¹. The charge of the arsenic atom in AsCl_3 is equal to 0.54, and that in $[\text{HAsCl}_3]^+$ is 0.98. Therefore, the As atom, despite its positive charge, exhibits the nucleophilic properties due to the unshared electron pair.

The data presented suggest that the reactions of 10-alkyl(aryl)phenoxarsines proceed through transition states (with synchronous anionoid detachment of iodine) under charge control when, due to the great difference between both E_{HOMO} of (10-alkyl(aryl)phenoxar-

sine as the donor (-8.7 eV) and E_{LUMO} of methyl iodide as the acceptor (-0.43 eV), processes occur via this route even if the reagents contain no atoms with especially high charges.⁹ Since the reaction occurs in acetone (aprotic polar solvent), it is quite probable that the approach of the organoarsenic compound and methyl iodide molecules results in the formation of the transition state of the S_N2 type.⁵ The scheme of the reaction can be presented as follows (Scheme 1). The As atom in the product reaches the maximum valence, which provides a comparatively high thermal stability of the salt.¹

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