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TRIPHENYLPHOSPHINE ANION RADICAL

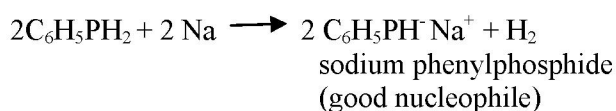
Abstract. According to the experimental data, the scheme of transformations of triphenylphosphine interaction with alkali metals should include stage of one-electron transfer from metal and the formation of a primary triphenylphosphine anion-radical $\text{Ph}_3\text{P}^{\cdot-} \text{M}^+$.

Therefore, during the lecture on organoelemental chemistry for students of chemical specialties of higher educational institutions should be noted that in the preparation of organic derivatives of alkali metals and tetraphenyl diphosphine from triphenylphosphine in a reaction with alkali metals, at the first stage the anion- radical of triphenylphosphine is formed.

The EPR spectrum of the anion radical of tetraphenyl diphosphine formed during the decomposition reaction of the triphenylphosphine-potassium anion-radical in 1,2-dimethoxyethane was studied.

Key words: anion-radical, triphenylphosphine, tetraphenyl diphosphine, electron paramagnetic resonance, organoelemental chemistry.

The most common types of organic derivatives of trivalent phosphorus are the phosphines R_3P , R_2PH , and RPH_2 in the molecule of which phosphorus is directly attached to the carbon. Hydrogen atoms with phosphorus have quite pronounced acidic properties in order to interact with metallic sodium, giving a salt (sodium phosphide) and hydrogen. Thus, during the reaction of phenylphosphine with sodium, the phenylphosphide anion $\text{C}_6\text{H}_5\text{PH}^-$ is formed, which is a strong nucleophilic reagent [1]



Summarizing the study of the reduction of triphenylphosphine with an alkali metal, Brit and Kaiser [2] proposed a triphenylphosphine splitting scheme that does not include the formation of an anion radical (AR).

In the reduction of triphenylphosphine with alkali metals (K and Na) in 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) at -70°C with the EPR method, we found an almost identical EPR spectrum [3], as Il'yasov did [4] with electrochemical restoration, Fig.1. In DME, the spectrum is described by the following hyperfine structure constants (HFS):

$$a_p = a_H^{\text{para}} = 2,5 \text{ rc}, a_H^{\text{ortho}} = 1,25 \text{ gauss}$$

An analysis of the hyperfine structure of the spectrum shows that the unpaired electron is uniformly delocalized throughout the molecule. In Figure 1, under the spectrum, quantum numbers corresponding to the projections of the total spin 3 para-protons ($I_H=1/2$) and one nucleus of phosphorus ($I_P=1/2$).

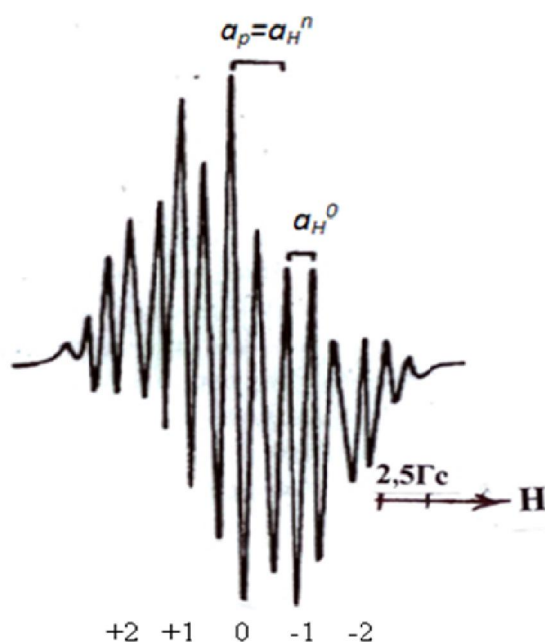
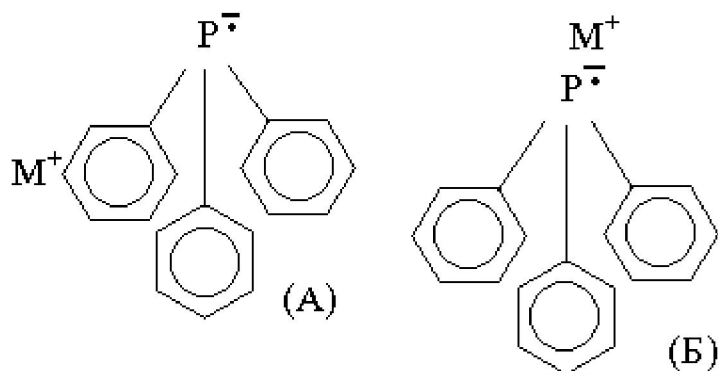


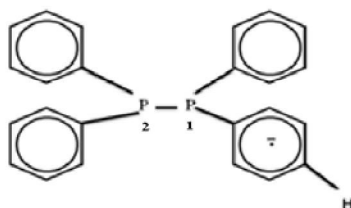
Figure 1 - EPR Spectrum of the anion radical of triphenylphosphine - potassium in DME at -60°C

In this connection, one can imagine two ways of locating the metal cation near the AR, which ensure a uniform distribution of the unpaired electron over the phenyl rings. In structure A, the cation is located near the phenyl nucleus and migrates at a high frequency between all three equivalent positions. In structure B, the cation is attached to the phosphorus atom and occupies a stationary symmetrical position with respect to the phenyl rings. This arrangement of the cation will also ensure a uniform distribution of the density of the unpaired electron throughout the molecule.

In favor of the second structure is the absence of the effect of a decrease in temperature on the nature of the electron delocalization. This means that the motion of the cation does not have a significant effect on the nature of delocalization of the unpaired electron.



Primary anion radicals are of low stability and turn into secondary radical anions as the temperature rises. This is evidently manifested in a change in the green coloring of the primary anion radicals to yellow. Figure 2 shows the EPR spectrum of the secondary anion radical. An analysis of a simple hyperfine structure shows that an unpaired electron interacts with two nuclei with an HFS constant of 7.15 gauss, with two cores with an HFS constant of 4 gauss and with one core with a HFS constant of 1.25 gauss.



We supposed that the HFS constant of 7.15 gauss refers to a single proton in the para-position of phenoxyl and to a phosphorus atom ($I_p=1/2$). Then the HFS constant of 4 gauss is naturally attributed to two ortho-protons. The magnitude of the constants and the nature of the distribution that should be reconstructed on their basis correspond to the parameters obtained by Gerson when studying the dimethylphenylphosphine anion radical [5].

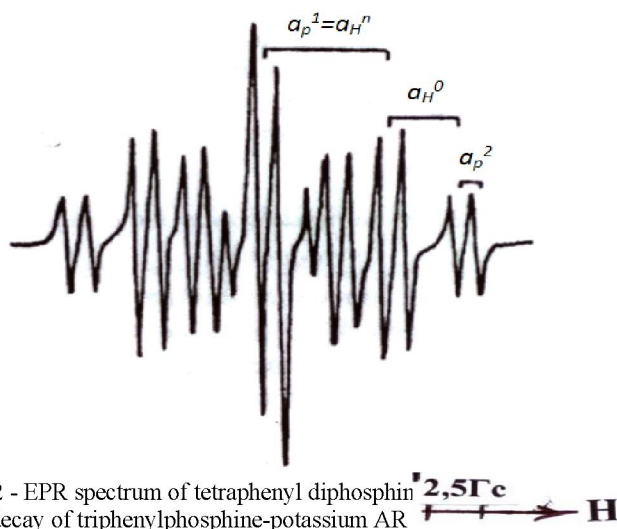


Figure 2 - EPR spectrum of tetraphenyl diphosphine
the decay of triphenylphosphine-potassium AR

According to the data of Britt and Kaiser [6], noting the formation of diphosphines, the EPR spectrum of the secondary anion radical can be attributed to the AR of tetraphenyldiphosphine. This assumption makes it possible to classify the doublet splitting with the HFS constant of 1.25 gauss to the second atom of phosphorus.

To confirm the above assumptions, we investigated the EPR spectrum of AR of secondary particle obtained from paradeuterated triphenylphosphine. Analysis of the obtained spectrum, Figure 3, convincingly confirmed the assignment of the HFS constants. The triplet spectrum has become a doublet, which confirms the equality of the HFS constants from phosphorus and proton in the para-position. The splitting constant for deuterium in accordance with the ratio of the magnetic moments of the proton and deuteron is 1.1 gauss and is close to the interaction constant with the second phosphorus atom.

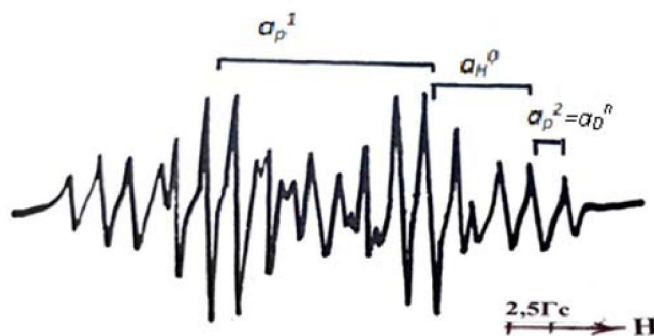
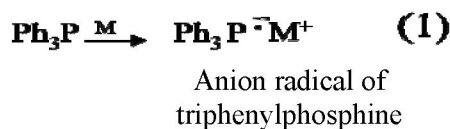


Figure 3-EPR spectrum of AR of the para-deuterotetraphenyl diphosphine formed during the decomposition of AR of para-deuterotriphenylphosphine-potassium in DME (at -30°C)

The obtained results indicate a change in the site of cation localization upon transition from triphenylphosphine AR to tetraphenyldiphosphine AR. In AR of tetraphenyl diphosphine, the cation is located near one phenyl nucleus, and the frequency of its migration to other phenyl rings is small in comparison with the splitting values.

As follows from the experimental data, the scheme of transformations of triphenylphosphine in the interaction with alkali metals [2] should include a single electron transfer from the metal and the formation of the primary anion radical of triphenylphosphine



Therefore, during the lecture on organoelemental chemistry [7-10] for students of chemical specialties of higher educational institutions, it should be noted that upon receiving the organic derivatives of alkali metals and tetraphenyl diphosphine from triphenylphosphine with alkali metals, the anion radical of triphenylphosphine (1) of the very first stage is formed.

Conclusions

1. As follows from the experimental data, the scheme of transformations of triphenylphosphine in the interaction with alkali metals should include a single electron transfer from the metal and the formation of the primary triphenylphosphine anion radical.

2. The EPR spectrum of the anion radical of tetraphenyl diphosphine formed during the decomposition reaction of the triphenylphosphine-potassium anion radical in 1,2-dimethoxyethane was studied.

REFERENCES

- [1] Ternay A. Contemporary organic chemistry. M.: Mir. 1981. T. 2. 651p. (in Russ.).
- [2] Britt A.D., Kaiser E.T. Phys. Chem. **69**, 2775 (1965).
- [3] Nasirov R., Solodovnikov S.P., Kabachnik M.I. The study of the reduction and cleavage of triphenylphosphine by alkali metals by the EPR method// Bulletin of the Academy of Sciences of the USSR, Chemical series. **1976**. №10. p. 2387-89. (in Russ.).
- [4] Ilyasov A.V., Kargin Yu. M., Morozova I. D. Spectra of EPR of organic ion - radicals. -M.: Nauka. 1980. 168p. (in Russ.).
- [5] Gerson F., Platner G., Bock H. Helv. chim. acta **53**, 1629 (1970).
- [6] Britt A.D., Kaiser E.T. J. Org. Chem. **31**, 112 (1966).
- [7] Kabachnik M.I. Chemistry of organophosphorus compounds. Selected Works: In. 3т./ Institut. elementoorganicheskikh soyedineniy A.N. Nesmeyanova RAN. -M.: Nauka, **2008**. (in Russ.).
- [8] Greenwood N., Earnshaw A. Chemistry of elements. т. I. -M.: BINOM. Laboratory of knowledge. **2008**. 607p. (in Russ.).
- [9] Sharutin V.V., Sharutina O.K., Senchurin V.S. Chemistry of organoelement compounds. Chelyabinsk: Publishing center YUUrGU. **2014**. 78p. (in Russ.).
- [10] Pavlov G.P., Vasilieva T.V., Osipova M.P., Vasiliev A.N. Chemistry of organoelement compounds/Chelboksary: Publishing house CHGU. **2011**. 78p. (in Russ.).

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ҮШФЕНИЛФОСФИННІҢ АНИОН-РАДИКАЛЫ

Аннотация. Тәжірибелік зерттеулерден үшфенилфосфиннің сілтілік металдармен әсерлесу кезінде, оған металдан бір электронның ауысуы орын алады, осының нәтижесінде анион-радикал деп аталатын бөлшек түзіледі $\text{Ph}_3\text{P} \xrightarrow{\text{M}} \text{Ph}_3\text{P}^{\cdot-}\text{M}^+$.

Сондықтан, химия мамандығы студенттеріне элементоорганикалық химиядан дәріс оқу кезінде сілтілік металдардың органикалық туындыларын және төртфенилкіфосфинді үшфенилфосфиннен сілтілік металдармен әсерлесуі кезінде, алғашқы сәтте үшфенилфосфин анион-радикалының түзілетіндігін ескерту керек.

Үшфенилфосфин – калий анион-радикалының 1,2-екіметоксиэтанда ыдырауы кезінде төртфенилкіфосфин анион-радикалының түзілуінің ЭПР спектрі зерттелген.

Түйін сөздер: анион-радикал, үшфенилфосфин, төртфенилкіфосфин, электрондық парамагниттік резонанс, элементоорганикалық химия.

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АНИОН-РАДИКАЛ ТРИФЕНИЛ-ФОСФИНА

Аннотация. Как следует из экспериментальных данных, схема превращений трифенилфосфина при взаимодействии с щелочными металлами должна включать стадию одноэлектронного переноса от металла и образование первичного анион-радикала трифенилфосфина $\text{Ph}_3\text{P} \xrightarrow{\text{M}} \text{Ph}_3\text{P}^{\cdot-} \text{M}^+$.

Поэтому, в ходе чтения лекции по элементоорганической химии для студентов химических специальностей высших учебных заведений следует отметить, что при получении органических производных щелочных металлов и тетрафенилдифосфина из трифенилфосфина с щелочными металлами образуется анион-радикал трифенилфосфина самой первой стадии.

Изучен спектр ЭПР анион-радикала тетрафенилдифосфина, образующегося в ходе реакции распада анион-радикала трифенилфосфин-калия в 1,2-диметоксиэтаноле.

Ключевые слова: анион-радикал, трифенилфосфин, тетрафенилдифосфин, электронный парамагнитный резонанс, элементоорганическая химия.

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