Lecture 2. Free radicals and atoms, their formation. Carbenes.

The purpose of the lecture: to give information about the structure, production and properties of free radicals, atoms and carbenes.

Expected results: students gaining knowledge about the structure, features and chemical activity of free radicals and atoms, carbenes.

Let us dwell in more detail on free radicals, the main participants in chemical reactions, and on their reactivity. In chemical reactions, the chemical bonds in molecules are rearranged, and some bonds are replaced by others. In a large number of cases, restructuring is due to the rupture of some of the existing ones and the formation of new electron pairs. Such processes are homolytic. For example, in the reaction of a hydrogen atom with chlorine molecules

$$Cl : Cl + H \cdot \rightarrow Cl \cdot + H : Cl$$

In addition to the ability to recombine, free radicals easily react with other molecules, detaching atoms or groups of atoms, for example

$$CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O$$

It should be noted that among particles with unpaired p-electrons there are those in which the tendency to recombination is weakly expressed or practically absent. They are considered to be molecules. These include particles with an odd number of electrons: NO (15 e.), NO_2 (23 e.), ClO_2 (33 e.) And an oxygen molecule that has two unpaired p-electrons in the ground state.

Unpaired electrons are located on non-binding orbitals and equally belongs to both extreme C atoms. The structure of the allyl free radical can be represented as

 - unbound orbital

$$H_2C \text{---} CH \text{---} \dot{C}H_2$$

Due to the delocalization of unpaired electrons, free allyl is significantly less reactive than free propyl $-CH_2-CH_2-CH_3$ with locally bound valency.

Free radicals can also be stable. These include diphenylpicrylhydrazyl

and semiquinone resulting from the oxidation of a doubly charged hydroquinone anion

Isomethane decomposes relatively easily with the formation of two CH_3 free radicals

$$CH_3-N=N-CH_3 \rightarrow 2CH_3^{\cdot} + N_2$$

$$Fe^{2+} + HO:OH \rightarrow HO^{\cdot} + FeOH^{2+}$$

it is already flowing violently at 0°C under conditions when the hydrogen peroxide solutions are completely stable.

Acetone decays with the action of light with a wavelength of 200 nm to form

$$CH_3COCH_3 + h\nu \rightarrow \cdot CH_3^{\cdot} + \cdot COCH_3$$

Carbenes

Carbenes are compounds of divalent carbon. These are unstable highly reactive compounds with six valence electrons and the general formula $R^1R^2C\text{:}$ (two substituents and an electron pair). There are two states of carbenes: singlet and triplet. Most carbenes exist for a very short time, although stable carbenes are also known. Carbenes can be fixed in an argon matrix at very low temperatures.

The most common nomenclature of divalent carbon compounds is carbene nomenclature. In this nomenclature, compounds are considered as derivatives of the simplest of them - methylene, for which its "non-carbene" name is preserved. The names of the derivatives of the latter are built on the principles of "substitution" nomenclature, for example:

: CCl_2 – dichlorocarbene,

: CHCOOEt – ethoxycarbonylcarbene,

: CClMe – methylchlorocarbene,

: $C=C=CH_2$ – vinylidencarbene,

: PhCCl – phenylchlorocarbene,

: CPh_2 – diphenylcarbene.

For cyclic compounds with a carbene atom in the cycle, the prefix "carbene" is used, for example:

 - carbenacyclopentane,

 - 1-carbenecycloheptatriene-2,4,6,

 - 1-carbenacyclopentadiene-2,4.
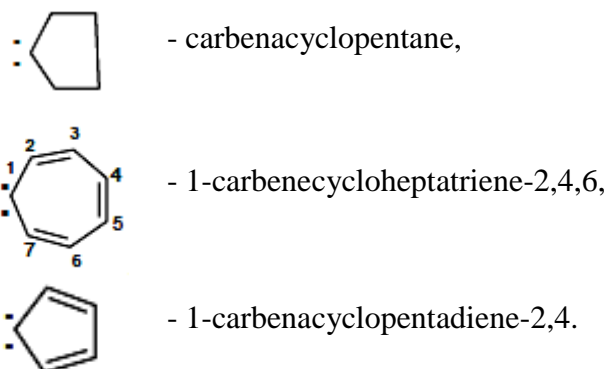
"Methylene" nomenclature is used much less frequently, for example: $:CCl_2$ – dichloromethylene, PhMeC – methylphenylmethylene.

It was proposed to use the methylene nomenclature for all triplet particles, while the carbene nomenclature should be retained only for singlet intermediates. However, the difficulty of determining particle multiplicity makes this proposal unacceptable.

In those cases where multiplicity must be indicated, they are indicated by the words "singlet", "triplet", or by a superscript digital index in front of the carbene carbon atom, or by using two parallel or antiparallel arrows, for example:

$$\text{singlet: } {}^{1}CH_2 \text{ or } \uparrow\downarrow CH_2; \text{ triplet: } {}^{3}CHPh \text{ or } \uparrow\uparrow CHPh.$$
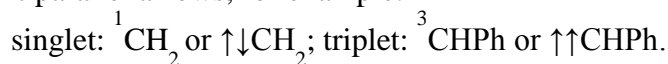
The image of the singlet and triplet states of carbenes with the help of "paired" or "steamed" points in accordance with the usual image of free electrons, for example, did not find application.

$$:CH_2 \text{ – singlet, } \cdot CH_2 \text{ – singlet.}$$
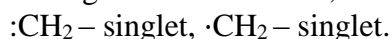
IUPAC developed the so-called γ-convention - a "universal" nomenclature for intermediate molecules containing an atom in an unusual valence state (carbocation, carbanion, radical, carbene). According to this convention, an atom in an unusual valence state is denoted by the symbol λ^n, where n is the maximum number of bonds for a given atom (for carbenes n = 2, for radicals n = 3). This symbol is preceded by a digit indicating the location of the atom, for example:

$$CH_3CH_2\text{-:}C\text{-}CH_2CH_3 \qquad\qquad\qquad :CCl_2$$
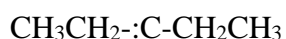
$$3\lambda^2\text{-pentane} \qquad\qquad\qquad \text{dichloro-}\lambda^2\text{-methane}$$

This system is contrived; it suffices to indicate that for carbanions, carbocations and radicals, the maximum number of bonds is the same and equal to three.

More logical and universal is the "yliden" nomenclature, according to which the carbene center is indicated by the end of the ylidene with the corresponding digital designation, for example:

$$:CCl_2 \qquad\qquad\qquad :CH\text{-}CH=CH_2$$
$$\text{dichloromethylidene} \qquad\qquad \text{propylene-2-ylidene-1}$$

Such a nomenclature is optimal for cyclic carbenes, and for simple ones, a carbene nomenclature is more convenient. The term "carbenes" is used as a generic name for the entire class of these intermediates.

The term "carbenoid" used for carbenes of the type SiRR', GeRR' and its difference from the term "carbene" is the same as between the concepts metal and metalloid, lanthanum and lanthanide.
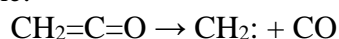
Subsequently, various carbene complexes and their labile precursors of the type of α-halogenated lithium compounds, which easily undergo α-elimination of the lithium halide molecule with the formation of a weak salt complex of carbene, became known as carbenoids. Carbenoids are understood to mean "molecules that directly react as carbenes or manifest themselves as sources of carbenes". Carbenes and their weak complexes are chemically identical.
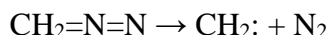
Getting carbenes

Historically, the first method for generating carbenes is the elimination of hydrogen halide from trihalomethanes under the action of strong bases. Using this method, the first carbene, dichlorocarbene (J. Hein 1950), was obtained as an intermediate:
$$CHCl_3 + C_4H_9OK \rightarrow CCl_2{:} + C_4H_9OH + KCl$$
In addition, there are other methods for producing carbenes. The simplest carbene can be obtained by decomposition of ketene:
$$CH_2=C=O \rightarrow CH_2{:} + CO$$
The most common method for generating carbenes is the photolytic, thermal, or transition metal catalyzed decomposition of aliphatic diazocompounds. So, as a result of the decomposition of diazomethane, the simplest carbene is formed:
$$CH_2=N=N \rightarrow CH_2{:} + N_2$$
The thermal or photochemical decomposition of tosyl hydrazones, derivatives of carboxylic acids, is a similar method for generating mono- and dialkylcarbenes. In this case, diazo compounds act as intermediates