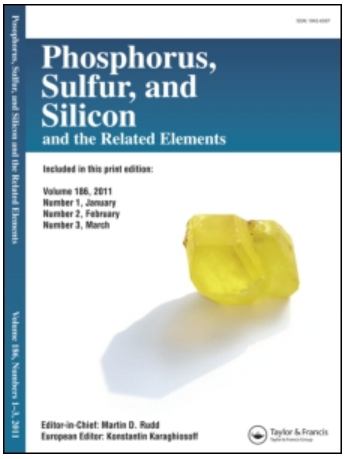

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The Phenylphosphinidene C_6H_5P is Stable Under Unimolecular Conditions - A Theoretical Prediction

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THE PHENYLPHOSPHINIDENE C_6H_5P IS STABLE UNDER UNIMOLECULAR CONDITIONS - A THEORETICAL PREDICTION

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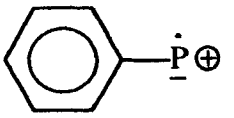
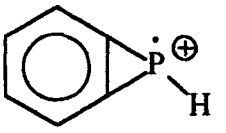
As members of the family of low-coordinated phosphorus compounds, the phosphinidenes (**RP**) containing subvalent phosphorus (σ^1,λ^1-P) are of current interest. Until now, no **Organophosphinidene RP** (R=Alkyl, Aryl) is known to be stable in the condensed phase. As the results of trapping experiments are questioned, the formation of **RP** as intermediates is still doubtful [1]. The mass spectrometric decay of some organophosphorus compounds yields radical cations $[C_6,H_5,P]^{+\bullet}$ m/z 108. For these species structures **1** and **2** are conceivable:



1



2

Using *ab initio* MO-calculations we were able to show that both ions correspond to minima on the potential surface of $[C_6,H_5,P]^{+\bullet}$. Surprisingly, **1** proved to be more stable than its counterpart **2** by 87,8 kJ/mol (HF/6-31G** basis set incl. ZPVE correction). The potential barrier was calculated to be 153,4 kJ/mol. In case of the corresponding neutrals, the phosphinidene form was evaluated to be 132,6 kJ/mol more stable. Thus, **1** should be a suitable precursor for generating phenylphosphinidene in the rarefied gas phase by Neutralization-Reionization mass spectrometry. **Latest Results**: In cooperation with **J. K. Terlouw** (McMaster University, Hamilton, Canada) we found that the ion m/z 108 generated by electron impact on $C_6H_5PBr_2$ has the connectivity **1** according to the observed structure diagnostic decays. By NRMS the ion can be neutralized and C_6H_5P has proved to be stable in the dilute gas phase.

[1] F. Mathey in: M. Regitz, O. J. Scherer: Multiple Bonds and Low Coordination in Phosphorus Chemistry; Georg Thieme Verlag, Stuttgart, New York (1990).