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RADIOLYSIS OF SOLID INORGANIC SALTS WITH OXYGEN-CONTAINING ANIONS

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ABSTRACT:

Data on radiation transformations in the group of salts that have been studied in detail have been systemized and are discussed in the basic groups formed by the alkaline metal nitrates, nitrites, chlorates, bromates, and perchlorates.

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RADIOLYSIS OF SOLID INORGANIC SALTS WITH OXYGEN - CONTAINING ANIONS

The level, tempo, and volume of research in the area of the radiation chemistry of inorganic compounds have steadily increased in recent years. In connection with this, the volume of information contained in the special literature about these problems at the present time is very great. For publications that appeared up to 1962 this information has been systematized by V. V. Sviridov [1]. More recent surveys of this area are lacking.

At the same time it is just these recent years that have been characterized by the deepening of research and by the use of spectroscopy of various ranges and fine analytical methods of studying the products of radiolysis that have brought about the possibility, which did not exist earlier, of discussing the details of the radiolysis mechanism of certain groups of salts. This is most applicable to the radiolysis of oxygen-containing compounds, a complex and, as a rule, multi-stage process including the formation of a large number of intermediate paramagnetic particles.

Among the oxygen-containing inorganic salts the most steady attention has been attracted by the group of radiation unstable compounds, the radiolysis investigation of which is convenient from the methodological point of view (simple structure and the ability to produce monocrystals, the presence in the products of radicals and molecules that can be spectroscopically computed and determined, etc.). The radiolysis patterns of this salts have been studied in the relatively greatest detail, but the methods and devices used in this and the results and conclusions obtained, besides being interesting in themselves, can be used (in the methodology and formulation) for the radiolysis study of other compounds.

In accordance with the presentation in this survey, the data on radiation transformations in the group of salts that have been studied in most detail in this way have been systematized and are discussed in the basic groups formed by the alkaline metal nitrates, nitrites, chlorates, bromates, and perchlorates. In addition to this, special attention has been paid to the latest research and the views that have been formulated on the basis of it.

II. Radiolysis of nitrates

The most intensively studied of all the inorganic salts with oxygen—containing anions are the nitrates. In addition, in this group of salts the alkaline metal nitrates have been studied in the most detail of all [2-10]. The nitrates of silver [2, 11], alkaline earth metals [2, 12-13], and lead [2, 14-16] have been studied in less detail.

1. Products of radiolysis

a) Results of chemical analysis

The generally used method for determining the end products of the radiolysis of nitrates is nitrite determination according to the diazotization reaction after dissolving irradiated nitrate in water. In the overwhelming majority of publications, both the ones that appeared after the publication of Sviridov's monograph [1] and the ones that he examined in his book, analysis of irradiated nitrate solutions was conducted only on nitrite. In the publications where an analysis was made of the gases produced during solution (e.g., [2, 7, 16]), it was shown that the gaseous product of radiolysis is oxygen. The relationship $G(NO_2^-)/G(O_2) \simeq 2$ is maintained in all cases, with the exception of the initial stage of the radiolysis of lead nitrate [16].

However, as was shown by Cunningham [7], radical products, such as O^-, O_2^-, NO_2, and NO, can also contribute to the output of a radiolysis product determined to be nitrite by the diazotization reaction. Actually, by comparison of the results of two methods of analysis (ceric and diazotization) it was established in this paper that when KNO_3 and $NaNO_3$ are irradiated at 77°K the strictly nitrite radiation chemical output amounts to, at most, not more than half of the value obtained by the diazotization method of analysis on nitrite. This deviation is less when potassium nitrate is irradiated at room temperature, but it remains considerable in the case of $NaNO_3$. It appears that it can be considered demonstrated that the basic products of radiolysis at room temperature, in any case for the nitrates of potassium and sodium, are NO, NO_2^-, $+NO_2$, and oxygen. As is shown by Cunningham [7], the presence of nitrogen in the gaseous products of radiolysis that was noted in paper [17] is the result of the desorption of air during nitrate irradiation. It should be mentioned that the oxygen tested after dissolution of irradiated nitrate in water is present in the crystalline lattice at small doses, apparently not only in the form of molecules or atoms but also in the form of O^-, O_2^-, and O_2^{-2} ions, which also explains to a certain extent its maintenance in the lattice in the course of irradiation. In connection with this, it seems that the assumptions [18] about the possibility of the formation of a metal in the course of nitrate irradiation are unacceptable.

Since the chemical analysis of irradiated nitrates is conducted after they are dissolved in water, in the process of which the chemical state of the radiolysis products can vary, it is difficult by this method to detect both the initial products of radiolysis and the final nitrate products in the lattice. More trustworthy information about them can be obtained by studying the optical absorption spectra and electron paramagnetic resonance spectra of nitrates, in as much as these methods do not require the destruction of the crystalline lattice.

b) Optical absorption in irradiated nitrates

One of the first papers on the study of optical absorption in irradiated $NaNO_3$ was Pringsheim's paper [19]. At the temperature of liquid nitrogen an absorption band was detected with a maximum at 335 millimicrons, and at room temperature, besides this band, another one appears with a maximum at 355 millimicrons.

The author assigned the first of these bands to the electron surplus center and the second to NO_2^- ions, since sodium nitrate, to which nitrite was added in the melt, also has an absorption band with a maximum of about 355 millimicrons. Absorption maximums at ~350 millimicrons were also detected by Johnson [16] while studying reflection spectra in irradiated KNO_3 and $Pb(NO_3)_2$. Cunningham's paper [4] was dedicated to a more detailed study of this problem in the case of KNO_3; therefore an examination of this paper in more detail seems interesting to us. In fig. 1 taken from paper [4] is presented the absorption spectrum of a

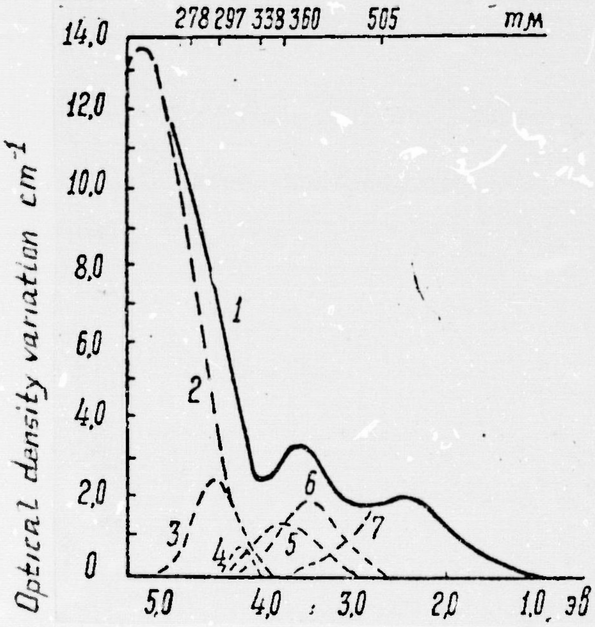

Fig. 1. Optical absorption spectrum in KNO_3 irradiated by gamma rays at 4.2°K [3]. The points present the experimental values. Curve 1 was obtained by summation of curves 2, 3, 4, 5, 6, and 7.

crystal of KNO_3 irradiated at 4.2°K. In the range of doses less than 10^{20} electron volts/gram, six absorption bands with maximums at the 520, 355, 325, 290, 268, and 250 millimicron wave lengths were detected at both 4.2°K and 77°K. Study of the behavior of these bands during irradiation with light of a definite wave length and variation of temperature and also comparison with the behavior of electron paramagnetic resonance signals during this kind of treatment permitted the author to identify these absorption bands.

Thus, for example, the bands at 268 and 250 millimicrons easily decrease when a crystal irradiated at 4.2°K is stored at this same temperature for 30 minutes. Further storage, however, for another hour does not cause variation of absorption at these wave lengths. A 16 hour cooling at 77°K of a crystal irradiated at this same temperature decreases absorption two times at 268 and 520 millimicrons and three times at 250 millimicrons. On the basis of analogous behavior of electron paramagnetic resonance signals [3, 4] assigned to NO_2^{-2} ion radicals and NO_3 radicals and also on the basis of experiments with the decoloration of these bands and electron paramagnetic resonance signals, absorption at 268 and 520 millimicrons was assigned to NO_2^{-2} ion radicals and absorption at 250 millimicrons, to NO_3 radicals.

Irradiation with light of the 520 to 680 millimicron wave length decreased absorption at 520, 290, 268, and 250 millimicrons. Since light of this wave length must absorb NO_2^{-2} ion radicals, the weakening of absorption at 520 and 268 millimicrons was assigned to an NO_2^{-2} decrease on account of ionization. However, the weakening of the bands at 290 and 250 millimicrons was explained by a decrease in the concentration of vacancy centers on account of the capture of an electron freed during the ionization of NO_2^{-2}. In this way these experiments also confirmed the above mentioned identification of the absorption bands at 520, 268, and 250 millimicrons. It must be noted that the absorption bands at 325 and 355 millimicrons during this treatment remain unchanged. This was explained by the electron excess nature of the centers responsible for these bands. When crystals are stored at 77°K, absorption also decreases at 325 millimicrons; moreover, if the crystals with the bands assigned to NO_2^{-2} previously decolored by light are subjected to roasting, then the decrease of absorption at 325 millimicrons is accompanied by the appearance and increase of absorption at 270 and 520 millimicrons.

On the basis of these data and data relating to the behavior of the electronic paramagnetic resonance signal assigned to NO_3^{-2} [3], the absorption band at 325 millimicrons was attributed to NO_3^{-2} ion radicals.

The center responsible for the 290 millimicron band, which is stable at the temperatures of liquid helium and liquid nitrogen but is burned off by heating to room temperature, was not identified. As for the absorption band at 355 millimicrons, which Pringsheim [19] assigns to nitrite ions and which is stable when the crystal is heated all the way up to room temperature, it is also not identified in this paper. The attribution of this band to NO_2^- ions in paper [4] is subject to doubt, since because of the exceedingly small coefficient of extinction of nitrite at 355 millimicrons the absorption caused by these ions in the obtained in this paper, which were determined chemically, lie outside the limits of error of the experiment. In a more recent paper [20] this absorption band (C-center) is identified by Cunningham as the hydroxy hyponitrite ion $N_2O_3^{-2}$.

When KNO_3 was irradiated by a dose of more than 10^{20} electron volt/

grams, an additionally appearing absorption band was detected at 410 millimicrons. Since the electron paramagnetic resonance signal assigned to NO_2 [3] also appears at doses that exceed 10^{20} electron volt/grams, this absorption band was assigned to NO_2. The decoloration of the NO_2^{-2} band by light with a wave length of more than 520 millimicrons also causes a decrease of the 410 millimicron band, which is apparently conditioned by the capture of an electron by the NO_2 molecule It is appropriate here to note that papers [21, 22] established the lack of the signal assigned to NO_2 in KNO_3 irradiated at the temperature of liquid nitrogen, if the initial nitrate does not contain nitrite or if pure nitrate is not heated to room temperature between irradiations. However, it appears that this result does not contradict Cunningham's data, since the doses used in paper [21] were less than 10^{20} electron volt/grams although in a more recent paper of these authors [5] NO_2 was detected in KNO_3 irradiated at 77°K by a dose of $2 \cdot 10^{19}$ electron volt/grams.

In sodium nitrate [20] irradiated at 77°K an absorption band with a maximum at 335 millimicrons was detected (fig. 2). However, analysis of the form of the curve and experiments with decoloration by UV light permitted the author to identify two particles responsible for this band (NO_2^{-2} and NO_3^{-2}) and detect absorption at $\sim$410 millimicrons assigned to NO_2. It is interesting to note that paper [20] noted an inhibiting influence of Ag^+ ions introduced into the KNO_3 and $NaNO_3$ lattice on the growth of absorption bands related to nitrogen-oxygen centers.

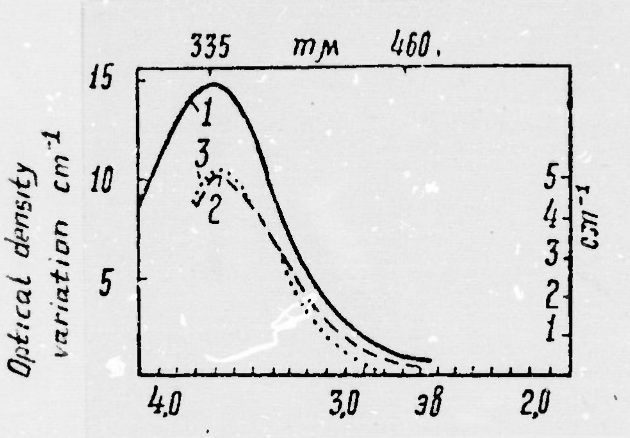

Fig. 2. Absorption of light in $NaNO_3$. 1) x-ray irradiation at 77°K for 75 minutes (right scale); 2) gamma ray irradiation at 77°K for 30 minutes (left scale); 3) the same thing as 2) after irradiation with light with $\lambda > 510$ mμ at 77°K for 40 minutes.

c) Electron paramagnetic resonance spectra in irradiated nitrates

The electron paramagnetic resonance signals in irradiated sodium nitrate [24-29] and potassium nitrate [3, 5, 7, 21, 22] have been studied in a relatively detailed manner. Information also exists on the electron paramagnetic resonance spectra in irradiated silver nitrate [11], strontium nitrate [12], and lead nitrate [15]. In all the studied nitrates the presence of NO_2 was established. The NO_3 radical was detected in KNO_3 [3, 5], in $NaNO_3$ [26], and in $Pb(NO_3)_2$ [15], and NO_3^{-2} was detected in KNO_3 [3, 5, 21, 22] and in $Sr(NO_3)_2$ [12]. A similar paramagnetic particle was detected also in $AgNO_3$; however the unpaired electron in this case was not located only on the anion but was also split on the silver nucleus [11]. The presence of NO, NO_2^{-2} and O_2^- in irradiated KNO_3 has been shown only in paper [3]. Thus, in one and the same nitrate and in the same or similar conditions various authors have detected various paramagnetic particles. Thus, for example, when KNO_3 is irradiated at 77°K with a dose of less than 10^{20} electron volt/grams, which Cunningham considers the threshold for the formation of NO_2, Zeldes [5] identified the presence of NO_3^{-2}, NO_3, and NO_2 when only NO_2^{-2} [3] was detected by Cunningham. Although the doses in these papers differed by about an order, one cannot explain the difference in the results quoted by the author just by the difference in the dose of irradiation. These discrepancies are more markedly apparent from the characteristics of the spectra assigned to paramagnetic particles in irradiated KNO_3 presented in table 1.

Table 1

Characterization of e.p.r. spectra of paramagnetic particles in irradiated KNO_3

Assumed radical	g-factor value	Hyperfine structure constants (gauss)	Bib. ref.	Remarks
NO	2.008 2.010 2.005	3.5 4.0 31	[3]	Initial product at 77°K and 4°K.
NO_2	1.9996 1.9932 2.0055 1.999	62.9 50.3 48.7 113	[21] [3]	Heat to room temp between 2 irrad. at 77°K or presence in KNO_2 nitrate. KNO_3 powder, dose $>3 \cdot 10^{20}$ eV/g.
NO_3^{-2}	2.025 2.025 2.008	9 9 9	[3]	4°K, $3 \cdot 10^{18}$ eV/g dose. Lacking at 77°K, decreases by 2 when cooled at 77°K for 2 hrs.
	2.0057 2.0057 2.0015	63.4 31.8 31.8	[21]	77°K, $4 \cdot 10^{19}$eV/g dose H||a.
NO_2^{-2}	2.006 2.006 2.002	61 32 32	[3]	Initial product at 4°K and 77°K. Axis of crystal c ⊥ axis of rotation and || H.
NO_3	2.006 2.006 2.001	0 0 0	[3]	4°K

Table 1 (cont)

NO_3 (cont)	2.0232	2.0232	2.0031	4.3	3.5	3.5	[5]	77°K quickly decaying at this temp.
O_2^-		1.958			0		[3]	Singlet. Appears during heating to 77°K of crystal irrad. at 4°K or during measurement at 4°K of crystal irrad. at 77°K

In spite of the fact that the electron paramagnetic resonance spectra in irradiated $NaNO_3$ have been studied in many papers, only the spectrum assigned to nitrogen dioxide is reliably deciphered. In two papers [26, 29], in addition to NO_2, NO_3 radicals were identified. As is obvious from table 2, in which are presented the characteristics of electron paramagnetic resonance signals in $NaNO_3$ and the conditions of irradiation, different spectra are assigned to the NO_3 radical. Gesi and Kazumata [26] assign to this radical a spectrum analogous to the one found in irradiated KNO_3 by Cunningham [3]. Adde, however, identified NO_3 in agreement with Zeldes [5] (Cf. NO_3 spectra in tables 1 and 2).

In this way, the presence of NO_2 and NO_3 in irradiated $NaNO_3$ can be considered established. If the data in tables 1 and 2 are compared, then it is obvious that the presence of NO_2 also in KNO_3 does not arouse doubt. In paper [27] it was shown that the matrix shows practically no influence on the characteristics of a spectrum of electron paramagnetic resonance specified by NO_2. Therefore the presence of NO_2 also in other nitrates occasions no doubts, since the characteristic electron paramagnetic resonance spectrum is observed also in them, as is obvious from table 3.

Table 2

Characteristics of electron paramagnetic resonance spectra in NaNO$_3$

Irradiation conditions	Para-mag. particle	$g_\parallel\langle 111\rangle$	$g_\perp\langle 111\rangle$	$A_\parallel\langle 111\rangle$	$A_\perp\langle 111\rangle$	Bib. ref.	Remarks
300°K 10-250Mrad	NO$_2$	2.0059	1.9982	48.0	58.4	[25]	
77°K	NO$_2$	2.0058	1.9964	50.5	59.1	[27]	
170°K	NO$_2$	2.0056	1.9966	51.1	58.4	[28]	
300°K	NO$_2$	2.0050	1.9970	53.0	57.8	[28]	
300°K	NO$_2$	2.006	1.9989	53	59	[26]	Disappears at 400°K
300°K 10^7-10^8r.	?	2.006	2.0097	0	0	[26]	"
300°K "	?	2.0064	2.0147	0	0	[26]	Stable higher than 530°K
300°K "	?	2.006	2.0237	0	0	[26]	Disappears at 400°K, at 300°K
77°K "	NO$_3$	2.0004	2.0053	0	0	[26]	irreversibly changes into the 3 preceding
77°K 10^{18} eV/g	NO$_3$	2.0022	2.0217	4.11	3.51	[29]	
77°K and 300°K	?	2.0030	2.0225	0	0	[29]	

In comparing the data presented in tables 1, 2, and 3, it is not hard to notice certain contradictions in the identification of separate paramagnetic particles. In connection with this the following remarks seem appropriate to us.

1. If the spectral characteristics of definite paramagnetic particles remain the same or similar in the lattices of various nitrates (which, it seems, actually does take place), then the electron paramag-

Table 3

Characterization of electron paramagnetic resonance spectra in irradiated alkaline metal nitrates

Paramagnetic particle	Irradiated salt	g-factor value			Hyperfine splitting constants (gauss)			Bib. ref.	Remarks
		g_x	g_y	g_z	A_x	A_y	A_z		
NO_3	$AgNO_3$	2.009	1.9978	2.0039	50.7	48.5	69.6	[11]	Irradiation at 77°K. Spectrum increases parallelly with disappearance of Ag^{+2} spectrum when crystals are heated from 77°K to 140°K.
"	$Sr(NO_3)_2$	1.9975	1.9975	2.0054	59	59	50	[12]	Room temperature. Formed at $\sim 10^7$ r or at $\sim 10^5$ r, if nitrate contains nitrite.
"	$Pb(NO_3)_2$	1.995	1.995	2.004	57	57	50	[15]	Room temperature.
NO_3	$Pb(NO_3)_2$	2.029	2.029	1.998	~ 1	~ 1	~ 2	[15]	"
NO_3^{-2}	$AgNO_3$	2.002	2.007	2.000	35.8	37.1	67.4	[11]	Temperature 77°K. Unpaired electron not located only on NO_3^- but also has hyperfine splitting on the Ag.
"	$Sr(NO_3)_2$	2.0081	2.0081	2.0027	0	0	1.2	[12]	Room temperature. Dose $\sim 10^5$ r.

netic resonance spectrum assigned by Cunningham to NO_2^{-2} in KNO_3 [3], by Zeldes to NO_3^{-2} in KNO_3 [22], by Mosley and Moulton to NO_3^{-2} in $AgNO_3$ [11], by Jaccard to NO_3^{-2} in KCl containing nitrate [23] must be attributed to one of these paramagnetic particles. The same thing also applies to the identification of the spectra assigned by Cunningham in KNO_3 [3] and by Zdansky and Sroubek in $Sr(NO_3)_2$ [12] to the particle NO_3^{-2}, and by Livingston and Zeldes in KNO_3 [5] and by Golding and Henchman in $Pb(NO_3)_2$ [15] to the particle NO_3. This problem was given a rather detailed examination in the paper of Atkins and Symons [30]. On the basis of comparison of the characterizations of this spectra with the spectra of isoelectronic radicals they assigned the first spectrum to NO_3^{-2} radicals and the second to NO_3^0 radicals.

2. The spectrum assigned by Cunningham [3] and Jaccard [23] to NO radicals is attributed in paper [30] to NO_2^{-2} particles.

In paper [7], however, Cunningham demonstrated by chemical analysis and electron paramagnetic resonance an NO accumulation with a dose of acceptable convergence. These data are shown in fig. 3. On the strength of this and also as a consequence of the exceedingly strong anisotropy of the hyperfine splitting constant, Cunningham's point of view on this problem is probably closer to reality.

As for the identification of NO_3 and NO_3^{-2} radicals, as yet it is difficult to give a preference for any of the opinions on this score that exist in the literature. Some sort of independent demonstration of their presence in the crystal, as also in the case of NO, would likewise be desirable. The existing data on optical spectra, of course, could serve

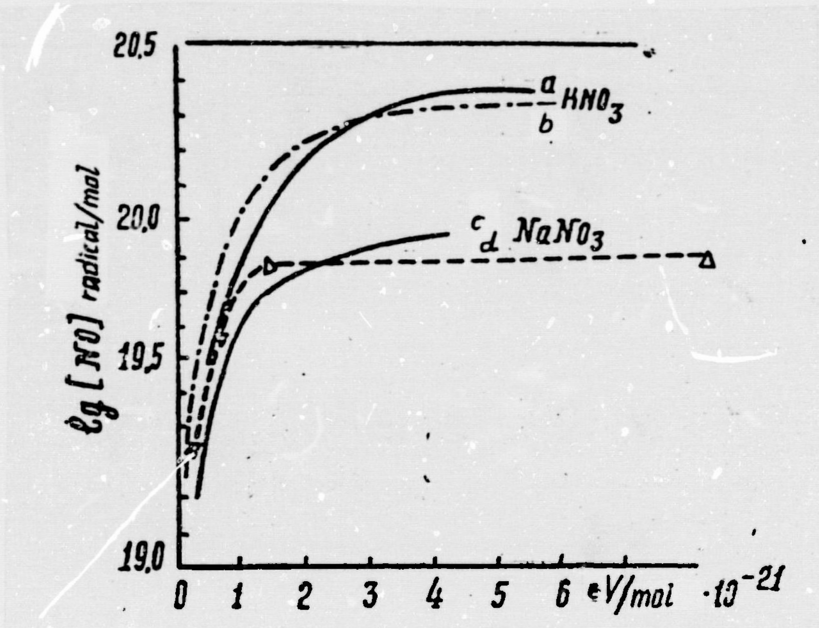

Fig. 3. Formation of NO in KNO$_3$ and NaNO$_3$ irradiated at 77°K. Curves a and c are the results of chemical analysis. Curves b and d were obtained by the electron paramagnetic resonance method.

as some confirmation of Cunningham's point of view, but these data cannot be considered completely independent of electron paramagnetic resonance since absorption belt identification was made in some measure on the basis of electron paramagnetic resonance data. As we have seen above, these contradictions are inherent also in the identification of electron paramagnetic resonance spectra in irradiated NaNO$_3$.

2. Kinetics of radiolysis

It has already been mentioned above that the products of the radiolysis of nitrates are nitrogen oxides and oxide anions and oxygen and not just nitrite and oxygen, as was assumed until the publication of Cunningham's paper [7]. However, in this same paper it was demonstrated that the concentration of radical products (NO, in particular) quickly reached saturation both during irradiation at 77°K (fig. 3) and at room temperature. On the basis of this and also in view of the lack of data on the kinetics of the accumulation of the separate products of radiolysis that contribute to the concentration determined by the diazotization reaction, we will examine below the kinetic patterns of the radiolysis of nitrates according to nitrate output. Here it should be borne in mind that the value $G(NO_2^-)$ includes in itself several values [7]: $G(NO_2^-)$, $G(NO_2)$, $G(NO)$, $G(O^-)$, and others.

a) Relation of radiation chemical output to absorbed dose

The independence of $G(NO_2^-)$ from the dose for separate nitrates has been noted in many papers [7, 8, 10, 16, 18, 31-33]. Along with this, however, in certain cases a lessening of radiation chemical output with an increase of dose was detected. This course is more characteristic of the radiolysis of potassium nitrate [32, 34, 35], whereupon in this case the accumulation of nitrite is described by two intersecting straight lines having different slope. As was demonstrated by Johnson's papers [2, 32], the deviation from linearity of the accumulation of nitrite with dose increase is, generally speaking, intrinsic for any nitrite, but the approximation of this relation to a straight line is possible only in a range of small doses that are different for different nitrates. Hence this fact also becomes understandable, that in the case of KNO_3 nonlinearity of NO_2^- accumulation with the dose is especially often detected since for KNO_3 deviation from linearity already sets in with a dose amount equal to $3 \cdot 10^{21}$ eV/g when in the case of $NaNO_3$ this dose is equal to $\sim 2 \cdot 10^{22}$ eV/g and was not achieved in many papers.

In the paper of Cunningham and Heal [35], in which doses of more than 10^{23} eV/g were used, a decrease of $G(NO_2^-)$ with dose increase was also observed in a series of nitrates. For KNO_3 the kinetics of radiolysis were described by the equation

$$\alpha = 1 - e^{bD}, \qquad (1)$$

where α is the potion of decomposed nitrate, and D is the absorbed dose.

This problem was studied in more detail for the nitrates of potassium, cesium, sodium, barium, lead, and silver by Johnson [2, 32]. In these papers, using the following kinetic diagram of decomposition:

$$MNO_3 \rightsquigarrow MNO_2 + O, \qquad (2)$$

$$O + NO_2^- \rightarrow NO_3^-, \qquad (3)$$

$$O + NO_3^- \rightarrow NO_2^- + O_2 \qquad (4)$$

and from the assumption about the stationary concentration of oxygen atoms, a second order equation for nitrite accumulation was obtained in the form

$$a[NO_2^-]^2 + [NO_2^-] = bD, \qquad (5)$$

where a and b are constants for the given salt, and D is the absorbed dose.

The applicability of equation (5) seems to be satisfactory for $CsNO_3$, $NaNO_3$, $Ba(NO_3)_2$, and $Pb(NO_3)_2$. As an illustration figure 4 shows the experimentally found accumulation of nitrite and oxygen in $NaNO_3$ and the nitrite accumulation calculated according to equation (5). In opposition to what has been presented, description of radiolysis in the cases of KNO_3 and $AgNO_3$ by this equation seemed impossible. It must be noted that equation (5) was obtained without consideration of variation of concentration during the course of irradiation. From the radiolysis diagram presented above (equations 2-4) with consideration of $[NO_3^-]$ non-steadiness an equation of the following form was obtained in paper [2]:

$$a \lg (1 - \alpha) + \frac{\alpha}{1 - \alpha} = bD \qquad (6)$$

where $= \frac{[NO_2^-]}{[NO_3^-]_0}$; and a and b are constants, and D is the absorbed dose which seemed applicable for description of nitrite accumulation in KNO_3.

For the kinetics of the radiolysis of $AgNO_3$ no suitable equation from the diagram of decomposition according to reactions (2-4) was able to be found.

It is not difficult to notice that all three kinetic equations (1, 5, 6) at sufficiently low doses can be simplified with a certain approximation in an expression of the form

$$[NO_2^-] = bD \qquad (7)$$

which is observed in the majority of papers that utilized small absorbed doses.

The applicability of the kinetic equations derived from the radiolysis diagram (2-4) can of course in no way serve as confirmation of the mechanism of radiolysis according to reactions (2-4) only suggest that at large doses of irradiation it is necessary to consider the reverse reactions.

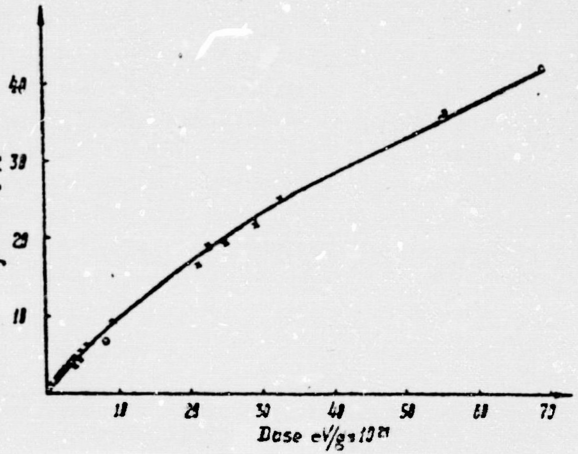

Fig. 4. Formation of nitrite in $NaNO_3$ [2]. o, x are experimental points presenting $[O_2]$ and $1/2[NO_2^-]$ respectively. The continuous line was calculated according to equation (5).

b) Influence of size of dose and linear energy loss

The influence of the size of dose on the radiolysis of nitrates has been studied in passing during the solution of other problems in papers [10, 33, 35]. This problem was, however, specially examined by Johnson [36]. When the dose size was changed from 10^{17} to 10^{20} eV/g on samples of the nitrates of potassium, sodium, cesium, and lead, it was shown in this paper that it had no influence on $G(NO_2^-)$, just as it was shown in other papers [10, 33, 35] in the area of other dose sizes and other forms of radiation.

It is interesting to note that the G values obtained in this paper by using electrons with energies between 1 and 0.5 MeV agree with the values obtained for gamma irradiation. Thus, the conclusion that dose size does not influence the radiation chemical output of nitrite in a wide range of values (from $\sim 10^{15}$ to 10^{20} eV/g sec) permits the single-value integration of results on the influence of form of radiation on

$G(NO_2^-)$. In table 4, which is borrowed from the paper of Hochanadel [10], are presented the $G(NO_2^-)$ values obtained by radiolysis of nitrates with various forms of radiation. The closeness of the $G(NO_2^-)$ values obtained by the action of x-rays and gamma rays at 150°C to the $G(NO_2^-)$ values obtained by the action of alpha rays permitted the author to reach a conclusion about the formation of thermal wedges in the tracks of alpha-particles. Therefore, the increase of the radiation chemical output of nitrite with increase in linear energy loss was attributed to local overheating along the tracks of heavy particles. From the relation of $G(NO_2^-)$ to temperature during irradiation with light forms of radiation, the apparent energy of activation was estimated at 2.8 kcal/mol.

Table 4

Influence of linear energy loss on $G(NO_2^-)$ in nitrates [10]

Irradiated salt	Alpha-particles 3.4 MeV		Gamma-rays Co^{60}		X-rays 44.5 keV	
	25°C	120°C	30°C	150°C	15°C	150°C
$LiNO_3$	0.7		0.02-0.2	0.03-0.4	0.02	
$NaNO_3$	1.3	1.1	0.27	1.0	0.4	1.1
KNO_3	2.2		1.5	3.0	2.0	3.0
$CsNO_3$	1.4		1.6	2.3	1.4	1.2
$BaNO_3$	1.6		1.8	1.6	1.8	1.8

c) Role of the nature of the cation

From the very first papers devoted to the problem being examined, a definite relation was noted of $G(NO_2^-)$ to the nature of the cation in nitrates which is lacking in the case of aqueous solutions. The generally accepted explanation of this relation at the present time is an account of the influence of the free volume of the lattice on the probability of the reverse reaction (3). This problem has been examined in sufficient detail in preceding surveys [1, 37]; therefore we will not dwell on it in detail. It is expedient to note, however, that, in spite of the existing correlation between $G(NO_2^-)$ and the amount of free volume, the causes should not be sought in the variation of $G(NO_2^-)$, for example, along the series from $LiNO_3$ to $CsNO_3$ only in the difference of the amount of free volume in this same series, especially in the initial stage of radiolysis. Apparently the substantial role must be played not so much by the spacial characteristics of the lattice as by the electron characteristics, since radiation interacts with the electron shells comprising the lattice. In all the papers examined here, attention only on the interaction of radiation and the nitrate ion is emphasized. Therefore it should be expected that $G(NO_2^-)$ would increase with an increase of the electron portion of the anion in a series of salts of one type, for example, alkaline metal nitrates. Probably, as a consequence of the contrary relation, which has been observed in experiment, this problem remains without due attention in the literature. In our view, together with NO_3^- a substantial contribution must be made by the interaction of radiation and the cations to the output of the products of radiolysis. A similar point of view has already been expressed in the literature [3, 4, 38] without giving details and was experimentally confirmed for the first time on a sample of $AgNO_3$ [11].

Actually, if the formation of the products of radiolysis in nitrates were conditioned only by the interaction of NO_3^- with radiation, then $G(NO_2^-)$ calculated on 100 eV of energy absorbed only by the anion would have to be the same in one and the same salt when different irradiations were used. We have calculated the radiation chemical outputs of nitrite for 100 eV of energy absorbed only by the cation $G^c_{(NO_2^-)}$ or the anion $G^a_{(NO_2^-)}$ on the basis of published data on $G_{(NO_2^-)}$ for KNO_3 and $NaNO_3$. These data are presented in table 5. Analysis of this table permits expression of the following considerations:

Table 5

Influence of cations on $G(NO_2^-)$ in nitrates

Salt	Type of radiation	$G^a(NO_2^-)$	$G^c(NO_2^-)$	Lit. source for G^a and G^c calculation
KNO_3	gamma - Co^{60}	2.4±0.2	4.0±0.3	[32-34]
KNO_3	x-ray - 45 keV	24.5	2.1	[35]
KNO_3	x-ray - 200 keV	22.8	2.4	[8]
KNO_3	alpha - 3.4 MeV	3.4	6.1	[10]
KNO_3	e - 1.0 and 0.5 MeV	2.3	4.2	[36]
$NaNO_3$	gamma - Co^{60}	0.25±0.05	0.7±0.1	[32, 34]
$NaNO_3$	x-ray - 45 keV	0.8	0.7	[35]
$NaNO_3$	x-ray - 200 keV	0.6	0.7	[8]
$NaNO_3$	e - 1.0 and 0.5 MeV	0.3	0.8	[36]
$NaNO_3$	alpha - 3.4 MeV	1.7	5.5	[10]

1. As should be expected, for Co^{60} gamma rays and electrons, the

energy absorption of which is proportional only to the electron density, both $G^a_{(NO_2^-)}$ and $G^c_{(NO_2)}$ [sic] coincide in one and the same salt.

2. The radiation chemical output of nitrite for the anion in the case of x-rays is different by an order from $G^a_{(NO_2^-)}$ in the case of gamma irradiation in KNO_3 and by three times in $NaNO_3$, but the corresponding values of $G^c_{(NO_2^-)}$ are different by only two times for KNO_3 and coincide for $NaNO_3$. Since the patterns of energy absorption of soft x-rays and Co^{60} gamma-rays strongly differ, it is exactly here that the contribution of the anion and the cation to the nitrite output must appear. These results therefore permit speaking about the largest contribution of the cation to nitrite output and not that of the anion.

3. The strong difference in $G^c_{(NO_2^-)}$ values for KNO_3 and $NaNO_3$ and also the variance of $G^a_{(NO_2^-)}$ and $G^c_{(NO_2^-)}$ for alpha-rays with the corresponding values for gamma-rays and electrons permits the conclusion that the processes of the interaction of the cation with radiation are not the natural source of radiolysis. Substantial influence is apparently also shown by spacial factors in the case of light forms of radiation and by track phenomena in the case of alpha particles.

d) Influence of other factors

Data on the $G_{(NO_2^-)}$ value obtained by various authors, as has been shown in Sviridov's monograph, differ very strongly. Recently some experimental facts have come into existence that permit an examination of the possible causes of the discrepancy of results of various authors. One of the possible causes could be non-uniform dispersion of irradiated nitrates. In paper [2], for example, it was noted that different $G(O_2)$ was observed in crystals of different dispersion. Since the presence of captured oxygen facilitates the flow of reverse reactions, dispersion must also show an influence on $G_{(NO_2^-)}$. We have studied this problem in more detail [8] and have demonstrated that the influence of the dimensions of irradiated crystals is especially great for slightly dispersed powders and, moreover, not only $G(O_2)$ but also $G(NO_2^-)$ increases with dispersion increase.

In this same paper we also studied the influence of heterophasal admixtures of semiconductor oxides on the rate of KNO_3 and $NaNO_3$ radiolysis. Here it was shown that oxides with the least operation of the output of the electron ϕ most strongly accelerate radiolysis, while oxides with a large ϕ retard it. Since the catalytic activity of the oxides irradiated by us correlates with the operation of the output of the electron, it was surmised that up-to-the-time additions of electrons $(I_{add} < I_{salt})$ accelerate radiolysis, while acceptor oxides as regards nitrates retard decay.

Similar data were obtained by Cunningham [20, 31] with homophasal addition of $AgNO_3$ in the lattice of irradiated sodium nitrate. The decrease of radiolysis rate of sodium nitrate in the presence of Ag^+ ions in the lattice was related to the acceptor properties of Ag^+. On the other side, the introduction of Tl^+ ions, which are electron donors, as was shown in [9], accelerates the radiolysis of KNO_3. Although the experimental data in this scheme are still not sufficient to make uniform conclusions about the mechanism of the influence of admixtures, it can be stated that the purity of the irradiated salt as well as the dispersion of the crystals shows a substantial influence on radiation chemical stability.

3. Mechanism of radiolysis

The observed relationship $G(NO_2^-) / G(O_2) \approx 2$ and also the correspondence of the kinetics of nitrite accumulation and oxygen accumulation to the equation derived on the basis of reactions (2-4) served as a basis for interpretation of the mechanism of the radiolysis of nitrates according to the equations presented above. However, recently in the papers of Cunningham [4, 7, 20, 31] and in papers on the study of electron paramagnetic resonance spectra in irradiated nitrates that have been examined above, the complexity both of initial and of secondary radiation chemical processes in the irradiation of nitrates has been convincingly demonstrated. The contradictions in the interpretation of electron paramagnetic resonance spectra in irradiated nitrates that have been noted above basically concern the identification and not the presence of one or another kind of paramagnetic particle. Therefore, at the present time the possibility exists of describing separate hypothetical stages of the radiolysis of nitrates by relying on the experimental data examined above.

As the initial processes the processes of ionization and excitation must be named:

$$NO_3^- \rightsquigarrow NO_3^{-*},\ NO_3,\ \bar{e}, \qquad (8^a)$$

$$Me^+ \rightsquigarrow Me_e^{++} + \bar{e}. \qquad (8b)^1$$

footnote
on next
page.

Since the excitation of the electron envelopes of the cation does not lead to chemical reactions, the process $Me^{+} \rightsquigarrow \rightarrow Me^{+*}$ can be disregarded.

Even if the formation of NO_3 by irradiation of nitrates has been experimentally observed by many authors (tables 1, 3), reaction (8^b) has been experimentally established only in paper [11]. It must be said that NO_3 can apparently be formed not only as a result of reaction (8^b) but also because of the following reaction:

$$Me^{++} + NO_3^- \rightarrow Me^{+} + NO_3 \qquad (9)$$

which confirms the role of the cation which was examined above. The NO_3 radicals formed in reactions (8^a) and (9) are already unstable at 77°K (at room temperature NO_3 is found only in lead nitrate [15]) and be broken down according to reactions:

$$NO_3 \rightarrow NO_2 + O \qquad (10^a)$$

$$NO_3 \rightarrow NO + O_2 \qquad (10^b)$$

or serve as traps for thermalized electrons:

$$NO_3 + e \rightarrow NO_3^{-*} \rightleftarrows NO_2^- + O. \qquad (11)$$

Since stationary concentrations of NO_3 and thermalized electrons are insignificant, reaction (11) has small probability. On the other hand, Cunningham [3, 7] found that NO is an initial product and NO_2 appears

---

[1] Here and later Me^{+} designates the normal cation (Na^{+} K^{+} Sr^{++} Ba^{++} etc.) and Me^{++} designates the ionized cation, i.e., one that has lost an additional electron (Na^{++} K^{++} Sr^{++} etc.).

at large absorbed dose values. In papers [21, 22] it has also been noted that NO_2 is a secondary product. Therefore, reactions (10^a) and (11) seem to have low probability in distinction to (10^b).

The decay of NO_3^{-*} obtained by reactions (8^a) and (11) apparently must make a definite contribution to the products of radiolysis. Since the affinity of NO_3 to the electron exceeds the energy of the N-O bond, the splinter atom of oxygen must have excess kinetic energy of about 0.2 eV, it it is calculated that the energy of the affinity of the NO_3 radical to the electron is localized on a definite bond. On the other hand, the effect of the screen should appear to the greatest extent in a solid. As a consequence of the mentioned causes, the excitation energy of NO_3^{-*} will be partially dissipated on the crystalline lattice and a part of the NO_3^{-*} will decay to nitrite and oxygen atoms.

The secondary electron, being thermalized in the course of inelastic and elastic collisions, is stabilized in some trap. Traps like this can be defects originally existing in the lattice, products of cation or anion ionization, radiolysis products produced by secondary (see below) processes (O, O_2, NO_2, etc.), and, finally, normal lattice points. In the last case it is naturally expected that for nitrates of alkaline and alkaline earth metals the thermalized electron will be stabilized on the anion and not on the cation, since the oxidation-reduction potential of N^{+5} / N^{+4} must be much higher than for Me^+ / Me. Accordingly, the basic initial product, besides NO_3, will be the result of the stabilization of a thermalized electron; namely,

$$NO_3^- + \bar{e} \rightarrow NO_3^{-2} \qquad (12)$$

or, in the case of $AgNO_3$ where the cation is also an effective electron acceptor,

$$AgNO_3 + \bar{e} \rightarrow (AgNO_3)^-.$$

Reaction (12) has been confirmed in many papers [3, 4, 5, 11, 12, 20, 21, 26] and takes place only at 77 or 4°K. Upon heating higher than 77°K, NO_3^{-2} disappears. If irradiation was conducted at 300°K, this ion radical was not observed in any nitrates except $Sr(NO_3)_2$ [12].

The relative contribution of conversions of oxidized radical particles with a lack of an electron (reactions 8-11) and reduced radical particles with an excess electron (12-16) to the output of the final products of radiolysis is as yet hard to evaluate. It is exceedingly probable that these two groups of reactions lead to different products. As was already mentioned above, the relative significance of the separate reactions within each group is also not uniform.

It should be mentioned that the rate of the reactions examined above is only a function of the dose and the electron portion of the cation and anion. The majority of these must be independent of the free volume, since they are irreversible processes. In paper [7] it was actually found that G(NO) in KNO_3 and $NaNO_3$ was uniform for irradiation at 300°K and differed very insignificantly for irradiation at 77°K. This fact is experimental proof of the role of the cation that was examined above and agrees with lack of dose size influence on radiolysis of nitrates.

In our opinion, the spacial factors must to a large degree be expressed in the secondary processes, including interaction of the products of reactions (8-16). It is seen in fig. 3 that [NO] in $NaNO_3$ reaches saturation already at a dose of about $1 \cdot 10^{21}$ eV/mol when the corresponding dose in KNO_3 is about two times larger, and the stationary concentration of NO in $NaNO_3$ is also less than in KNO_3. Thus the reactions of NO decay become dependent on lattice parameters. According to Cunningham, these reactions could be:

$$NO + O \rightarrow NO_2, \qquad (17)$$

$$NO + O_2^- \rightleftarrows NO_3^{-*} \rightleftarrows NO_2^- + O. \qquad (18)$$

$$NO + NO_3 \rightarrow N_2O_4^* \rightleftarrows 2NO, \qquad (19)$$

$$NO + NO_2^{-2} \rightarrow N_2O_3^{-2}. \qquad (20)$$

Besides,

$$O + O \rightarrow O_2. \qquad (21)$$

Accordingly it should not be thought [1] that radiolysis of nitrates is not accompanied by the formation of vacant lattice joints. However, the formation of molecular oxygen with excess overlaps the formation of vacancies and creates interior pressure in the crystals, which leads to breakdown in the crystalline lattice. Apparently ionization of the cation also plays a not insignificant role in the process of the disordering of the lattice. Since reaction (9), for example, is strongly exothermal, the energy produced in this can be converted into thermal energy of the cation, which leads to displacement of it from the lattice joint. The variations observed in paper [32] in the density and heat of the solution of irradiated $NaNO_3$ and KNO_3 occur in agreement with these hypotheses.

In as much as the radiolysis processes of potassium nitrate and sodium nitrate have been studied in relatively greater detail, our discussions basically concern exactly these processes. Obviously, these discussions can without great risk be transferred to the nitrates of alkaline earth metals. As for the nitrates of heavy metals or metals showing variable valence, caution is necessary in the interpretation of the mechanism, since in this case completely different electron-ion processes can happen, the importance of which emerges from an examination of the influence of admixtures on the radiolysis of nitrates [8, 20, 31, 39].

III. Radiolysis of nitrites

The nitrites of alkaline metals are very radiation stable compounds. According to recent results obtained in this field [41], irradiation of $NaNO_2$ to doses of ∿250 Mrad does not lead to the appearance of an optically noticeable quantity of electron color centers, colloid metal, or gaseous products of radiolysis. The natural paramagnetic molecules induced by radiation are NO_2 and N_2O_4 (in interpretations [40-43]). The electron paramagnetic resonance spectrum of $NaNO_2$ irradiated at 77°K, according to [40, 42], consists of three lines of equal intensity with complete splitting of 136 gauss. Authors [40, 42] with sufficient basis attribute this strongly anisotropic triplet to an NO_2 molecule lying in plane bc of the crystal [44]. NO_2 molecules obtained at low temperature are unstable and completely disappear when the crystals are heated to room temperature.

Irradiation of $NaNO_2$ crystals at room temperature leads to consequences somewhat different from those that take place at low temperatures. The electron paramagnetic resonance spectrum of $NaNO_2$ irradiated with doses of about 100 mrad consists in this case of an anisotropic triplet and a superposable quintet. The NO_2 molecule computation made by the authors of [43] and study of the symmetry of the triplet have shown that it relates to NO_2 lying in plane ac of the crystal, that is, unfolded by 90° in relation to the position of NO_2 in low temperature radiolysis. The five-component spectrum with a component intensivity ratio of 1:2:3:2:1 most probably yields an $N_2O_4^-$ ion radical, the unpaired electron of which has equal planes on both nitrogen nuclei. The symmetry of $N_2O_4^-$ and the character of the kinetic curve of acumulation of $N_2O_4^-$ permits the assumption [41] that the ion radical is formed as a result of shift of the NO_2^- anion (or, more probably, the NO_2 molecule) to the neighboring cation vacancy (with a 180° turn) and by the formation of an N-N bond in plane bc. In this vacancies can be used that either already existed in the crystal before irradiation (most cases) or were induced by radiation. In accordance with this point of view, the lack of $N_2O_4^-$ in low temperature irradiation of $NaNO_2$ can be connected with retardation of NO_2 rotation and the small number of vacancies in nitrite at 77°k.

Enumerated data correspond well with existing published results on optical spectra (in the visible and infrared ranges) in irradiated $NaNO_2$ [44-46]. At room temperature the absorption spectrum of irradiated $NaNO_2$ has a wide maximum in the 550 to 400 millimicron range relating to NO_2. Study of spectra in polarized light has confirmed the conclusion about the distribution of the molecule at room temperature in the ac plane of the crystal.

IV. Processes in the irradiation of chlorates, bromates, and iodates

Radiolysis of alkaline metal chlorates, bromates, and iodates has received far from uniform study. While the composition of the final products of radiolysis, final product outputs, and the kinetics of accumulation and disappearance of molecular products of the first two groups of salts have been studied in sufficient detail in recent years, similar information on iodates is lacking. Optical spectra and electron paramagnetic resonance signals are described in the literature only for chlorates, papers of this kind on bromates have the character of brief reports, but the behavior of iodates is absolutely unstudied. This kind of non-uniformity in the study of the properties of these materials is connected with the greater radiation stability of the bromates and iodates and, in the case of the latter group, with the more complex structure and formation of the lattice.

1. Composition of the products of radiolysis

After the first papers on the radiolysis of chlorates [17, 62], which established the presence of oxygen, Cl^-, and ClO_2^- in the products, the problem of the composition of the products of radiolysis was first examined in detail by Heal [58].

By analysis of solutions of irradiated $KClO_3$ and from absorption spectra of crystals, the following product composition was determined by him: O_2, Cl^-, ClO^-, ClO_2^-, ClO_4^-, and also the presence in small quantities of Cl_2O_6 and ClO_2. In this, O_2, Cl^-, ClO^-, and ClO_2^- were determined immediately, and the presence of ClO_4 was hypothesized from data on the deficit of free (O_2) and bound oxygen in the products and was confirmed by study of the infrared light spectra of the irradiated salt. But the conclusion about the presence of Cl_2O_6 and ClO_2 was made from analysis of optical spectra. In the same paper it was shown that the enumerated oxychloride products in actuality are formed in a solid and do not appear during solution of irradiated crystals. This is testified to by the presence in optical absorption spectra of $KClO_3$ of bands belonging to oxychloride molecules (see below).

In the first papers on the radiation chemistry of bromates [68, 69] it was established that irradiation of bromates in a nuclear reactor by mixed radiation (gamma-rays, fast and slow neutrons) leads to accumulation of the products of radiolysis (Br_2, Br^-, BrO^-, BrO_2); moreover the value of $G(BrO_3)$ is constant (accumulation of products linearly with dose of irradiation). In more recent papers [71-74] it was shown that the forms of oxidized radiolytic products of bromine in irradiated bromates are analogous to the oxychloride products found by the radiolysis of chlorates, namely, Br^-, Br_2, BrO^-, and BrO_2^-. Among the products is also O_2, but the presence of BrO_4^- has not been conclusively established.

2. Kinetic patterns of radiolysis

The G values of some of the products of the radiolysis of potassium chlorate, first found in papers [17, 62], are for irradiation of the salt by x-rays at room temperature 1.57, 1.2, and 0.4 for oxygen, ClO_2^-, and Cl^- respectively. Radiolytic oxygen is completely retained in the $KClO_3$ lattice (to 8% of conversion, after which disintegration of crystals happens). Cl^- and Cl_2^- accumulation is linear in the region of doses radiated in [62] and depends on the temperature of heating after irradiation.

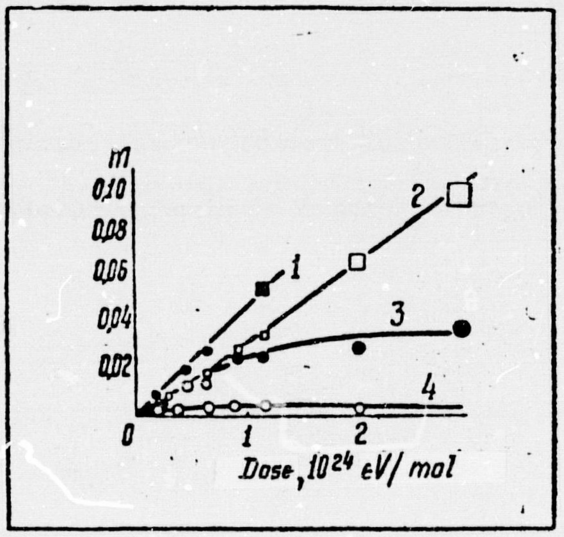

Fig. 5. Accumulation curves of the basic products of radiolysis in $KClO_3$ at room temperature. 1) O_2; 2) Cl^-; 3) ClO_2^-; 4) ClO^-.

The accumulation curves of the basic products of the radiolysis of $KClO_3$ obtained first in [58] are shown in fig. 5. The values of the "initial" radiation output (G at a dose of $0.38 \cdot 10^{23}$ eV/g) calculated from these data and also according to the results of carrying out radiolysis at -196°C are

a) at t = 25°C - 1.3, 0.5, 2.0, 2.5, 0.2;

b) at t = -196°C - 1.1, 0.5, 1.5, 2.0, and 0.2 for Cl, ClO^-, Cl_2^-, O_2, and ClO_2 respectively.

The following is characteristic of the kinetics of the radiolysis of $KClO_3$:

1. Constant rate of Cl^- and O_2 accumulation and saturation of the curves of ClO_2^- and ClO^- accumulation,

2. Insignificant influence of temperature in the 77 to 300°K range on the G values, and

3. Probable formation of ClO_4^- or Cl_2O_5 in noticeable quantities.

In a single paper [63] on the radiolysis of chlorates it was shown that the radiation output G_{Cl^-} in the case of $NaClO_3$ under the action of heavy radiation (alpha-particles) is 2.12 (at room temperature) and, in opposition to the effects with gamma-radiation, does not vary after the irradiated salt is heated. On the basis of this fact the author of [63] framed a hypothesis about the large role of thermal effects (in the track) in the radiolysis of chlorates by alpha-radiation.

Among the papers on the radiolysis of chlorates there is a group of papers studying the Szilard-Chalmers effect in this class of compounds [64-66]. Among the products in chlorates irradiated by neutrons the presence is noted of Cl^-, ClO_2^-, ClO^-, Cl_2, and ClO_4^-; the Cl^{36} isotope formed according to the reaction (neutron, gamma-ray) is almost completely retained in the Cl^- form. In paper [65], on data on the distribution of induced activity (i.e., Cl^{36} content) in the ClO_3^- and ClO_4^- forms, the conclusion was made that the production of ClO_4^- by oxidation of ClO_3^- was more probable than by the reaction of Cl^- oxidation.

In the process of the radiolysis of $KBrO_3$ under the action of mixed reactor radiation the portion of decomposed bromate increases linearly with irradiation dose increase [68-69]. In this, according to [70] G_{Br^-} + 1 ± 0.1 for gamma-radiation and fast electrons of the broad spectrum of energies and amounts to 23 to 30 (G_{Cl^-}) for mixed neutrons.

The most detailed examination of the the radiolysis of alkaline metal bromates is in the recent papers of Boyd and coauthors [71-74]. Data on the output of basic products of radiolysis under the action of Co^{60} gamma-radiation [71] are presented in table 6.

Table 6

G_0 values of the radiolysis of bromates in alkaline metals when irradiated by Co^{60} gamma radiation.

Salt		Products	
	$G(BrO_2^- + BrO^-)$	$G(Br^-)$	$G(-BrO_3^-)$
$LiBrO_3$	0.21	0.13	0.23
$NaBrO_3$	0.64	0.88	1.48
$KBrO_3$	0.46	1.07	1.53
$RbBrO_3$	0.82	1.02	1.85
$CsBrO_3$	0.49	2.23	2.73

Br^- accumulation, linear in the initial stage of radiolysis (roughly to $1 \cdot 10^{23}$ eV/g), later begins to happen at a gradually decreasing rate for all bromates except $LiBrO_3$. The degree of deviation from linearity increases along the series from $NaBrO_3$ to $CsBrO_3$. For these latter the following relation of output (y) to absorbed dose (x) is true:

$$y \doteq k_1 x / 1 + k_2 \cdot \sqrt{x}.$$

To a still greater degree in the course of radiolysis the $G(BrO^- + BrO_2^-)$ value decreases.

In the 77 to 358°K temperature range the radiolysis rate is only slightly dependent on the irradiation temperature. The ratios $G(Br^-)$ / / $G(Br^-)$ and $G(-BrO_3^-)$ / $G(-BrO_3^-)$ at 357 and 77°K are least for $CsBrO_3$ [1, 16] and maximum for $RbBrO_3$ [1, 47]. For $CsBrO_3$ the rate of Br^- accumulation is practically also independent of the size of the dose of irradiation. The isotope composition (for $LiBrO_3$) and the method of obtaining compounds (for $LiBrO_3$ and $RbBrO_3$) only weakly influence the radiolysis rate of bromates.

One of the central conclusions of paper [71] is the authors' establishment of a correlation between the amount of free volume and the radiation stability of bromates that is similar to the one that obtains for a series of other inorganic salts [75]. This correlation, however, is only true for a group of similar compounds (the alkaline metal bromates).

In a more recent paper [72] Boyd and coauthors have established that the G values of the radiolysis products of bromates in a field of neutron irradiation is considerably higher than in the case of gamma-irradiation. As a consequence of this and in order to clarify the problem of the specifics of the flow of radiolysis under the influence of neutrons, these same authors made a detailed study of the radiolysis of bromates in a field of mixed reactor radiation [73]. It was analytically established that at the total absorbed dose more than half needed internal irradiation of bromates by radiation that is regenerated by the unstable products of the reaction (neutrons, gamma-rays) and by recoil nuclei. In mixed reactor radiation the portion of "pure" gamma-radiation is more than 50% of the total dose absorbed by the bromates. The amounts of radiation products obtained by radiolysis in this kind of conditions are presented in table 7.

Table 7

G values of the basic products of the radiolysis of bromates in a field of reactor radiation

Salt	Products			
	$G(-BrO_3^-)$	$G(Br^-)$	$G(BrO^-)$	$G(BrO_2^-)$
Li^7BrO_3	0.47			
$NaBrO_3$	1.4	0.59	0.22	0.59
$KBrO_3$	1.3	0.63	0.2	0.54
$RbBrO_3$	2.4	0.96	2.23	0.31
$CsBrO_3$	3.4	0.61		
$LiBrO_3$	1.4	0.58	0.26	0.47

Comparison of the data in tables 6 and 7 shows that for all bromates, except $LiBrO_3$, the output of products by gamma-radiation and reactor radiation is very close. The output increase for $LiBrO_3$ is connected with the high efficiency of Li^6 nuclei in the capture of neutrons. The isotope composition of $LiBrO_3$ in this case, naturally, in distinction to the situation during gamma-radiolysis influences the rate of the process.

Among the alkaline metal bromates radiolysis has been studied in most detail for $CsBrO_3$ [74].

The kinetic patterns of product accumulation seem in this case to be qualitatively similar to those that obtain for $KClO_3$ (see above). The accumulation curves of oxybromide products run with saturation in such a way that at doses on the order of 10^{24} eV/g their output practically becomes equal to zero. In distinction to oxybromide products Br^- and O_2 accumulation is linear all the way to high doses. Cooling phenomena are strongly expressed. In connection with this the relative content of Br^- and bromine oxides in the products depends on the temperature of radiolysis. The outputs of all the products do not depend on the size of the dose of irradiation. The temperature relation of the rate of radiolysis for $CsBrO_3$ has proven to be complex. This is connected with the complexity of the cooling processes in bromates that happen both with the formation of the final products of the process and also with reverse oxidation of products to BrO_3^-.

3. Electron paramagnetic resonance spectra and optical spectra in irradiated salts

At the present time the form of the electron paramagnetic spectrum has been given relatively detailed study only in potassium chlorate and sodium chlorate irradiated with comparatively small doses (< 10^6 rad). Data on signals in $CsClO_3$ and $RbClO_3$ are extremely limited and, as for bromates and iodates, there is only a general indication of the possibility of observing signals in these salts and a brief description of the form of these signals in powdered materials [47].

The electron paramagnetic resonance spectrum in irradiated chlorates of alkaline metals has a complex form (fig. 6) and it still has not been deciphered completely and with sufficient correctness.

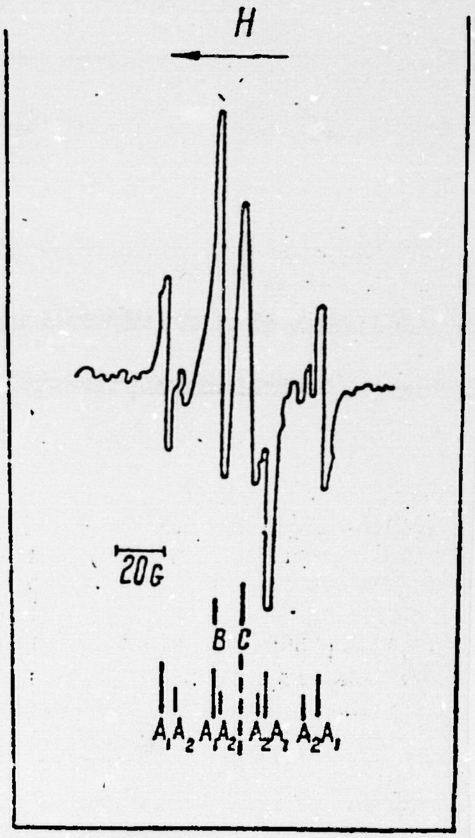

Fig. 6. Electron paramagnetic resonance spectrum of irradiated $NaClO_3$ (irradiated and taken at room temperature). A_1 and A_2 are two quartets (Cl^{35} and Cl^{37}); B and C are singlets.

Concerning the identification of each signal in the spectrum, as a rule, contradictory opinions exist in the literature.

After qualitative description of the signals in irradiated $KClO_3$ [48], the electron paramagnetic resonance of this salt was first studied in detail by Hasty and coauthors [48, 50]. According to [48] the spectrum of $KClO_3$ irradiated at 20°C consists of two groups of lines of a broad central singlet with a g-factor greater than 2 and a group of strongly anisotropic quartets with relatively less intensivity, which the authors relate to one singlet. Sixteen lines of the spectrum completely disappear when the crystals are heated to 105°C; moreover, the crystal becomes a nontransparent milky color.

The results of the author's computations of the hyperfine structure values of the quartets gave them a basis for hypothesizing that this signal relates to a ClO - ClO_3^- grouping with a generalized valence electron. In this case the ClO radical is obtained as a result of the breakdown of ClO_3^0. The four quartets realized in the spectrum relate to different combinations of Cl^{35} and Cl^{37} isotopes in the ClO - Cl_3^- complex, having different nuclear magnetic moment values. The authors attribute the central singlet to the O_2^- radical (without any clear bases for this). On the other hand, the authors of [49] think that the central singlet in the spectrum of irradiated $NaClO_3$ should (as also in the case of $KClO_3$) be attributed more probably to the O_3^- radical ($g = 2.003$ to 2.015) than to the O_2^- radical, since the latter possesses a large anisotropy, which is not characteristic of the singlet in the $NaClO_3$ spectrum. Unlike [48], paper [49] in addition to the singlet and the complex multi-quartet spectrum demonstrated the presence of a weakly split doublet (table 8) and two other lines hidden by quartets. The first doublet was hypothetically attributed to the ClO_2 ($g = 2.01$ according to [51]) and the second, to oxygen or an oxygen formation (table 8).

In this same article the authors concluded that there was no signal in $NaBrO_3$ irradiated with gamma-radiation.

Atkins and coauthors, having studied the analogy between the spectra of oxychloride radicals (ClO, ClO_2, and ClO_3) frozen in different matrices and the form of the electron paramagnetic resonance signals in irradiated chlorates and perchlorates, think that the false signal in chlorates is with greater probability related to the formation of $Cl - ClO_3^-$ than to the $ClO - ClO_3^-$ ion radical. As for the central singlet, the authors of [51] definitely relate it to O_3^- on the basis of the lack of a similar signal in KO_3 and because of the correlation with the optical spectrum of ozonide.

Table 8

Character of electron paramagnetic resonance signals in irradiated chlorates

Paper	Radicals			
	$O_3^-(O_2^-)$	ClO_2	ClO	ClO_3^0 $ClO - ClO_3^-$
[58]	g = 2.00			
[49]	g = 2.00 A = 11 gauss	g = 2.01 A = 57	g = 2.022	g = 2.0023
[51]		g = 2.0102		
[52]	g = 2.008			
[53]	g = 2.0338			g = 2.0124
[61]		g = 2.0032		2.003

In a more recent paper devoted to electron paramagnetic resonance spectra in irradiated $NaClO_3$ [52] it was shown that at doses of irradiation to ~10^5 roentgen three paramagnetic centers are noticeable. Upon further irradiation their number grows. In opposition to [48] and [51] the authors relate the multi-quartet spectrum (found also in all the preceding papers) to the ClO_3 radical on the basis of the fact that the established form of the center - a pyramid with its axis along the <111> direction of the crystal - corresponds to the form of ClO_3^0 situated in the normal place of the chlorate anion. This axial symmetry established experimentally for the center does not permit attribution of it to ClO_2 which more probably has rhombic symmetry [51]. A similar conclusion about the nature of the signal was arrived at in [61], where, in addition to it, three centers were detected in $KClO_3$, one of which was attributed to ClO_2^0. Besides the complex signal, the authors found two other central singlets which they did not identify.

The position of the g-factor of one of the singlets ($g = 2.008$) is close to the position of the signals attributed in papers [48] and [49] to the O_3^- ion radical. The center corresponding to the second signal ($g_{||} = 2.007$; $g_{\perp} = 2.02$) was not established.

The results obtained in [53] show that the character of the electron paramagnetic resonance signals in powdered salts irradiated at room temperature are qualitatively similar in all the chlorates of alkaline and alkaline earth metals. However, the g-factor values found in this paper for the centers differ from those found earlier for monocrystals. Not framing any new hypotheses about the identification of the signals, the author withholds his point of view on this question [48].

As follows from what has just been presented, a single point of view on the question of models of the centers responsible for absorption in chlorates in the superhigh frequency range does not exist.

At the present time it is apparently possible with sufficient definiteness to decipher the central singlet, assigning it to O^-. Among the proposed models of the multi-quartet spectrum the ClO_3^0 radical is more probable.

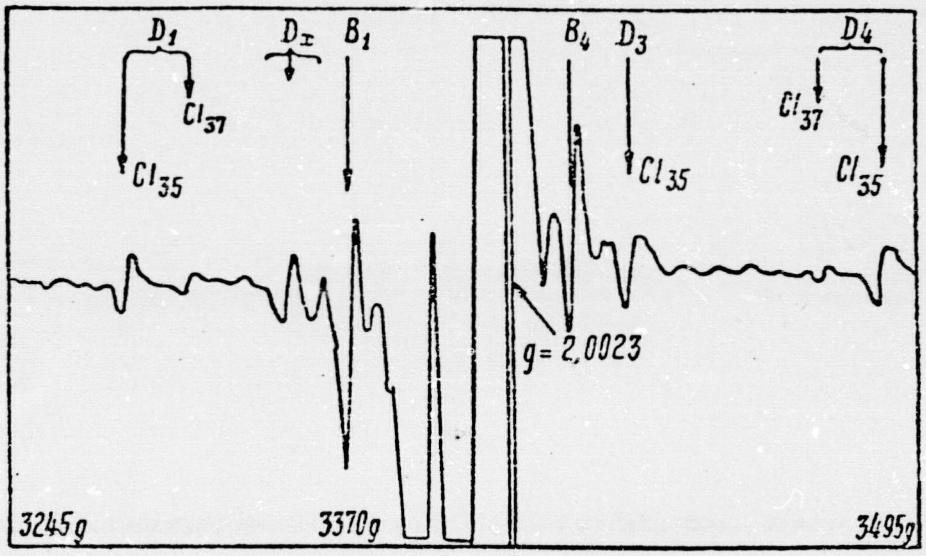

Fig. 7. Electron paramagnetic resonance spectrum of irradiated $KClO_3$ ($\vec{H}$ [111]), D - multi-quartet signal.

Unlike the work done earlier in papers [47, 54], for the first time information about the electron paramagnetic resonance spectra of alkaline metal chlorates irradiated and exposed at 77°K and data about the kinetics of accumulation and the patterns of cooling of signals in a series of chlorates and about the connection of the rate of accumulation and the parameters of the crystalline lattice were obtained. Irradiation of salts at low temperatures with large doses (to 10^8 rad) provided for the first time the possibility of obtaining signals in bromates and iodates and of sharply observing signals in $KClO_3$ that had not been detected before.

Papers [55, 57], which are fundamentally brief reports, describe nuclear quadrupolar resonance signals on Cl^{35} nuclei in the chlorates of potassium and sodium.

The authors note a broadening of the lines after irradiation of the chlorates, which is a consequence of the disturbance of the crystalline field by the radical and ion products of radiolysis. The conclusion of one of the papers about the larger value of G during irradiation of $NaClO_3$ by neutrons in comparison with radiolysis by gamma-radiation is interesting.

Information on the optical absorption spectra in irradiated salts of the $MeHalO_3$ type is extremely limited.

Heal, after studying the absorption spectra of fine monocrystalline plates of $KClO_3$ [58] irradiated with x-rays to high doses ($\sim 10^{23}$ eV/g), established the presence in the spectra of three absorption bands - at 260 mμ, 310 mμ, and in the 450 mμ range. By analogy with the position of the absorption bands of oxychloride anions in aqueous solutions [59] he related these bands to ClO^-, ClO_2^-, and Cl_2O_6 respectively. Their presence was confirmed by analysis of a solution of the irradiated salt. Unlike Heal's data, papers [48] and [60] noted only one intensive band in irradiated $KClO_3$. Its maximum was at 461 millimicrons and it was stable at room temperature. In the same conditions paper [60] observed two absorption peaks in $NaClO_3$, shifted into the shortwave region of the spectrum. More careful study of the coloration of $NaClO_3$ at room temperature, which was done in [67], has demonstrated that three absorption regions are produced in the spectrum of an irradiated salt - at about 260 millimicrons and with maxima at 302 and 420 millimicrons. These centers are not induced by irradiation of chlorate by light (220 to 400 millimicron region) and by additive coloring and heating of crystals in an oxygen atmosphere. The absorption centers are optically stable but are destroyed by heating the irradiated crystal to 140°C.

Absorption in the region of wave lengths less than 260 millimicrons and at 302 millimicrons naturally, as also in $KClO_3$, joins with ClO^- and ClO_2^-. If one considers that in irradiated $NaClO_3$ all the absorption bands are shifted into the shortwave region of the spectrum relative to the bands in $KClO_3$, then it is possible to suppose that the 420 millimicron band in $NaClO_3$ is analogous to the band at 460 millimicrons in $KClO_3$. In paper [48] the maximum in $KClO_3$ at 460 millimicrons is attributed to an O_2^- center situated in an anion vacancy. Finally, paper [53] contains still another hypothesis, according to which the color of irradiated chlorates (unfortunately, the author does not say which absorption band he is talking about) is attributed to $ClO - ClO_3^-$ centers.

The discrepancy existing between the data in [58] and that in [48, 53, 60] can be connected with the fact that in the latter papers irradiation was carried out with comparatively small doses, which apparently did not permit the obtaining of bands from a series of products. As for a model of the center responsible for the 460 millimicron band, Cl_2O_6 or O_3^- molecules should be considered the most probable.

4. The mechanism of radiolysis

The data presented above on the optical absorption and electron paramagnetic resonance spectra and also on the character and accumulation of the final products in the radiolysis of chlorates of alkaline metals provides a basis for the construction of a hypothetical mechanism of the radiation decomposition of this group of compounds. The stated propositions are admissible in the largest measure only for potassium chlorate and sodium chlorate, in as much as the necessary experimental data has been obtained only for these two salts.

In the radiolysis of chlorates the following fundamental stages are probable:

$$1.\ \mathrm{ClO_3^-} \rightsquigarrow \mathrm{ClO_3^{-*}} \left| \begin{array}{ll} \to \mathrm{ClO^- + O_2}, & (a) \\ \to \mathrm{ClO_2^- + O}, & (b) \\ \to \mathrm{Cl^- + O_2 + O}, & (c) \\ \to \mathrm{ClO + O_2^-}, & (d) \\ \to \mathrm{ClO_2 + O^-}; & (e) \end{array} \right.$$

$$2.\ \mathrm{ClO_3^-} \rightsquigarrow \mathrm{ClO_3^0} + e^*;$$

$$3.\ e^* \to e;$$

$$4.\ \mathrm{ClO_3^0} \to \left| \begin{array}{ll} \to \mathrm{ClO_2 + O}, & (a) \\ \to \mathrm{ClO + O_2}, & \\ \to \mathrm{Cl + O_2 + O}; & (b) \end{array} \right.$$

$$5.\ \mathrm{ClO_3} + e \to | - \text{products } 1,\ a - 1,\ e;$$

$$6.\ \mathrm{O_2^- + O \to O_3^-},$$

$$\mathrm{O_2}/\square\, a + e \to \mathrm{O_2^-}/\square\, a;$$

7. $O + O \rightarrow O_2$; (a) $Cl + Cl \rightarrow Cl_2$; (b)

8. $ClO_2^- \rightarrow Cl^- + O_2$, (a)

$ClO^- \rightarrow Cl^- + O$; (b)

9. $ClO_2^- + O_2 \rightarrow ClO_3^- + O$, (a)

$ClO^- + O_2 \rightarrow ClO_3^-$; (b)

10. $ClO_3^- + O \rightarrow ClO_4^-$.

As the primary stages of radiolysis both excitation (1) and ionization (2) of anions are probable. In the dissociation of excited ClO_3^{-*} a wide range of oxychloride products, determined analytically or spectroscopically, can be formed (reactions 1a - 1e). The formation of oxychloride anions (stages 1a - 1c), however, appears more probable than reactions (1d) and (1e) in virtue of the fact that oxychloride formations [76] have a higher affinity to the electron than oxygen does. The products formed in this have been clearly determined analytically (see above), but the presence of part of them immediately in the crystals has been established also by studying the optical absorption spectra in irradiated crystals.

The experimental facts that confirm ionization in chlorates are the following:

1. the presence of a multi-quartet signal in the spectra of irradiated $NaClO_3$ and $KClO_3$ related, most probably, to ClO_3^0;

2. the formation in radiolysis of small quantities of Cl_2O_6 [58] produced by biomolecular interaction of ClO_3^0.

After ionization the excited electron loses its energy (electron thermalization, stage 3), after which it is caught by one of the traps.

The ClO_3^0 radical, since it is an unstable formation, can be thermally decomposed (especially by radiolysis in the region of elevated temperatures); the ClO and ClO_2 radicals formed in this can exist in the products of radiolysis, however the question as to whether they are present as intermediate or final formations is answered clearly only for ClO_2^0.

In view of the high affinity of the ClO_3^0 radical for the electron (E = 3.96 eV, according to [76]), their recombination can also lead to rupture of the bonds within the radical. The possibility of this is determined to a considerable extent by the relationship between the energy of ClO_3^0 affinity to the electron and the energy of the rupture of the Cl - O bonds in chlorate. The latter value in $KClO_3$ amounts to 2.38 eV [17]. Accordingly, it can be assumed that the recombination has the character of a dissociative joining of the electron to ClO (reaction 5).

In the electron paramagnetic resonance spectra of irradiated chlorates one of the singlets is related to the oxygen radical [illegible]. This provides the basis for the introduction of reaction 6, in which, judging by the latest papers, stage (6a) seems more probable.

By analogy with the bromates the annealing of the products of radiolysis that apparently takes place also in the very process of radiolysis at medium and high temperatures happens both by means of the thermal conversion of unstable products (reactions 8a and 8b) and with reverse oxidation of oxychloride products by radiolytic oxygen (reactions 9a and 9b). As the first events in the radiolysis of chlorates reactions (1) and (2) apparently proceed parallelly.

Determination of the further fate of the ClO_3^0 radicals formed in stage (2) - whether decay or dissociative recombination with an electron - is definitely impossible at the present time. However, data on the lack of influence of dose size on the accumulation of paramagnetic particles in chlorates permit the surmise that the more probable process is the decay of ClO_3^0 (reaction 4). In connection with this and in correspondence with the above presentation it can be expected that the formation of neutral oxychloride radicals (ClO, ClO_2) and anions (ClO^-, ClO_2^-) in chlorates happens by different reactions (4 and 1 respectively).

In as much as a series of papers has demonstrated the presence of the ClO_4^- anion in the products of the radiolysis of chlorates and since paper [65] contains confirmation of the formation of ClO_4^- by the full oxidation of the chlorate anion, reaction (10) must be introduced conjecturally.

In a similarly drawn up diagram of radiolysis Baberkin [62] also considers it probable that the excitation and ionization that bring about the formation of the products of radiolysis proceed parallelly, but he thinks that the role of the ionization processes is insignicant.

In paper [58] Heal examines only chlorate anion excitation as the initial process; however, the list of fundamental stages of radiolysis examined by him does not take into account the formation of a series of radical products, the presence of which was established later by electron paramagnetic resonance.

The formation of Me^{++} cations as the initial products in the radiolysis of chlorates by the reaction

$$Me^{+} \rightarrow Me^{++} + e \qquad (11)$$

and the further interaction of Me^{++} with the neighboring anion

$$Me^{++} + ClO_3^{-} \rightarrow Me^{+} + ClO_3^{0} \qquad (12)$$

is apparently possible in principle just as that which was proposed above for nitrates. For chlorates, however, evaluation of the contribution of the cation to the total product output is as yet impossible.

The formation of radicals and final molecular products by the radiolysis of alkaline metal bromates has been studied in relatively very much less detail than in the case of chlorates. The literature has clarified to a sufficient degree only the problem of the composition and accumulation of bromide and oxybromide anions with a low degree of bromine oxidation. In connection with this the mechanism of bromate radiolysis presented in [72-73] looks less definite and substantiated than the list of fundamental stages that can be presented for the chlorates. It is reasonable to suppose (and comparison of the composition of the molecular products of chlorate and bromate radiolysis confirms this) that the character of the fundamental stages of the radiolysis of bromates must basically be similar to that which obtains in the radiolysis of chlorates. The differences in radiolysis mechanisms that exist for these two groups of salts can be definitely established only by careful comparative study of the optical and electron paramagnetic resonance spectra of the salts.

V. Radiolysis of perchlorates

Among the groups of salts examined in this review the perchlorates are the least resistant to the action of radiation. As the products of the radiolysis of potassium perchlorate after dissolving the irradiated salt in water Heal [77] identified Cl^-, Cl_3^-, and O_2. However, Baberkin [62] found that chloride appears only after the heating of irradiated samples to higher than 270°K. Paper [77] had also hypothesized the formation of hypochlorite and chlorite, the presence of which in the irradiated perchlorates of alkaline and alkaline earth metals was experimentally demonstrated in later papers [38, 78, 79]. Accumulation of the fundamental products of radiolysis with absorbed dose departs little from linearity. The radiation chemical output values of the products of the radiolysis of the perchlorates of various metals are presented in table 9.

As is seen from this table, the fundamental products of the radiolysis of perchlorates are chlorate and oxygen. The remaining products are formed with relatively small outputs. In papers [38, 78] it is demonstrated that $G(-ClO_4^-)$ in $KClO_4$ and $NaClO_4$ is almost independent of temperature in a wide range of temperatures. From table 10, taken from the paper of Prince and Johnson [78], it can be seen that $G(ClO_2^-)$ and $G(ClO_2)$ decrease monotonically with increase of temperature of $KClO_4$ irradiation and $G(ClO^-)$ passes through the maximum. The author attributed these facts to the thermal decomposition of these products.

Table 9

Radiation chemical outputs of the products of the radiolysis of perchlorates at room temperature

SALT	$G(ClO_3^-)$	$G(ClO_2^-)$	$G(ClO_2)$	$G(ClO^-)$	$G(Cl^-)$	$G(O_2)$	$G(-ClO_4^-)$	REFERENCE
$LiClO_4$	2,80	0,15	0,59	0,10	0,12	2,15	3,76	78
$NaClO_4$	3,57	0,17	0,11	0,09	0,42	2,96	4,36	[78]
$NaClO_4$	2,8	0,75	0,08	0,1	0,43	—	4,2	[38]
$KClO_4$	2,99	0,18	0,12	0,09	0,45	2,68	3,83	[78]
$KClO_4$	—	—	—	—	0,94	—	3,46	[79]
$RbClO_4$	4,06	0,20	0,12	0,14	0,75	3,84	5,27	[78]
$RbClO_4$	—	—	—	—	1,14	—	4,86	[79]
$CsClO_4$	5,28	0,22	0,10	0,17	1,07	5,28	6,84	[78]
$CsClO_4$	—	—	—	—	1,94	—	8,84	[79]
$Mg(ClO_4)_2$	4,29	0,14	0,07	0,03	0,15	2,62	4,67	[78]
$Ca(ClO_4)_2$	3,44	0,00	0,51	0,08	0,12	1,99	4,15	[78]
$Sr(ClO_4)_2$	3,90	0,19	0,14	0,11	0,19	2,61	4,53	[78]
$Ba(ClO_4)_2$	1,76	0,84	0,42	0,12	0,06	2,18	3,20	[78]

Table 10

Influence of irradiation temperature on the radiolysis of $KClO_4$ [78]

t° C	$G(-ClO_4^-)$	$G(ClO_3^-)$	$G(ClO_2^-)$	$G(ClO_2)$	$G(ClO^-)$	$G(Cl^-)$	$G(O_2)$
−196	4,0	2,7	0,58	0,18	0,00	0,5	3,0
−80	4,0	2,8	0,49	0,17	0,00	0,6	2,7
−16	3,7	2,8	0,26	0,06	0,06	0,5	2,4
−8	3,5	2,6	0,26	0,09	0,06	0,5	2,6
0	3,4	2,6	0,20	0,07	0,06	0,5	2,2
20	3,7	2,9	0,19	0,09	0,08	0,5	2,5
72	4,1	3,3	0,19	0,09	0,00	0,5	2,7
260	4,9	4,2	0,00	0,00	0,00	0,7	2,0
295	3 8	2,9	0,00	0,00	0,00	0,9	1,0

The electron paramagnetic resonance method has also confirmed the instability of ClO_2 molecules at temperatures higher than 340°K [80]. At room temperature, besides ClO_2 [80, 81], paramagnetic particles of O_3^- and an unidentified radical have been detected in irradiated $KClO_4$. Additionally at 77°K ClO_3 radicals appear [80]. The ClO_3 radical was also found in irradiated NH_4ClO_4 [82-84] at room temperature. However in these conditions it is very unstable. The presence of other paramagnetic particles formed by irradiation of $KClO_4$ were not detected in NH_4ClO_4. Besides ClO_3, in irradiated ammonium perchlorate NH_3^+ ion radicals are formed, which are stable at 300°K [82-86]. It must be noted that not only do the intermediate products of the radiolysis of ammonium perchlorate and potassium perchlorate differ, but also the final products determined by chemical methods. Thus in papers [87, 88] it was demonstrated that the fundamental products of the radiolysis of NH_4ClO_4 are Cl_3 and Cl^-, which is connected with the oxidation of the ammonium ion. However, in the perchlorates of metals of the first and second groups of the periodic table the nature of the cation shows an influence only on the value of the radiation chemical output. The dependence of $G(-ClO_4^-)$ on the nature of the cation, as also in other layers, is attributed to variation of the amount of free volume in the crystalline lattice [78, 79]. The fact that draws attention to itself is that in the case of perchlorates the influence of the nature of the cation is very much less expressed than in the case of, for example, the nitrates. Apparently this is connected with the fact that in the radiation chemical stability of the perchlorates in the series of cations of alkaline and alkaline earth metals overwhelming significance is possessed not by free volume but by the electron allotment of the cation and anion [38]. However, there is as yet insufficient information existing in the literature for a confident interpretation of the mechanism of the radiolysis of the perchlorates. The accumulation of experimental results similar to the data on the electron paramagnetic resonance spectra in irradiated perchlorates [80-85] and the optical absorption spectra [59] permits a more detailed study of the intermediate stages of the radiolysis of perchlorates. From this point of view the diagrams of the separate intermediate stages presented in paper [78, 80] should be viewed as very hypothetical.

VI. Annealing of radiation dislocations

Many researchers, mainly in recent years, have undertaken the study of the processes of the restoration of the properties and stoichiometric composition of irradiated materials under the action of a different kind of influences on the irradiated compounds.

The papers written in this vein form two groups of research efforts with several different problems set before them.

The majority of the papers are devoted to the study of annealing phenomena in preparations (mainly inorganic, oxygen-containing, radiation stable salts) irradiated by slow neutrons. Mainly they examine the problems of isotope separation with the use of the Szilard-Chalmers effect and the variation during isotope diffusion among the separate chemical forms in the irradiated materials. In view of the oblique relationship of this problem to the subject of the radiation chemistry of solid compounds and also because of the appearance recently of two similar surveys in this field [89, 90], we will not examine the problems of the annealing redistribution of recoil nuclei in detail in this paper.

A comparatively small number of the papers under examination are devoted to the problems of the variations during the post-radiation annealing of the concentration of the products of radiolysis in solid salts.

1. Annealing phenomena in irradiated nitrates

The majority of the papers on the annealing of the products of radiolysis are written with the use of barium nitrate and the nitrates of several heavy metals as their subjects. The first qualitative observations of the annealing of the radiation products in nitrates-however, were obtained on KNO_3 [91]. In this and in following papers variation was studied during concentration of nitrite in nitrates irradiated with gamma-radiation or fast electrons.

The material existing in the literature is exclusively devoted to the kinetics of thermal annealing; post-radiation variation of the products under the influence of other facts has been given extremely feeble study.

In paper [92] it was established that during heating of crystals of $Pb(NO_3)_2$ at $t = 150°C$ the concentration of nitrite in them decreases with a rate that is highest in the intial period of the annealing and acquires a constant value after 30 to 40 hours of heating. Oxygen from the air does not participate in the annealing; the thermal decomposition of $Pb(NO_3)_2$ - $Pb(NO_2)_2$ solid solutions at 150°C is not observed [93]. All this provided the authors a basis for assuming that in the annealing of irradiated nitrates nitrate oxidation happens via the molecular oxygen product of radiolysis. It has been established in a series of papers that dislocations of the crystalline lattice of nitrates play a very important role in annealing. Any kind of treatment of irradiated crystals that causes an increase of defects in them can be a cause of an increase in the rate of annealing.

Thus in [94] it was shown that the pressing (40 T / cm^2) of irradiated $Pb(NO_3)_2$ powder causes a noticeable increase in the rate of annealing. A (quantitatively) similar effect was produced by the pulverization of irradiated lead nitrate, which was carried out before it began to be heated at 150°C [95]. In both cases the acceleration was characteristic of the initial (fast) stage of annealing, but the constant rate of the process in the later stages remains unchanged. In this case the pulverization of the crystals itself causes only very weak annealing, but pressing of irradiated $Pb(NO_3)_2$, on the other hand, itself leads to a considerable decrease of nitrite concentration. The annealing portion in this case is 0.141 for a pressing pressure of 10 T / cm^2 and 0.181 for 20 T / cm^2 [14]. The authors connect the acceleration of annealing after pressing hypothetically with the formation at high non-uniform loads of a considerable number of point [13] vacancy defects and interpunctal ions [13], which play an important role in annealing [93, 96].

Study of annealing in irradiated $Ba(NO_3)_2$ [13] has shown that in this case the process happens at temperatures higher than for $Pb(NO_3)_2$. Unlike $Pb(NO_3)_2$ complete cessation of annealing after 20 to 40 hours of heating and less process depth (i.e., greater radiolysis irreversibility) is characteristic for barium nitrate. Some results on the thermal annealing of the nitrates in irradiated $TlNO_3$ and the nitrates of the alkaline metals are contained in [39, 97, 98]. The data presented in these papers show that the rate of annealing in nitrates depends both on the macroproperties of the crystalline lattice [98] (free volume) and on the microdislocations and defects of the matrix, the content of which can be regulated by the introduction of heterovalent admixture ions into the nitrates [39].

The dependence of the rate of annealing on the macroproperties leads to a patterned variation in the rate and depth of annealing in the nitrates of alkaline metals along the series from $NaNO_3$ to $CsNO_3$. Moreover, the temperature coefficient of the rate of annealing in the nitrates is substantially greater than the analogous value for the rate of radiolysis. As a consequence of this the serial dependences of the rate of radiolysis of the alkaline metal nitrates at elevated temperatures and during irradiation with alpha-particles (high temperatures in the tracks) seem to be expressed remarkably more weakly [10]. On the other hand, the important role of microdislocations is pointed out by the variation of the rate of annealing during the introduction into the lattice of the nitrates of the higher valence cations that accompanies the increase in the number of cation vacancies in the nitrates.

2. Annealing phenomena in other oxygen-containing salts

The various forms of the oxidation of haloids that are formed during the radiolysis of oxyhaloid compounds are thermally unstable products and can undergo various transformations during storage of the irradiated salts. The kinetics of this kind of transformations in sodium chlorate is described in [63, 99]. The heating of $NaClO_3$ in the 100 to 210°C temperature region leads to an increase of Cl^- output on account of the thermolysis of the oxychloride products of radiolysis (ClO_2, - ClO_2^-). But maintenance of the irradiated salt at 50°C causes more complex variations of G_{Cl^-} in this time, i.e., a quick initial increase of G_{Cl^-} and a succeeding fall to a value less than that of G_{Cl^-} in chlorate that has not been put aside. The complex character of the kinetic curve of annealing provides a basis for the hypothesis that along with the process of the decomposition of oxyhaloid forms a substantial role in heating is played by the concurrent recombination reactions of these forms with oxygen captured by the matrix, which leads to the reduction of the anion that had been broken down by radiation. Papers [71, 74, 100, 101] present experimental results that confirm the discharge during annealing of oxidized haloid forms via these two channels simultaneously and at rates that do not differ very much from each other (for $CsBrO_3$ and $KBrO_3$).

Annealing, which probably takes place in the form of the thermal decompositon of oxychloride products is characteristic also of the perchlorates of alkaline metals [78], although in this case the problem of the character of the annealing (oxidation or thermolysis) was not specially studied by the authors. The result communicated in [78] permit the assumption that in the perchlorates, in a way similar to that which obtains in alkaline metal nitrates [98], the rate of annealing substantially depends on the free volume of the crystalline lattice; moreover, it is greatest in the perchlorates that have the maximum free volume.

The existence of this kind of correlation for the nitrates and perchlorates of alkaline metals permits posing the question of the generality of the connection between the annealing rate of the products of radiolysis and the amount of free volume in the lattice for the entire class of inorganic salts. The existence of this connection is understandable for the case when annealing takes place as the recombination (but not the thermolysis) of radiolytic products. Improvement in the mutual diffusion conditions of the products in a series of salts of one type parallelly with free volume increase must naturally cause an increase of the annealing rate in this same series.

Substantial interest is presented by papers which study the influence of a different kind of actions on radiation stable salts (mainly chromates, bichromates, and phosphates) after they have been irradiated by slow neutrons [102-108]. In these papers it was established that treatment of the irradiated salts by softer radiation (light, gamma-rays, fast electrons), as well as pressing or pulverizing them, causes succeeding thermal annealing of the products of the Szilard-Chalmers reaction. Just as in the similar experiments with nitrates described above, the detailed mechanism of this kind of stimulating influences is not clear.

The effectiveness of retention of the products of the Szilard-Chalmers process is also substantially influenced by admixture ions introduced into the lattice of the crystal [109, 110]. The authors think that this points out the important role of fundamental ion and electron processes in the implementation of annealing in inorganic salts irradiated by neutrons.

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[Note: Items marked by an asterisk (*) are transliterated and / or translated as applicable in a separate list following the main list.]

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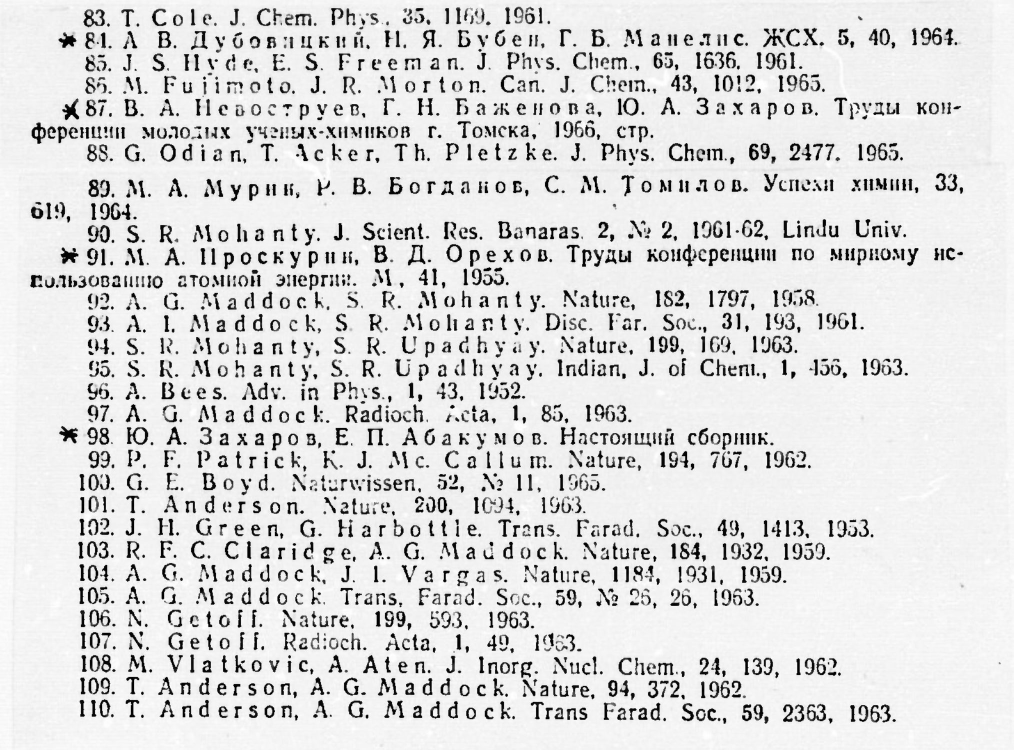

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