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Modeling of the Elementary Step of Chemical Transformation of Crystals: II. Application to Decomposition of Metal Azides

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The model set forth in Part I for analyzing the elementary chemical step (ECS) in the case of solid state reactions is applied to an examination of the thermal decomposition, photolysis, and radiolysis of metal azides. A comparison is made of various possible elementary chemical transformations of the structural units (SU) of the crystals of these salts. At the same time, correlations in orbital symmetry and spin are analyzed, and correlation diagrams (CD) that identify the electronic terms of the SU and the products of their transformation are constructed. On the basis of an analysis of the ECS, the mechanism of the chemical step of decomposition of the salts tested is formulated and an interpretation is given to various experimental data (composition and yield of products, catalysis and autocatalysis, effect of magnetic field, etc.).

1. Thermal Decomposition of Metal Azides

The effectiveness of the proposed model for the elementary chemical step (ECS) and the information content of such an approach can be demonstrated in the example of decomposition of salt-like inorganic azides. A large number of studies has been dedicated to the study of azides and there is much experimental material on the kinetics of decomposition and physical chemical properties (see, for example, (*1–7*)). Intensive research into the azides stems from their applied value; at the same time, metal azides are a convenient model for study in depth of the decomposition mechanism (*2*, p. 246). The experimental data, however, have not yet been interpreted on the basis of an analysis of the elementary steps of transformation. The azides can serve as an illustration of the unfortunate situation in theory when the detailed mechanism of decomposition is discussed without substantiated selection of the ECS.

1.1. Structural Units in the Azides

In the case of ionic azides (the most typical among them are the azides of the alkali and alkaline earth metals), the N_3^- azide ions and the metal cations emerge as the structural units (SU). The azide ions in these crystals can be rather specifically identified (*8*). They are linear and symmetrical; the parameters of their geometry depend weakly on the cation (*4–6*). The electronic structure of the linear N_3^- is examined in Refs. (*9–14*) within the framework of MO theory. The excited states $^1\Sigma_u^-(\sim 230$ nm), $^1\Delta_u(\sim 190$ nm), $^1\pi_{g,u}(\sim 155$ nm), and $^1\Sigma_u^+(\sim 145$ nm) have been determined experimentally (*15*). In the first excited states the azide ion preserves its linear geometry (*10*). The ionization threshold in the ionic crystals equals 7 to 8.6 eV (*4*, *6*, *15*). The formation enthalpy of N_3^- equals 35 kcal/mole (*16*). In analyzing the structural and geometric relations in the crystals, the azide ion can be considered as an ellipsoid of revolution with

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axes equal to 5.1, 3.5, and 3.5 Å (*5*). The azide ions have closed electron shells, i.e., they belong to the class of "saturated" SU. Adiabatic transition from the SU of the crystal to free N_3^- leads to an ion in its ground state of $^1\Sigma_g^+$. In the case of azides with considerable covalent character (the azides of lead, silver, thallium, copper, etc.), the SU are "unsaturated," and a problem arises of selecting the initial approximation (the state of the free azide grouping). In the extreme case of completely covalent azides, it is natural to take some state of the N_3^0 radical as the initial approximation; however, one should consider that the electronic distribution of free N_3^0 undergoes strong perturbation in the transition to the state of an SU of the crystal.

In the case of partially covalent azides, electron excitation is possible in the form of "positive holes of conductivity." The presence of hole conductivity when heated and under the influence of light has been established experimentally for azides of lead, silver, and thallium, which have a comparatively narrow forbidden band and low-lying acceptor levels (*17*, *18*). The formation within these units of N_3^0 radicals corresponds to localization of the "holes of conductivity" in specific anionic units. The parameters of these radicals are close to the parameters of N_3^0 radicals in the gaseous phase (*19–21*), in solutions (*20*), and in matrices of solid alkaline metal halides (*23*). The fact is that redistribution of the electronic pattern, which can be represented as the transition of an electron from the azide group to the cation, corresponds to formation of mobile "holes" and localized N_3^0 radicals. This leads to Coulomb loss and to a substantial decrease in the covalent bond of the components (*24*), i.e., to "isolation" of the azide groupings. N_3^0 in the ground and first electronically excited states has linear geometry. The ground state is identified as $^2\pi_g$. Experimentally the electronically excited state has been found to be $^2\Sigma_u^+$(~270 nm) (*19–21*). The formation enthalpy of N_3^0 equals 105 to 135 kcal/mole (*16*).

Hole conductivity on heating to the decomposition temperatures of the ionic azides has not been experimentally established. This is due to both a very broad forbidden band in these azides and small mobility of N_3^0 in the "hole" mechanism. The formation of N_3^0 radicals in the case of ionic azides is possible only under the influence of uv irradiation with energy >8.6 eV or of an ionizing radiation. Thus, their formation was apparently recorded by EPR during radiation decomposition of barium azide (*25*).

1.2. Monomolecular Transformations of SU in Azides

In analyzing the ECS in azides, an examination of the transformation of the complex SU, i.e., azide groupings, is of basic interest. Cations can also take part in this transformation. In the case of partially covalent azides, thermally activated decomposition is possible from the ground (electronic) state of the N_3^0 radical. It is suggested here that a step of electronic excitation and formation of N_3^0 radicals precedes the elementary act of N_3^0 transformation. In crystals with an essentially ionic character of the bond, the formation of N_3^0 requires large expenditure of energy (more than 105 kcal/mole), so that there are no bases to suggest that the N_3^0 radicals participate in the ECS. In this case, thermal activation from the ground state of N_3^- should be analyzed. (In Refs. (*26*) and (*27*), however, the mechanism of thermal decomposition of barium azide, a typically ionic compound, is dealt with on the basis of transformation of free N_3^0 on the surface. In conformity with what is set forth here, the analysis carried out in Refs. (*26*) and (*27*) and applied to barium azide strikes us as being incorrect. Moreover, in those studies "nonadiabatic" transitions between terms were not examined.)

Monomolecular transformation of N_3^- and N_3^0 from ground states with formation of products in ground states can be presented by the equations:

$$[M^+(^1S) + N_3^-(^1\Sigma_g^+)] \rightarrow N_2(^1\Sigma_g^+) + [M^+(^1S) + N^-(^3P_u)] \quad \Delta H = 67\ \text{kcal/mole}, \quad (1)$$

$$N_3^0(^2\pi_g) \rightarrow N_2(^1\Sigma_g^+) + N(^4S) \qquad \Delta H = 7.5 \text{ kcal/mole.} \quad (2)$$

(Here and in what follows, numerical values of the enthalpy change ΔH are given in conformity with data cited in the handbook of Part I.) Along with Eqs. (1) and (2), other paths of monomolecular transformation can also be described. Analysis shows that Eqs. (1) and (2) express monomolecular transformations which require minimal E_a. Both transformations are spin "forbidden" and the transformation expressed by Eq. (2) is also "forbidden" by orbital symmetry (*28*), i.e., the indicated transformations are "nonadiabatic" with transition coefficient $\kappa < 1$ and E_a, which is not determined by the magnitude of ΔH. Since the transitions under discussion are similar to the N_2O transition examined in Part I and also correspond to a simple change of configuration, one may expect that a satisfactory evaluation of E_a can be obtained by the correlation diagram (CD) method. In this respect we assume that for the reaction the energetically most favorable path of transition is examined and that the CD on this path reveals the main potential barrier ("peak") that determines E_a. The CD corresponding to the reactions described by Eqs. (1) and (2) are presented in Fig. 1. (In this case, one may not construct a CD of the orbitals but rather a CD of states, using the tables of Wigner-Witmer presented in Ref. (28)). Because the desired terms are an approximation of the electronic terms of the crystal and the reacting SU are the bearers of properties of the crystal which are important for ECS, the level of the ground (electronic) state corresponding to $[M^+(^1S) + N_3^-(^1\Sigma_g)]$ is given by the formation enthalpy of the azide of a monovalent (alkali) metal (~10 kcal/mole). All other levels are viewed relative to this, which is conditionally reflected by the fact that the levels are classified with respect to an azide grouping cation pair. Here and in what follows the particles studied in the crystal are bracketed. The levels shown are determined by the formation enthalpy of the particles and also by spectroscopic values of the corresponding excitations. Levels $^3\Sigma_u^-$ for N_3^- and $^4\Sigma$ for N_3^0 are not known and are approximated from the energies of the corresponding singlet and doublet states (*6*, *19*). (One should keep in mind that the electron levels of excited states of the system as a whole actually form band patterns. However, the levels that interest us are local as a result of the fact that transformation takes place in defect areas of the crystal. The electron levels of products, especially metals, can have band character.) In the approximation of levels indicated above, it has been established from the CD that $E_a^{(1)} \approx 90$ kcal/mole and $E_a^{(2)} \approx 30$ kcal/mole.

Participation of the cation in the activated

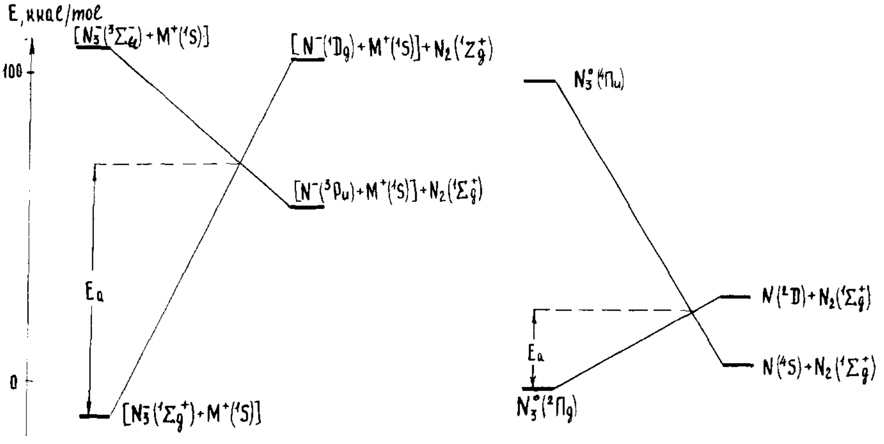

FIG. 1. Correlation diagrams for the monomolecular decomposition of N_3^- and N_3^0.

complex (AC) makes possible partial or full transition of the electron from the azide ion. However, even in the case of full transition of the electron, a decline in $E_a^{(1)}$ is not realizable since metal atoms and nitrogen, which have high enthalpies of formation, are formed. Only a simultaneous convergence of three N_3^- can lead to onset in the elementary act of states of the nitrogen atoms corresponding to formation of nitride (the formal charge on the nitrogen is 3−), which is very unlikely. In establishing the rate constant of the chemical step it is necessary to allow that $\kappa < 1$. It may be surmised that $\kappa \sim 10^{-1}$ to 10^{-2}, i.e., it has the same order of magnitude as the value established for the decomposition of N_2O discussed in Part I (*29*). (Let us call attention to the fact that according to data available in (*30*), the probability of intercombination nonradiating transition in the case of inorganic systems can significantly exceed that in the case of aromatic molecules. In the latter case, usually $\kappa \sim 10^{-6}$ is accepted, and this estimate is often also used without justification for the general case (*31*).)

1.3. Bimolecular Transformation as to Azide

In considering the CD, it is assumed that the "reaction coordinate" along with the electron term is approximated gives the configuration change of the ECS and selects the most convenient path of transformation in energy. As a result of the formal character of the reaction coordinate, it is necessary to study various possible AC configurations. Bimolecular transformations of N_3^0 radicals studied within the framework of the model of a two-dimensional quasi-gaseous reaction have been analyzed in Refs. (*26*) and (*27*). In Refs. (*26*) and (*27*) transitions which proceeded with formation of a linear (*l*) or cyclic (benzene-type) (*c*) intermediate N_6^0 complex were studied. On the basis of random reciprocal orientation of the spins of the interacting radicals, the state of the intermediate complex is a triplet with probability of 3/4 and singlet with probability of 1/4:

$$2N_3^0({}^2\pi_g) \rightarrow N_6^0({}^3\Sigma_u^+ \text{ or } {}^3B_u) \rightarrow 2N_2({}^1\Sigma_g^+) + N_2({}^3\Sigma_u^+), \quad (3)$$

$$2N_3^0({}^2\pi_g) \rightarrow N_6^0({}^1\Sigma_g^+ \text{ or } {}^1A_g) \rightarrow 3N_2({}^1\Sigma_g^+). \quad (4)$$

The states of the reactants, the intermediate complex, and the products correlate directly, so that the E_a of the transitions can result only from the ΔH. The transitions are exothermic. For the last reaction, $\Delta H = -(210\text{–}270)$ kcal/mole and for the reaction expressed by Eq. (3), $\Delta H = -(72\text{–}132)$ kcal/mole.

We have examined transformations that are bimolecular in azide groupings:

$$[2N_3^-({}^1\Sigma_g^+) + 2M^+({}^1S)] \rightarrow [2N_2^-({}^2\pi) + 2M^+({}^1S)] + N_2({}^1\Sigma_g^+) \qquad \Delta H \approx 60 \text{ kcal/mole}, \quad (5)$$

$$[2N_3^-({}^1\Sigma_g^+) + 2M^+({}^1S)] \rightarrow 2M^0({}^2S) + 3N_2({}^1\Sigma_g^+) \qquad \Delta H \approx 40 \text{ kcal/mole}, \quad (6)$$

$$2N_3^0({}^2\pi_g) \rightarrow 3N_2({}^1\Sigma_g^+) \qquad \Delta H \approx -210 \text{ kcal/mole}. \quad (7)$$

The enthalpy of the reaction expressed in Eq. (5) is estimated relative to the reactants assuming invariability of the Coulomb interaction. The value $\Delta H(N_2^-) = 64.4$ kcal/mole is used in doing so. We have examined the CD of the orbitals of the reactants and their AC as well as of the products and their AC; these diagrams are partially presented in Fig. 2. As a consequence of the diversity of crystalline metal azide structures, the CD for linear, ring-shaped, and T-shaped N_6^{2-} complexes were studied. Figure 3 shows the transition of the orbitals of azide ions into the orbitals of $N_{6,c}^{2-}$ with formation of σ- and π-bonds in this complex. In analyzing the correlations, we have used the forms of the orbitals and their relative energies as obtained from calculations according to the method of Ref. (*32*). Cor-

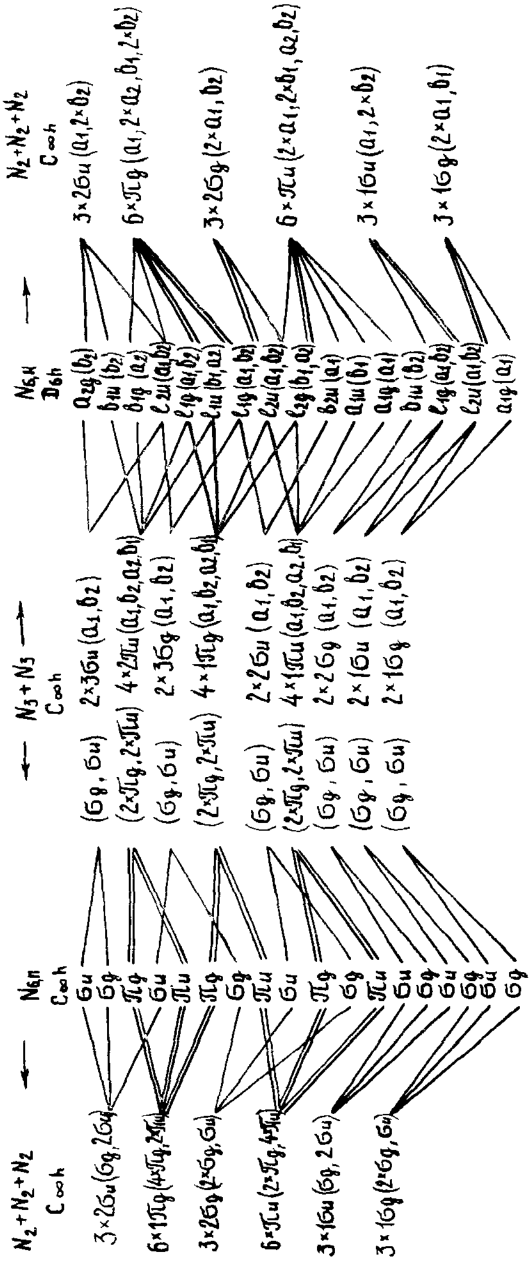

FIG. 2. Correlation diagrams for orbitals in the case of bimolecular interaction of azide ions.

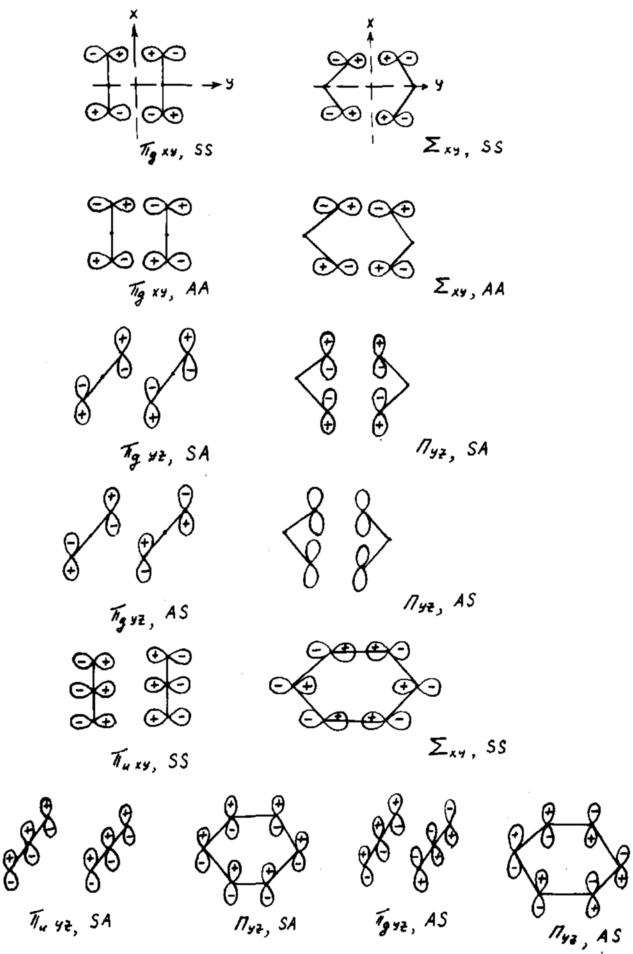

FIG. 3. The transfer of orbitals of bimolecularly interacting azide ions to the orbitals of ring-shaped N_6^{2-}.

relation diagrams were constructed for the states. From their analysis, it follows that transitions through N_6^{2-} are "forbidden" in orbital symmetry for all three configurations. Moreover, a transition is forbidden in spin, too; the last orbital of N_6^{2-} filled by electrons is doubly degenerate so that the ground state of this complex is a triplet, whereas the ground state of the two N_3^- before and during the interaction is a singlet.

Under the presumption that the order of the molecular orbitals does not change upon the removal of one or two electrons, the correlation diagrams were used in analyzing the correlation for N_6^- and N_6^0 in the indicated configurations in a corresponding decreasing in population density of the orbitals. The results of our study for the bimolecular interaction of N_3^0 do not agree with the conclusions of Refs. (*26*) and (*27*) due to differences in the approximations in calculating *M*O. The relative arrangement of the *M*O levels and, consequently, of CD depends on the approximation used in calculating *M*O, whereas the Woodward–Hoffmann rules preserve their validity even within the limits of precise functions of the Hartree–Fock approximation (*33*). In Refs. (*26*) and (*27*), the rough approximation of the simple Hückel method was used. According to our data, in bimolecular transformation of N_3^0, there are correlation "prohibitions" for all configurations of AC. However, the excited state of the products lies somewhat lower than the ground state of the reagents, so that a correlation barrier is practically nonexistent. True, an activation barrier in the interaction of N_3^0 should exist, being related, in any case, to Coulomb repulsion of the radicals. The order of magnitude of the E_a determined by the Coulomb repulsion of N_3^0 "holes" can be established in the following manner. Assume that the charge of the hole on the surface is $\leqslant 0.5$ of the charge of an electron and the distance of closest approach on attainment of which the N_3^0 complex is formed is of the order of a lattice constant, i.e., ~10 Å. These assumptions are based on the fact that the charge of the hole is an effective charge related to the environment of the N_3^0. In this case, $E_a \leqslant$ 10 kcal/mole.

As was shown in Part I, orbital "prohibitions" in a crystal apparently are stripped away (however, "prohibitions" in spin and those connected with band to band transitions are preserved)—due to combination of the orbitals of the SU of the crystals. On this basis, it is possible to assume that the bimolecular transformations expressed in Eqs. (5) through (7) can be viewed as "allowed" by orbital symmetry.

In analyzing the transformation expressed in Eq. (6), it is necessary to keep in mind the clear participation in it of cations. At the same time, in the course of the ECS a local transfer of electrons from azide ions to cations can take place, while redistribution of electron density in the N_3^- leading to electron transfer and change in configuration of the azide groupings takes place simultaneously (*34*). The displacement of cations during vibration–rotation convergence of the anions decreases the steric difficulties for this convergence, and the transfer of electrons to the cations diminishes the Coulomb repulsion of the azide groupings. Such a transformation is feasible in defect areas of the crystal where cations can emerge as acceptors of a pair of electrons and the configuration of the area favors restructuring of the geometry of the complex in the ECS process. As a first approximation in studying the ECS and modeling the AC, it is possible to begin with the structure of an ideal crystal. The relative orientation of N_3^- ions in a real crystal evidently has no significance since at transformation temperatures the azide ions spin freely. At sufficiently low temperatures the structure of the crystal can have an effect on the rate of the ECS. Since in the case under study in the process of energy exchange and formation of the activation barrier, the interaction with the environment of molecular groupings undergoing transformation is strong, we suggest absence of an activation barrier conditioned by correlation in orbital symmetry. The activation barrier can be obtained under consideration of the process of transferring the electron pair to the cations. The corresponding CD is presented in Fig. 4. The activation energy of the ECS defined by this diagram equals 55 kcal/mole (for azides of alkali metals) and significantly diminishes (by 10–20 kcal/mole) when the ECS proceeds on the interface with a product in the form of a metallic phase. In such a case, the formation enthalpy of the metal atoms decreases to the extent of the absorption heat of atoms on the surface—during absorption on the surface of the metal nucleus $\Delta H(M^0) \approx 0$. Consequently one should bear in mind that the evaluations conducted on the E_a for various possible realizations of ECS are overly high.

The transformation that is bimolecular in N_3^- and proceeds in two stages with transfer of one electron in each stage has to be examined:

$$[2N_3^-({}^1\Sigma_g^+) + 2M^+({}^1S)] \rightarrow$$

$$[N_2^-({}^2\pi) + M^+({}^1S)] + 2N_2({}^1\Sigma_g^+) + M^0({}^2S), \tag{8}$$

$$[N_2^-({}^2\pi) + M^+({}^1S)] \rightarrow N_2({}^1\Sigma_g^+) + M^0({}^2S). \tag{9}$$

The estimate of E_a from the CD constructed for the first stage and expressed by Eq. (8)

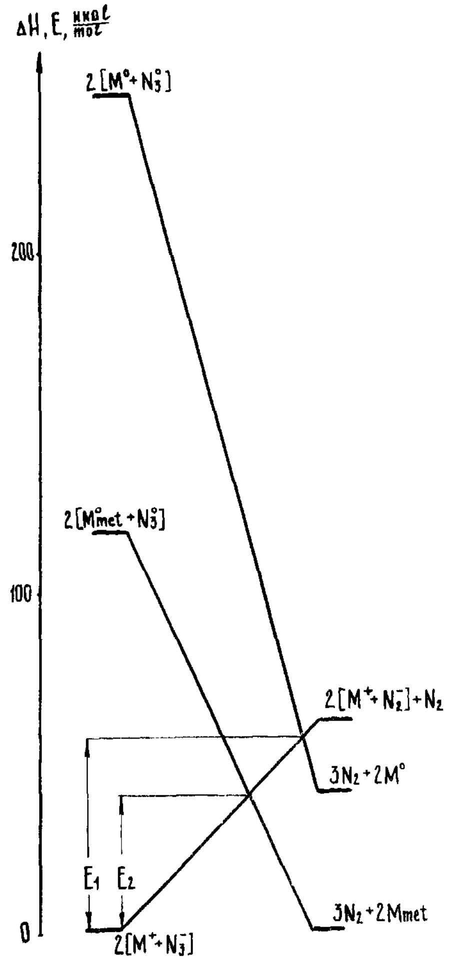

FIG. 4. Correlation diagram corresponding to bimolecular interaction of azide ions with a transfer of two electrons to the cation.

leads to a magnitude approximately equal to the E_a established for the transformation expressed in Eq. (6). Available experimental data (EPR spectra) are evidence of the instability of N_2^- and N_4^- when heated. Thus, the two-stage transformation expressed in Eqs. (8) and (9) can compete with the transformation expressed in Eq. (6).

It would be necessary to consider the interaction of N_3^0 and N_3^-. From analysis of the CD for N_6^- (all three different configurations), it follows that transformation through this AC is forbidden by orbital symmetry. Evidently, the participation of the cation in the ECS makes possible a transfer of an electron to it and can reduce the E_a. Such a reaction, in principle, is possible in the case of partially covalent azides when N_3^0 is actually formed. However, the question of the possibility of having the transformation under discussion is not clear since it is not possible to evaluate whether the hindrances to approach the azide groupings are reduced to a sufficient degree by the covalency of the metal–azide bonds if N_3^0 is one of the groupings. (We note at once that for photolysis of the azides such difficulties are absent. The square dependence of the rate of photolysis on the intensity of light is evidence of this; see the discussion of photolysis.)

The above evaluations of E_a permit us to compare transformations that are mono- and bimolecular in the azide grouping and show their relative role in the mechanism of reaction. Of important moment is the stability of the radicals conforming to electronic excitations favoring possible participation of electronically excited states (N_3^0) in the ECS of the thermal decomposition of the azides which we have examined. As follows from the preceding remarks, this stability is fostered by the presence of prohibitions during monomolecular decomposition.

1.4. Interpretation of Experimental Data

(*A*) *Thermal decomposition of ionic azides.* In agreement with what has been set forth above, a transformation that is bimolecular in N_3^- in the course of ECS is energetically more favorable than a monomolecular. The obtained estimate for E_a is compared with experimental values for the energy of nucleation for the alkali metal azides (*35*). The character of the ECS bimolecular in N_3^- allows us to give an explanation of the experimental fact that all azides decompose into metal despite the thermodynamic preference for decomposition into nitrides (*4*, *5*). It is even possible to describe concretely the significant autocatalysis observed in the experiment during decomposition of ionic azides. Thus, in Refs.

(*27*) and (*36*) values are indicated for E_a as ~60 kcal/mole for the beginning stage of the reaction and ~40 kcal/mole for the case of the reaction interfacing the phases during the decomposition of barium azide. As is shown in the CD illustrated in Fig. 4, the formation of the metallic phase effects a decrease in the ground level of the product by about 40 kcal/mole and a reduction in the energy exciting the reagents by about half (the energy of ionization of an anion on the boundary with a metal lowers by such an amount). This leads to a reduction of E_a for the ECS in the course of which metal atoms are formed. The formation of large nuclei observed in the experiment during the decomposition of ionic azides also is explained.

The following regularity takes place: The azides of bivalent (alkaline earth) metals all decompose with about the same speed at one and the same temperature (one may take 400°K as the temperature of perceptible decomposition). The situation is analogous in the case of azides of monovalent (alkali) metals, but in that case the corresponding temperature is different—about 600°K. The observed regularity may be related to the effectiveness of the cations as acceptors of the two electrons in the process of realizing the ECS: The effectiveness of the doubly charged electron trap is greater than a single one. Great effectiveness of electron acceptors is displayed in the reduction of the levels of the products on the CD illustrated in Fig. 4. A rough comparison of the effectiveness of the traps (acceptors) can be made by ionization potentials: The effectiveness of the two-charged cation can be characterized as the sum of the first and second ionization potentials ($I_1 + I_2$) and that of the single-charged as twice the ionization potential, $2I_1$. The ratio of these two sums for alkaline earth and alkali metals is about 1.7 and this magnitude is compared with the relation of the temperatures indicated above.

(*B*) *Thermal decomposition of azides with partially covalent character of the chemical bond.* The model study we have carried out leads to a conclusion on the various mechanisms of thermal decomposition of the metal azides depending on the character of the chemical bond in their crystal lattices.

In the case of azides with partially covalent bond character, a CD of the type illustrated in Fig. 4 leads to a still smaller value of E_a (~35 kcal/mole) than in the case of ionic azides. However, the bimolecular interaction of N_3^- in the case of covalent azides is practically nonexistent since the directed bonds of the azide groupings with the cationic sublattices strongly limit the mobility of the structure and its tendency to atomic regroupings. Thus, the mechanism of decomposition in the case of covalent azides should be connected to the formation of N_3^0. In this case, the electron transfer and the formation of "positive holes," i.e., the process

$$[N_3^-] \rightarrow [N_3^0] + e \qquad (10)$$

represents a separate step and the ECS takes place without participation of an electron trap (acceptor). From this point of view, the lack of a noticeable difference in the decomposition temperatures between mono- and bivalent covalent azides is explained.

E_a for the monomolecular decomposition of N_3^0 is near 30 kcal/mole. E_a for the bimolecular interaction of N_3^0 is roughly estimated to be less than 10 kcal/mole (the Coulomb repulsion of N_3^0). Taking into account the ΔH of formation of N_3^0 (10–20 kcal/mole) (*37*), the E_a for the bimolecular interaction approaches the E_a of the monomolecular decomposition of N_3^0. The rates of both realizations of ECS, in the roughness of our estimates, are difficult to differentiate, all the more since in the case of monomolecular transformation one should allow for $\kappa < 1$. However, the low E_a for the ECS corresponding to both cases of N_3^0 transformation agree with the conclusion about a different mechanism of decomposition of the covalent azides compared with the ionic metal azides.

The difference of mechanism for thermal decomposition of ionic and covalent azides allows us to explain a series of experimental data on covalent azides. It was established by Refs. (*38*) and (*39*) that in the case of thermal decomposition of these azides, effective catalysis of the decomposition takes place on addition of paramagnetic ions. There is no similar influence on the decomposition of the ionic azides. An effective acceleration of decomposition may be connected with removal of spin and orbital prohibitions for the reaction expressed in Eq. (2). The catalytic act can at the same time be repeated many times since the positive holes are mobile and no change of the catalyst takes place in the course of the reaction. The instability of transition metal azides may also be related to this circumstance. The separation of steps of electronic excitation from chemical in the case of covalent azides results in the fact that, in their thermal decomposition, autocatalysis by the product–metal develops not at all or very weakly, and the growth of the nuclei either ceases in early stages (for example, in the case of silver azide) or nuclei are in general not observed (for example, in the case of lead azide). Actually, the developing metal can accelerate the decomposition because of the lowering of the E_a on contact for the step expressed in Eq. (10), but this effect cannot develop as a result of presence in the covalent azides of acceptor levels that determine the energetics of positive hole formation (*37*).

(*C*) *The effect of the magnetic field on the rate of thermal decomposition.* The proposed modeling of the ECS allows us to interpret the experimentally observed (*40*) acceleration of thermal decomposition of barium azide and the constancy of the rate of decomposition of silver azide on application of a magnetic field with an intensity of ~1100 Oe. The absence of any effect in the case of silver azide can be understood on the assumption of a decomposition mechanism for this salt that is bimolecular in N_3^0. In such case, the ECS develops without change of multiplicity in the transformation process. In the case of barium azide typical of an ionic azide, the ECS develops with a transfer of two electrons to the acceptor and a change of multiplicity in the course of the elementary step. The effect of a magnetic field on the rate of thermal decomposition is interpreted (*41*) as the result of an effect of the field on the probability of intercombination transfers induced by spin–orbit interactions.

2. Photolysis and Radiolysis of Metal Azides

2.1. Photolysis of Azides

Differences in the mechanism of photolysis compared with thermal decomposition are primarily related to participation in the decomposition of electronically excited states and to the low temperatures at which processes with high E_a are not possible. In this case only reactions permitted by spin and symmetry are possible.

The various specific realizations for ECS may be written in the form of monomolecular decompositions of the type

$$[M^+ + (N_3^-)^*] \rightarrow [N + N_2^- + M^+] \quad (11)$$

or

$$[M^+ + (N_3^-)^*] \rightarrow [N^- + N_2 + M^+]. \quad (12)$$

In this case it makes sense to examine only the first excited states of the SU of the crystal even in the case where excitations develop at higher levels. We are guided here by the circumstance that, when particles in a solid body are excited, there takes place a rapid internal conversion to the first excited state which is relatively long-lived (*31*). This situation is postulated for organic molecules; it is, however, apparently also applicable, with rare exceptions, to the case of inorganic systems. The selection rules for internal conversion in the azide ion are fulfilled, and the levels of the excited states converge in proportion to the increase of excitation, so that the indicated situation should be applicable in the case of azides. Taking into account the indicated limitations, one may come to the conclusion that a more likely path of monomolecular decomposition is

$$[(M^+(^1S) + N_3^-(^1\Sigma_u^-)] \rightarrow [M^+(^1S) + N^-(^1D) + N_2(^1\Sigma_g^+)] \quad \Delta H \approx -10\,\text{kcal/mole} \quad (13)$$

("correlation prohibitions" are absent).

The following bimolecular transformations of excited azide ions are possible:

$$[2N_3^-(^1\Sigma_u \text{ or } ^3\Sigma_u^-)] \rightarrow [N_6^{2-}(^1A)] \rightarrow [N_2^-(^2\pi_g) + N_4^-(^2\pi_g)], \quad (14)$$

$$[2N_3^-(^1\Sigma_u \text{ or } ^3\Sigma_u^-)] \rightarrow [N_6^{2-}(^1A)] \rightarrow [2N_2^-(^2\pi_g) + N_2(^1\Sigma_g^+)]. \quad (15)$$

Bimolecular transformations in T-traps are also possible, for example, in anionic vacancies or their aggregates with formation of the corresponding color centers:

$$[2(N_3^-)^* + T] \rightarrow [N_6^{2-}\cdot T](^1A) \rightarrow [N_2^-(^2\Pi_g) + T\cdot e(^2S) + 2N_2(^1\Sigma_g^+)], \quad (16)$$

$$[2(N_3^-)^* + T] \rightarrow [N_6^{2-}\cdot T](^1A) \rightarrow [N_4^-(^2\pi_g) + T\cdot e(^2S) + N_2(^1\Sigma_g^+), \quad (17)$$

$$[2(N_3^-)^* + T] \rightarrow [N_6^{2-}\cdot T](^1A) \rightarrow [3N_2(^1\Sigma_g^+) + T\cdot e\cdot e(^1S)]. \quad (18)$$

The indicated reactions are permitted by spin and orbital symmetry. The total energy of the two excited anions is large so the reactions should proceed with a liberation of energy and without E_a.

One should keep in mind the possibility of transformation of the excited azide ion into N_3^0 after interaction with a lattice defect. Subsequently, a bimolecular interaction of N_3^0 not having to surmount the activation barrier is possible.

The photolysis of azides are studied experimentally over a broad spectral range, from $\lambda = 184.8$ nm to $\lambda = 800$ nm (*3–6, 23, 25, 42–44*). In the case of covalent azides (AgN_3, TlN_3, PbN_6) (*3–6, 42, 43*) this range includes energies sufficient for the formation of positive holes by means of excitation across the forbidden gap and on to the acceptor levels. The characteristic peculiarity of the photolysis of these azides is the presence of a hole photocurrent (*17*). An important fact established in Refs. (*42*) and (*43*) is the quadratic dependence between decomposition rate and the photocurrent. Here the dependence of photolysis rate on intensity changes within limits from quadratic to linear, whereas the photocurrent changes from linear to hyperbolic. Experimental data agree with a mechanism that is bimolecular in N_3^0 for the photolysis of these azides. Suppression of the monomolecular decay of N_3^0 and the bimolecularity of the ECS lead to a low quantum yield ($\sim 10^{-3}$).

During the photolysis of all ionic azides, except sodium azide, the dependence of rate on irradiation intensity is quadratic. In the case of sodium azide, this dependence is linear. The final products of photolysis are metal and nitrogen, while for all azides (except sodium azide) dark liberation of nitrogen takes place which depends quadratically on the intensity of the previous irradiation. The formation of N_2^- and N_4^- was registered by the EPR method. Formation of atomic centers of the type N or N^- was not detected. Only in Ref. (*23*), where photolysis was investigated in alkali halide matrices, i.e., under conditions which make bimolecular interaction of the anions difficult, was formation of N registered with small yield. In Ref. (*23*) it was considered that under the conditions of the experiment the primary reversible step is the reaction expressed by Eq. (12).

Thus, in the case of ionic azides, monomolecular transformation proceeds with low yield and the basic reaction is bimolecular interaction of the excited azide ions. In such a case, intermediate particles with even numbers of nitrogen atoms are formed. A rapid decline in the initial speed of photolysis can be viewed as evidence of the preference for an ECS with traps taking part.

2.2. Radiolysis of Azides

Differences in the mechanism of photolysis and radiolysis may be related above all to participation in the reaction of excited states of N_3^0 which are obtained from ionizing N_3^-. We suggest that in this case, too, one should examine only the first excited states $^2\Sigma$ and $^4\Sigma$:

$$[M^+(^1S) + N_3^0(^2\Sigma)] \rightarrow [M^+(^1S) + N(^2D) + N_2(^1\Sigma_g^+) \qquad \Delta H \approx -50 \text{ kcal/mole}, \quad (19)$$

$$[M^+(^1S) + N_3^0(^4\Sigma)] \rightarrow [M^+(^1S) + N(^4S) + N_2(^1\Sigma_g^+)] \qquad \Delta H < 0. \quad (20)$$

The ECS expressed in Eqs. (19) and (20) take place without surmounting activation barriers, so the bimolecular interactions could not be examined.

The state of $N_3^0(^2\Sigma)$ has been studied spectroscopically (*19–21*). Vibrational structure of the band is detected, corresponding to the electron transfer $^2\Sigma \leftarrow {^2\pi}$, while the lines have diffuse character, which is evidence of predissociation (*28*). The state of $^4\Sigma$ has not been identified experimentally. However, the very fact of predissociation of $^2\Sigma$ indicates the presence of a lower, easily dissociated state. A calculation of the quartet state is necessary since it should be formed, along with a doublet, under conditions of internal radiation by electrons during ionizing radiation action. The energy of transfer $^2\Sigma \leftarrow {^2\pi}$ is evaluated as equal to ~4.6 eV (~2700 Å).

For ionic type azides the ionization energy (the width of the forbidden gap) is ~8.6 eV, whereas for covalent azides it is ~4 eV. Thus, for ionic azides the transfer from the mechanism taking place during photolysis to the radiolysis mechanism expressed by Eq. (19) should take place at a quantum energy ≳13 eV (~94.0 nm), whereas for covalent azides this transfer can take place at a quantum energy of ≳8.6 eV (~145.0 nm). With participation of the quartet state, the transfer limit can be lowered somewhat. The value of the transfer limit can be compared with the data of Ref. (*45*), where a sharp increase in yield during decomposition of sodium azide by electrons when their energy equals 11.65 eV was established experimentally. This experimental fact can be interpreted as a transition at this energy to monomolecular decomposition of N_3^0 from the first excited (apparently $^4\Sigma$) state.

Radiolysis of heavy metal azides (lead and silver azides) has been studied in Ref. (*46*). It has been established that the speed of radiolysis depends linearly on the strength of the dosage; radiation-chemical yield is high and at normal temperature consists, for example, for lead azide, of ~30 molecules/100 eV. Electroconductivity of the irradiated azides also depends linearly on the strength of the dosage. Experimental data are in agreement with a monomolecular mechanism of decomposition of N_3^0. However, the radiation yield exceeds by more than twice the calculated value corresponding to decomposition according to Eqs. (19) and (20). This may be interpreted by the fact that the decomposition of $(N_3^0)^*$ induces a breakdown of the neighboring N_3^- through participation of the excited nitrogen atom:

$$[M^+(^1S) + N_3^-(^1\Sigma_g^+) + N(^2D)] \rightarrow [N_4^-(^2\pi) + M^+(^1S)] \rightarrow N_2(^1\Sigma_g^+) + N_2(^2\pi_g). \quad (21)$$

This reaction should be realized without an activation barrier.

The rate of radiolysis of ionic azides also depends linearly on the strength of the dosage. The radiation-chemical yield consists of 1 to 10 molecules/100 eV (*47–50*). It has been shown by EPR experiments that the intermediate metastable products are N, N_2^-, and N_4^- and also F and V centers. The presence of atomic centers, the high radiation yield, and the linear dependence on dosage are evidence in favour of the monomolecular mechanism of radiolysis expressed by Eqs. (19) and (20). N_2^- and N_4^- may be secondary products formed by

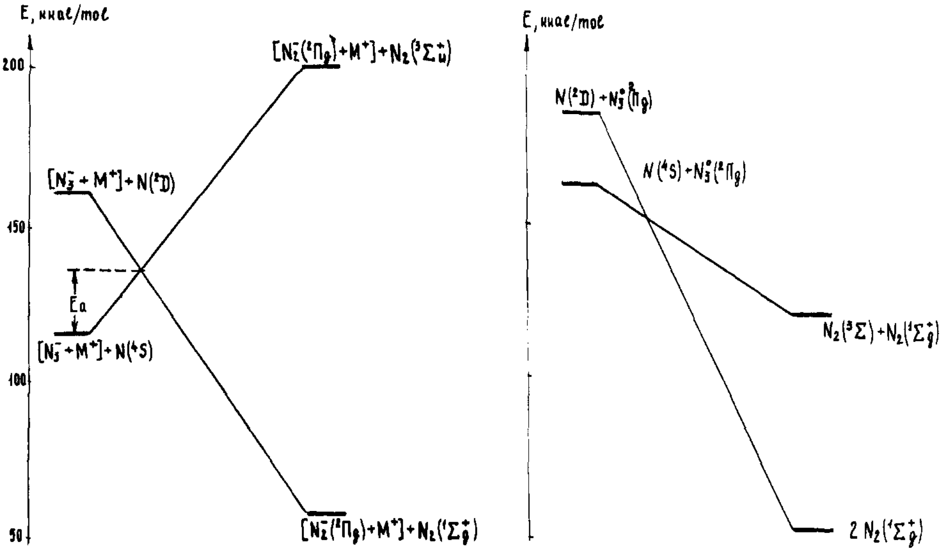

FIG. 5. Correlation diagrams corresponding to the interaction of nitrogen atoms with ionic and covalent azides.

mechanisms characteristic for photolysis or intermediate products formed according to Eq. (21).

2.3. The Interaction of Nitrogen and Hydrogen Atoms with Azides

Experiments were conducted to test the predictive power of the proposed model of solid state elementary steps. (The experiments were conducted with the participation of staff members of the Tomsk Polytechnic Institute, A. Ilyina, V. Styrova, and A. Kharlamova.)

Equations (22) through (25) and (26) through (28) describe the elementary steps of the interaction of hydrogen and nitrogen atoms with metal azides:

$$\mathrm{H}(^2S) + \mathrm{N}_3^-(^1\Sigma_g^+) \rightarrow \mathrm{HN}_3^-(^2A') \rightarrow \mathrm{NH}^-(^2\pi) + \mathrm{N}_2(^1\Sigma_g^+), \quad (22)$$

$$\mathrm{NH}^-(^2\pi) \rightarrow e + \mathrm{NH}(^3\Sigma^-), \quad (23)$$

$$\mathrm{NH}^-(^2\pi) + \mathrm{N}_3^-(^1\Sigma_g^+) \rightarrow \mathrm{H}^-(^1S) + \mathrm{N}_2^-(^2\pi) + \mathrm{N}_2(^1\Sigma_g^+), \quad (24)$$

$$\mathrm{NH}(^3\Sigma^-) + \mathrm{N}_3^-(^1\Sigma_g^+) \rightarrow \mathrm{H}(^2S) + \mathrm{N}_2^-(^2\pi) + \mathrm{N}_2(^1\Sigma_g^+), \quad (25)$$

$$\mathrm{N}(^4S) + [\mathrm{N}_3^-(^1\Sigma_g^+) + M^+(^1S)] \rightarrow [\mathrm{N}_2^-(^2\pi_g) + M^+(^1S)] + \mathrm{N}_2, \quad (26)$$

$$\mathrm{N}(^2D) + [\mathrm{N}_3^-(^1\Sigma_g^+) + M^+(^1S)] \rightarrow [\mathrm{N}_2^-(^2\pi_g) + M^+(^1S)] + \mathrm{N}_2, \quad (27)$$

$$\mathrm{N}(^4S) + \mathrm{N}_3^0(^2\pi_g) \rightarrow 2\mathrm{N}_2(^1\Sigma_g^+). \quad (28)$$

Figure 5 presents the CD corresponding to the interaction with nitrogen atoms. As follows from the correlation analysis, the interaction with hydrogen atoms does not need any E_a.

Experimental data agree completely with the conclusions resulting from the correlation analyis of the interactions examined. Thus, the unexcited nitrogen atoms easily decompose heavy metal azides and do not decompose sodium and potassium azides completely (at room temperature and a pressure of 0.1 Torr). According to the CD, an interaction with the ionic azides is possible without E_a only in the case of excited nitrogen atoms. In accord with the theoretical analysis, the unexcited hydrogen atoms easily decompose all azides.

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