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NEW APPLICATION OF OXIDATION-REDUCTION REACTIONS

Abstract. In this article, the application of new methods of oxidation-reduction reactions in three directions is considered.

Its first direction is in the role of an intermediate in the process of passage of organic reactions. When a weak CH-acid of triphenylmethane is reduced with sodium, in the first stage an anion-radical is formed and then a carbanion.

The second direction is the determination of vanadium metal in petroleum and petroleum products.In this direction, the photocolorimetric method was used before. Now, when burning oil residues from the ash formed (V_2O_5) by the interaction of hydrochloric acid, vanadium chloride is formed, which is determined by the EPR spectrometer. This new method is more efficient and accurate, compared to the conventional photocolorimetric method used in the laboratory.

In recent years, based on experiments conducted in the Atyrau region, a genetic link between nitrates and nitrite ionshasbeen established. Members of the circle tested the content of nitrate ions in plants using diphenylamine-4-sulfonic acid sodium salt. When exposed to reagents, the nitrate ion contained in the acidic juice of the plant is oxidized and stained from slightly violet to dark blue.

Keywords: anion-radical, electron paramagnetic resonance, vanadium, ash oil, photocolorimetric method, nitrate ion, nitrite ion.

Introduction. In the chemistry history, it has long been asserted that oxidation occurs when the elements are combined with oxygen. For example, many metals lose their properties under the influence of oxygen and are corroded (destroyed).

If the iron lies in moist air, then its surface is covered with red-brown rust:

$$2\text{Fe}+\frac{3}{2}O_2+nH_2O\xrightarrow{25^0C}Fe_2O_3\cdot nH_2O$$

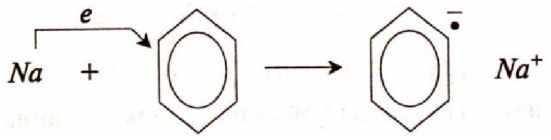
Likewise, all elements, apart from inert gases, react with oxygen and form oxides. Recently, complex physico-chemical devices and studies have shown that other chemical reactions lead to a similar conclusion. For example, metallic sodium not only reacts with oxygen, but also interacts with other compounds:

$$2\text{Na} + \overset{e}{\frac{1}{2}}\text{O}_2\rightarrow\text{Na}_2\text{O}$$

Also, sodium reacts with poisonous chlorine with the formation of an edible salt, having a unique taste and does not have its own smell:

$$2\text{Na} \overset{e}{+} \text{Cl}_2\rightarrow 2\text{NaCl}$$

Also, sodium reacts with benzene, and gives it one electron turning into an anion-radical of the organic salt [1]:



This compound has an unpaired electron that gives paramagnetic properties to benzene and has a negative charge.

When triphenylmethane reacts with sodium, it flows through the stage of the unstable anion-radical of triphenylmethane[2].

$$(C_6H_5)_3CH \xrightarrow{Na} (C_6H_5)_3CH^{\bullet -}Na^{+}$$

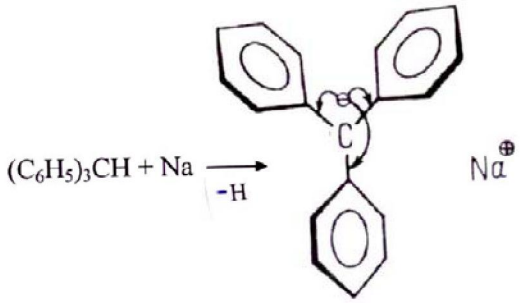
For sodium, this process is similar to each other. Since in four cases it gives up its valence electron and is oxidized.

In the first case - oxygen, in the second case - chlorine, in the third case - benzene, in the fourth case - triphenylmethane are oxidants. These reactions are simple methods of oxidation-reduction reactions.

Reaction of triphenylmethane with sodium

The mechanism of carbanion formation from the triphenylmethane compounds during the reduction with sodium occurs through the stage of the unstable anion-radical of triphenylmethane and is detected by the electron paramagnetic resonance (EPR) method.

Of the fatty-aromatic multinuclear compounds, the properties of the central carbon "methane" atom of triphenylmethane (TFM) are the most interesting. In the triphenylmethane itself, hydrogen bound to this carbon is relatively easily cleaved in the form of a proton under the action of sodium amalgam [3]:



triphenylmethyl anion
(red); λ=480 nm

The stability of carbanions (triphenylmethyl anions) with phenyl nuclei is due to the conjugation of the negative charge of the central carbon atom to the π-electron system of three benzene rings [3,4]. The triphenylmethyl anion is identified by UV spectroscopy in tetrahydrofuran (λ=480 nm)

The reaction of an alkali metal with triphenylmethane at low temperature (-110 °C) in tetrahydrofuran (THF) gives a new EPR spectrum consisting of 10 lines [2]:

$$N=2nI_H+1 = 2 \cdot 9 \cdot ½ + 1 = 10 \text{ line}$$

and the distance between the lines a=1,85 Gs (рисунок 1).

This unpaired electron in two rings is delocalized and magnetically interacts with equivalent four-ortho, four-paraand one-methine protons and, as a result, forms ten lines (the spin of the nucleus of hydrogenI_H = 1/2).

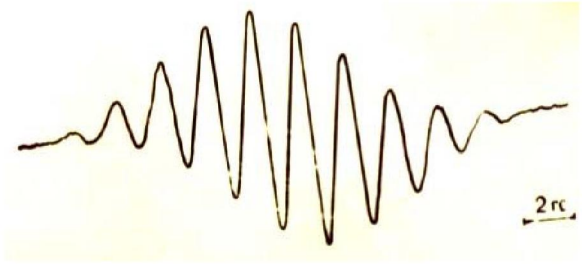


Figure 1 - The EPR spectrum of the anion-radical of triphenylmethaneof green color with sodium at a temperature of -110ºC.

As a result of the reaction of triphenylmethane with sodium, the anion radical of triphenylmethane (of dark greenish color) is unstable at low temperatures, and then the alkali metal replaces hydrogen and the carbanion is formed:

$$(C_6H_5)_3CH \xrightarrow{Na} (C_6H_5)_3CH^{\bullet -}Na^+ \longrightarrow (C_6H_5)C^-Na^+ + H^\bullet$$

The description of the proposed basic mechanism getting the unstable anion radical of triphenylmethane as a reaction intermediate was directly proved by EPR spectroscopy.

The proposed scheme is also confirmed by visual observations of the transition of the green color of the anion radical to the distinctive red color of the carbanion.

At the end of the last century, in the subject of organic chemistry in all higher educational institutions, it was known that the reaction of weak CH acids with alkali metals leads to the formation of carbanions, and no word is said about the intermediate particle. [3] When reading lectures on organic chemistry, it is necessary to clarify the mechanism of this reaction. Thiswillgreatlyincreasestudents' interestinscience.

Oxidizing ability of vanadium pentoxide included in the composition of oil ash with hydrochloric acid.

In order to improve the standard GOST 10364-63 chemical method for the determination of vanadium in oil and petroleum ash, we propose a more express method for estimating the total amount of vanadium in oil ash, based on the oxidizing capacity of V_2O_5 in an acidic environment of concentrated hydrochloric acid[5-7]:

$$V_2O_5 + 6HCl = 2VOCl_2 + Cl_2 + 3H_2O$$

In the resulting oxo-vanadyl group VO^{2+}, the central vanadium ion has one unpaired electron, as a result of which it has a paramagnetic property. The oxo-vanadyl ion VO^{2+} is highly stable and remains unchanged during the reactions, as evidenced by its EPR spectrum.

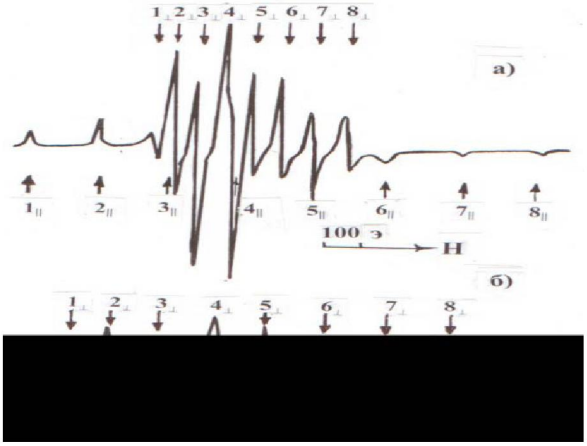


Figure2 - The EPR spectra of vanadyl chloride at -196 °C, obtained: a - from V_2O_5; b- from the ash of Kalamkas oil, of borehole #52, (here are written the hyperfine lines of the I⊥ - 8⊥vanadyl ion)

Figure 2a shows the anisotropic EPR spectrum of the resulting vanadium chloride formed from reactive vanadium oxide. The same spectrum was obtained from the ash of Kalamkas oil, borehole 52 (Fig. 2b) and other oils.

The concentration of vanadium, in the studied oil ash of the Caspian region, is determined by the isanotropic EPR spectrum of vanadyl chloride formed from vanadium pentoxide at liquid nitrogen temperature (-196°C) (Table 1).

Table 1 - The content of vanadium in oils and their ash, %

Oil	Ash output	The amount of vanadium in oil		The content of vanadium in ash
		XFA	EPR	
Kalamkas, 52	0.087	0.0154	0.0148	17.5
Botakhan,68	0.037	0.0025	0.0022	12.9
Karazhanbas, 851	0.09	0.029	0.026	28.9

As can be seen from Table 1, the results of determination of vanadium in petroleum oils by photocolorimetric (PEC) and EPR method in terms of oil, are consistent with the result of determination of vanadium in crude oils by XFA and EPR methods. The EPR method is more efficient and accurate than the traditional photocolorimetric method used in laboratories [8].

Genetic relationship between nitrite and nitrate ions

The research work for students interested in chemistry is mainly related to the needs of the Atyrau region.

The accumulation of nitrates and nitrites above the norm in crop mass, fodder, vegetables and in meat that are used as food can have an unprofitable effect on animals and human organisms, especially the properties of mutagenic nitrites in the human body is extremely dangerous.

Nitrates that enter the human or animal body when using vegetable food are restored to nitrite. The resulting nitrite ion blocks the oxygen supply to the cells and leads to serious illnesses in the body. The daily amount of nitrate for live weight should be from 300 to 320 mg or 4 mg/kg [9]. Members of the circle on the basis of their own experiments established a genetic link between the nitrates and nitrites ions[10-12]:

$$NO_3^- \underset{O}{\overset{H^\cdot}{\rightleftharpoons}} NO_2^-$$

In the course of the experiment, it was found that a simpler method of transition from nitrate to nitrite is the reduction of nitrate by hydrogen in the acidic medium.

$$2CH_3COOH + Zn \text{ (dry chemical)} = 2H^\cdot + Zn(CH_3COO)_2$$

$$KNO_3 + 2H^\cdot \text{(at the moment of allocation)} = KNO_2 + H_2O$$

We solve the inverse problem:

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = 5NaNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

The reducing properties of nitric acid and its salt are confirmed by the disappearance of the pink color $KMnO_4$.

We can test this equation by adding the Griss reagent to the solution.

Under the action of nitrite ions, the Griss reagent turns to red. Students developed an express visual technique for the mass analysis of nitrate ions in plant juices. To produce a visual scale, an aqueous solution of diphenylamine-4-sulfonic acid sodium salt was used with a known nitrate ion content[10].

Table 2 - Visual scale for determination of nitrate ion in test samples

Concentration of nitrate ion in solution, mg/l	**Colorofsolution**
<10	Bright blue
30	Blue
300	Dark blue

The development of express ions also requires, in addition to chemical knowledge, knowledge in physics (optics), biology, agrochemistryand ecology.

Conclusions

1.The mechanism of the formation of carbanion from the compounds of triphenylmethane during the reduction by sodium occurs through the stage of the unstable radical anion of triphenylmethane and is detected by the electron paramagnetic resonance (EPR) method.

The proposed scheme is also confirmed by visual observations of the transition of the green color of the anion radical to the distinctive red color of the carbanion.

2.It is proposed to use EPR - radiospectroscopy not only to estimate the amount of tetravalent vanadium in oils, but also to estimate the total amount of vanadium in oils. In the case of mass laboratory analyses characterized by selectivity, high accuracy and expressiveness, the proposed method has advantages in comparison with the photocolorimetric method of vanadium analysis in oils and petroleum products.

3. In the circle, students master and develop the technique for determining the content of nitrates and nitrites in crop materials.

REFERENCES

[1] Tuttle T.R., Weissman S.I. // J.Am.Chem.Soc. **1958**. **80**. P. 5342 – 5348.

[2] Nasirov R., Prokofiev A.I, Solodovnikov S.P, Kabachnik M.I. Anion-radical of triphenylmethane // Izvest.AN USSR, ser.Chem. 1973. № 9.S.1981.

[3] PerekalinV.V and Zonis S. Organic Chemistry. M .: Enlightenment. **1982**.464 p.

[4] Reutov OA, Kuri AL, ButinKP Organic chemistry. M .: Pilot, **2017**. 568 p.

[5] AkhmetovN.S. General and Inorganic Chemistry. M .: Higher School. **2001**.

[6] Nasirov R. General and inorganic chemistry. Almaty: Science. **2003**. 359 p.

[7] Greenwood N., Ernsho A. Chemistry of Elements (in 2 volumes) .M.:BINOM.Laboratory of Knowledge. **2008**.

[8] Nasirov R. Vanadium in oil and its use in the processing, search and extraction of hydrocarbons // Reports NAS RK. **2012**. №2.P.34 -38.

[9] GolubkinaN.A and Shamina M.A. Laboratory practical work on ecology. M.: FORUM: INFRA. M. **2004**.56 p.

[10] Nasirov R. Genetic link between ions // Kazakh school. **1988**, №1, p.64 - 67.

[11] Nasirov R., MazhitovS.M. Experimental work in the circle "Young chemist" // Chemistry in the school. **1989**. №5. P.108-109.

[12] Nasirov R., BaymukashevaG.K., MatveevaE.F. Experiment of interdisciplinary nature in the classroom / / Chemistry in school. **2008**, 4, P.64 - 70.

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ТОТЫҒУ – ТОТЫҚСЫЗДАНУ РЕАКЦИЯЛАРЫНЫҢ ЖАҢА ҚОЛДАНЫЛУЫ

Аннотация. Бұл мақалада тотығу – тотықсыздану реакцияларының жаңа қолданысы үш бағытта айқындалды. Оның бірінші бағыты жоғарғы оқу орындары химиясын оқуда органикалық реакциялардың жүру барысында интермедиат ретіндегі рөлі. Әлсіз СН – қышқылы үшфенилметанның натриймен тотықсыздануы кезінде ең бірінші сатыда анион – радикал түзілетіні ұсынылды, ал одан кейін карбанион өнімі алынады.

Екінші бағыт мұнай және мұнай өнімдерінде ванадий металын анықтау ісі. Бұл ретте осы кезеңге дейін фотоколориметрлік әдіс қолданылып келді. Енді мұнайды жағып оның күлінен (V_2O_5) қойылтылған тұз қышқылымен әсер ету арқылы хлорлы ванадийді алып, оны ЭПР – спектрометрмен анықтау ісі. Бұл жаңа әдіс зертханада қолданылып жүрген дәстүрлі фотоколорметрлік әдіске қарағанда аса тиімді және дәлдігіде өте жоғары.

Соңғы жылдары Атырау облысында өздері жүргізген тәжірибелер негізінде нитрат және нитрит ионы арасындағы генетикалық байланысты тағайындады. Үйірме мүшелері өсімдік суындағы нитрат ионды экспресті анықтау үшін екі фениламин- 4-сульфоқышқыл натрий тұзын сынақтан өткізді. Ол нитрат

ионының реактиві ретінде қышқыл ортада өсімдік сөліндегі нитрат-ион әсерінен тотығып, оның мөлшеріне сай әлсіз күлгін түстен сиякөк түске дейін боялатын өнім береді.

Түйін сөздер: анион – радикал, электрондық парамагниттік резонанс, ванадий, мұнай күлі, фотоколориметрлік әдіс, нитрат ион, нитрит ион.

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НОВОЕ ПРИМЕНЕНИЕ ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ РЕАКЦИЙ

Аннотация. В этой статье рассмотренопременение новых способов окислительно-восстановительных реакций по трем направлениям.

Его первое направление в роли интермедиата в процессе прохождения органических реакции. При восстановлении слабой СН-кислоты трифенилметана натриемв первой стадии образуется анион-радикал и после этого карбанион.

Второе направление - определение металла ванадия в нефтях и нефтепродуктах. В этом направлении раньше использовался фотоколориметрический метод. Теперь, присжигании нефтяных остатков из образовавшей золы (V_2O_5) взаимодействием соляной кислоты, образуется хлорид ванадия, который определяется с помощью ЭПР –спектрометра. Этот новый метод является более эффективным и точным, по сравнению с обычным фотоколориметрическим методом, применяемый в лаборатории.

В последние годы, основываясь на экспериментах, проведенных в Атырауской области, установили генетическую связь между нитратами и нитритными ионами. Члены кружка протестировали содержание нитрат-ионов в растениях с использованием дифениламин-4-сульфокислот натриевой соли. Нитрат-ионом в кислой среде растении при воздействии дифениламин-4-сульфокислот натриевой солиокисляется и окрашивается от слабо фиолетового до темно синего цвета.

Ключевые слова: анион – радикал, электронный парамагнитный резонанс, ванадий, зола нефти, фотоколориметрический метод, нитрат ион, нитрит ион.

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