SOME PRINCIPLES OF THE RADIOLYSIS OF CRYSTALLINE
INORGANIC COMPOUNDS

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Substantial experimental material has now been accumulated on the radiolysis of oxygen-containing salts, and attempts are being made to generalize the available data to explain the principles of radiochemical conversions. Thus, a relationship has been established between the radiochemical yields and the whole series of parameters of crystalline compounds (the free volume of the unit cell, the energy of the bond between atoms and the anion, the type of cation, the crystal lattice energy, etc. [1]), with the aid of which a comparative estimation of the radiation stability of certain monotypic salts can be performed.*

For example, the radiochemical yields (G) of most monotypic compounds are reduced in direct proportion to the decrease in the free volume of unit cell of the crystal lattice. However, for such salts as sulfates, selenates, carbonates, and a number of others, the interrelationship between the free volume and G cannot be followed [2-4]. The bond energy does not always play a decisive role in the radiochemistry of ionic crystals either (Table 1).

Consequently, a general approach (one or a sum of criteria) that would permit explanation of the observed differences in the behavior of various salts under irradiation still has not been found.

In this work we discuss the relationship between the value of the electron affinity (A0) of the primary products of radiolysis and the radiation stability of oxygen-containing ionic compounds. Earlier utilization of this parameter in the elucidation of radiochemical processes in inorganic salts was abandoned, although, as an analysis of the literature data shows, in certain cases it may be an extremely useful criterion for the evaluation of radiation stability.

The processes of radiolysis of inorganic compounds are customarily divided into primary and secondary. The primary processes for oxygen-containing salts consist chiefly of the excitation and ionization of anions or cations (or of the entire molecule), while the secondary processes pertain to the interaction of the products of excitation and ionization with one another or with the surrounding ions [1, 10]. Correspondingly, ionized ions of the crystal lattice, as well as particles obtained as a result of the decomposition of ionized or excited ions (molecules in the case of molecular crystals) can be assigned to the primary products of radiolysis.

It is very frequently difficult to determine the contribution of ionization and excitation in the primary stage of radiolysis; however, a group of salts in which ionized particles predominate among the primary products can always be indicated, while in other cases the products obtained as a result of cleavage of bonds in the anions predominate, i.e., ultimately (without going deeper into the mechanism of the primary event of absorption of radiation energy and the intermediate stages of its transfer), the primary products are formed according to reactions (1) and (2)

\[
\begin{align*}
\text{hv} \longrightarrow (K^\text{eX}, A') & \rightarrow K^{\text{eX}-m}, A^{\text{eX}+m} + (m + n) \text{e}^- \\
\text{hv} \longrightarrow (K^\text{eX}, A') & \rightarrow K^{\text{eX}}, B^{\text{eB}} + C^{\text{eC}}
\end{align*}
\]

where K, A (B) are the cation and anion, respectively, \(A^{zA} = B^{zB} + C^{zC}\); \(z\) is the charge of the given particle; \(m\) and \(n\) are the numbers of electrons leaving the cation and anion (the cation is the ionized metal).

*We have in mind compounds with the same anion but different cations.

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TABLE 1. Characteristics of Radiochemical Properties of Certain Oxygen-Containing Salts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy, eV</th>
<th>Type of radiation*</th>
<th>G (eV)</th>
<th>Literature reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KClO₄</td>
<td>---</td>
<td>2.06 (ClO₂-O)</td>
<td>Co⁶⁰</td>
<td>2.5</td>
</tr>
<tr>
<td>KBrO₃</td>
<td>6.51</td>
<td>&gt; 3.04 (BrO₂-O)</td>
<td>Co⁶⁰</td>
<td>1.3</td>
</tr>
<tr>
<td>KNO₃</td>
<td>6.94</td>
<td>2.21 (NO₂-O)</td>
<td>Co⁶⁰, X-ray</td>
<td>0.8</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>18.73</td>
<td>3.60 (SO₄-O)</td>
<td>Co⁶⁰</td>
<td>~0.04</td>
</tr>
</tbody>
</table>

*Room temperature.

According to the aforementioned, we can arbitrarily divide all inorganic salts into two groups: I) primary products are formed chiefly according to reaction (1); II) primary products are formed chiefly according to reaction (2). Thus, in the radiolysis of sulfates of the alkali and alkaline earth metals irradiated with γ quanta (Co⁶⁰) at the temperature -196 °C, ~ 96% of all the paramagnetic centers (PMC) arising are ion radicals SO₄⁻, and only ~ 4% are the sum (SO₃⁻ + SO₂⁻), i.e., the concentration of PMC formed as a result of cleavage of the bond in the primary step is extremely negligible [3, 11]. The same is observed in the radiolysis of selenates and carbonates [2, 4]. Consequently, according to the classification cited these salts can be assigned to group I. When the temperature is raised during or after irradiation, in these compounds secondary reactions leading to a decrease in the concentration of SO₄⁻, SO₃⁻, and CO₂⁻ and an increase in SO₃, SO₂, SeO₂⁻, SeO₃⁻, and CO₂ radicals, in the corresponding salts according to the schemes

XO₃⁻ + e⁻ → XO₂⁻ + O²⁻ (3)

or

XO₃⁻ + e⁻ → XO₂⁻ + O₂⁻ (4)

are accelerated on account of the liberation of electrons from traps, which is also observed experimentally [2-4].

Among the compounds of group II (the bond in the anion is easily broken) we can class, for example, nitrates, chlorates, bromates, and iodates of the alkali metals. In this case, under the action of ionizing radiation, the following reactions are realized:

XO₃⁻ → (XO₃⁻) * → XO₂⁻ + O⁻ (XO₂⁻ + O)

and probably

XO₃⁻ → (XO₃⁻) * + e⁻

XO₃⁻ + e⁻ → XO₂⁻ + O⁻ (XO₂⁻ + O)

With increasing temperature, as a result of secondary reactions there is a more profound "collapse" of the anion.

Evidently reactions (1) and (2) proceed to an equal degree in chlorates, bromates, and iodates of the alkaline earth metals, and it is expedient to class these compounds in an intermediate category (group III). We must note that such a division of oxygen-containing salts according to the nature of the formation of primary radiolysis products into three groups is of course arbitrary; however, assuming this, we can attempt to use the value of the electron affinity $\Lambda_0$ of the dominant primary radiolysis products as a parameter characterizing the radiation stability.

The following pattern is observed for the compounds of group I: the greater $\Lambda_0$ of the basic primary products, the higher the radiation stability. Thus, the values of $\Lambda_0$ for SeO₄⁻, SO₄⁻, and CO₂⁻ ion radicals in selenates, sulfates, and carbonates are related as ~1:1.3:2, respectively; the abovementioned salts are arranged in the same order with respect to radiation stability (Table 2). The observed interrelationship between $\Lambda_0$ of the primary products and the summary yield of PMC (see Table 2) can be explained by the fact that the higher the value of $\Lambda_0$, the less probable are reactions of the anion occurring with stripping of an electron of the type

XO₃⁻⁻ → XO₄⁻(m⁻) + e⁻

Moreover, there are very few products formed with cleavage of the bond in the anion in salts of group I, and the total yield of the ion radicals should be low.