JOURNAL OF SOLID STATE CHEMISTRY 26, 69–77 (1978)

Modeling of the Elementary Step in the Chemical Transformation of Crystals. I. Statement of the Problem; Description of the Model

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Received May 9, 1977; in revised form March 11, 1978

A model is proposed within the framework of activated-complex (AC) theory for analyzing the elementary chemical step (ECS) in the case of solid state reactions. By ECS is understood the synchronous restructuring (change in configuration, decomposition) of polyatomic structural units (SU) of the crystal or synchronous formation of new molecular groupings from poly- or monatomic SU. Simple physical observations lead to the conclusion that the ECS of solid state transformations does not have high molecularity. The mechanism which controls activation and deactivation is not directly considered. For activated SU that do not experience deactivation, it is suggested that interaction of these reacting SU with their surroundings in the crystal is constant throughtout the course of the ECS. In conformity with this, an analysis of elementary steps of chemical transformation in crystals leads to an examination of the transformation of groupings composed of a small number of the SU of the crystal. A comparison of the ECS is carried out based on a comparison of the energies of activation (E_a) corresponding to the transformations. The E_a for various paths of transformation are evaluated by using the correlation diagram (CD) method. In a correlation analysis, experimental data for crystals should be used. Orbital symmetry and multiplicity of terms should be examined on the basis of specific quantum chemical analysis. The problem is formally reduced to a molecular one; however, the separable SU are bearers of properties of the crystal which are important for the ECS (enthalpy of formation, symmetry, electron composition, spectroscopic properties, etc.).

1. Statement of the Problem

In contemporary chemistry of crystalline inorganic compounds there is lacking not only a coherent and strict theory of the purely chemical steps of the process on an atomic and molecular level, but also adequate simple modeling methods for analyzing the elementary chemical steps (ECS) which would allow them to be applied to an examination of specific important reactions. Apparently, this is caused not only by the complexity of solid state reactions, but also by their specificity, which demands for their resolution a broad drawing together of the concepts and methods of physics and solid state theory. Certainly, the mastery of them has enriched solid state chemistry and the corresponding period has been important and fruitful in the establishment of solid state chemistry. However, the traditions for analyzing chemical transformations, formed in this time, are such that an examination of specifically chemical steps of the process often remain neglected. In examining the mechanisms of reactions, basic attention as a rule is focused on electronic and ionic defects and on migration phenomena within the crystals.

In the case of chemical transformation of crystals, migrations of energy, charge, and mass, as well as factors determining reaction zone development are of great importance. However, the ECS is an essential and frequently limiting reaction. The ECS of the reaction

0022-4596/78/0261-0069$02.00/0

selects only quite specific changes in configuration and predetermines the course of transformation characteristic of the material. Besides the composition of the products, the ECS can also determine the dependence of speed of transformations of the same kind on the chemical nature and structure of the reagents and the influence of type of activation (light, heat, ionizing radiation) on the direction of transformation and the yield of the products. The role of intermolecular transformations comprising the ECS is especially great in the case of molecular crystals. Consequently, in analyzing the reaction capability of crystalline organic compounds, primary attention is centered on the examination of the purely chemical steps (see, for example, (*1*)).

Turning our attention to the important role of the ECS, we propose a model for consideration regarding the transformation of crystals. At the same time, an analysis of the elementary steps of purely chemical transformations is proposed. Electron migrations, which can be treated independently of the reconstruction of the atomic–ionic configuration, are excluded from the investigation. In formulating the model, gross simplifying hypotheses are used, but from that arises a scheme applicable to rather complex systems.

At the present time, even in the simplest case of unimolecular gas phase reactions, theory has a significant degree of idealized character. This is caused by the fact that neither the potential energy surface nor the mechanism of energy exchange between polyatomic molecules are known sufficiently well (*2*). In this circumstance we do not set ourselves the task of a coherent review of the dynamics of the chemical act in the crystal but use as a basis for the analysis activated-complex (AC) theory. There has been a series of investigations applying AC theory to solid state problems. Among them, the work of Shannon (*3*), in which one can find references to the work of predecessors, where he carries out an examination of the reactions of thermal decomposition of inorganic crystals, is especially interesting. In Ref. (*3*) he uses the usual expression for the rate constant K of the ECS according to AC theory:

$$K = \kappa \frac{kT}{h} \frac{Q_a}{Q} \exp(-E_a/kT), \qquad (1)$$

where κ is the transmission coefficient (adiabatic reactions were treated, i.e., $\kappa = 1$); Q_a and Q are the partition functions for the AC and the initial state of the crystal, respectively; k and h are the Boltzmann and Planck constants; and T is the absolute temperature. In the specific cases of calcium and magnesium carbonate, it is shown that based on established assumptions of the AC structure and its frequencies one can get values of the pre-exponential factor in Eq. (1) which agree well with experiment.

In Ref. (*3*) the main possibility of calculating the pre-exponential factor in Eq. (1) for solid state reactions is demonstrated. As for E_a, in Ref. (*3*) as well as in the great majority of other investigations within the framework of AC theory, E_a is viewed as an empirical parameter. However, such an approach for analyzing the mechanism of solid state reactions is unsatisfactory, in that the determination of E_a for the ECS in crystals is experimentally very much harder. At the same time, the magnitude of E_a is in the majority of cases the determining factor in choosing the preferred path of transformation in the course of the ECS. We focus attention on the problem of evaluating E_a.

2. A Description of the Model: Basic Simplifying Assumptions

2.1. Impracticality with ECS of High Molecularity in the Case of Crystals

We begin with the idea that representation of solid state theory of a crystal as a system of interacting structural units (SU) (*4*) is applicable as well to consideration of a crystal undergoing chemical transformation.

In the case of any single phase or multiphase system in the process of redistributing energy during activation and deactivation, a number of particles is involved which is larger than that which determines the molecularity of the elementary step. Since we are not concerned with the detailed dynamics of the ECS, the specific mechanism of energy redistribution which determines the ECS is outside the scope of our review. We note, however, that in the course of solid state transformation, activation of the SU takes place during the continuous and, generally speaking, strong and far-ranging interaction with the environment in the crystal. In the energy redistribution process, in such case, there generally participate a significant number of SU of the crystal which constitute the near and next near neighbors of the SU undergoing transformation in the course of the ECS. Moreover, for the realization of each elementary step, in the course of which the transformation of several SU of the crystal takes place, there should occur a close approach significant enough to assure required overlapping of electron clouds or change of this overlapping and, as a result, a restructuring of the system of chemical bonds between these SU as well as between the atoms (ions) entering into their composition. This close approach depends on oscillating-rotational movements of the SU in a configuration of the environment which is conducive to realization of the elementary step. At the same time, steric hindrances to movement of the SU in the crystal are so great that simultaneous approaches of more than two SU of the same type in a complex crystal which would assume restructuring of the system of chemical bonds are not very likely and almost excluded. Consequently, in analyzing the ECS in complex crystals, one can limit one's self to consideration of uni- and bimolecular transformations (of each SU of a specific type). The local character of the ECS in crystals is fixed by the environment examined and by the necessity of concentrating energy in the area where the elementary step is realized (*5*).

2.2. Basic Simplifying Assumptions

In AC theory it is assumed that for activated particles undergoing transformation, one may disregard exchange of energy with the environment in the transformation process. During this process, the potential of the mean force of interaction of the N particles ($N =$ the molecularity of the ECS) with the remaining particles of the system ($\bar{U}_n$) can be viewed as constant for the initial and transition states. It is assumed that the system of valence electrons of the aggregate of N particles both in the initial state and also in the course of the elementary transition corresponds to a single specific electronic term. The coordinates of the remaining particles, other than the N under study, can be discounted in analyzing the potential surface of the term (the configuration of this surface determines the minimal barrier for the transformation path that corresponds to the ECS, i.e., it determines the E_a for this ECS).

In the case of gas phase reactions, the assumption $\bar{U}_n =$ constant appears to be justified. The nature of the situation is determined by the fact that the particles of gas undergoing transformation are sufficiently isolated. Since isolation (in the sense of neglect of overlap of electron clouds) is clearly less in the case of crystals, the assumption that $\bar{U}_n =$ constant becomes less valid and will be realized all the better the larger the number of particles other than N indirectly experiencing transformation and included in an examination of the elementary step (*6*). In Ref. (*6*) it is suggested that the totality of N particles (SU) be expanded. However, if we keep in mind analysis of the potential surface only in connection with evaluation of E_a and not touch on the processes of energy distribution, then we may accept $\bar{U}_n =$ constant for the crystals as a rougher but still acceptable approximation. It is proposed also that after, according to the magnitude of E_a, the composition and structure of the AC for the most probable path of transformation are established, it is necessary, in a coherent study, to calculate the rate constant, using Eq. (1). We bear in mind that in evaluating the preexponential factor, one should, generally speaking, examine the entire crystal. Approaches of the type proposed in Ref. (*3*) can be used.

In the present work, there is absent a mathematical proof for applying the proposal under discussion to the case of ECS in crystals. Ultimately, a comparison with experimental conclusions that can be obtained on the basis of the model using this hypothesis can serve as a criterion for the possibility of essentially limiting the totality of the reacting SU in evaluating E_a for the ECS in the crystal. However, one can provide support for the hypothesis introduced. The ECS in the crystal has a collective character in the sense that the transformation of N-activated SU is realized only with a favorable configuration of the environment. The configuration of the environment should be such as to exclude deactivation and assure output of ECS products in the case of a decomposition of complex SU. In a rough way, these factors, which constitute the "cage effect," can be traced to the fact that the ECS is realized only in defect regions of the crystal at the expense of increasing values of the effective free volume (*7*). The increased free volume in the vicinity of the SU undergoing transformation can be viewed as an effective "isolation" of these SU. The resulting "isolation" of the reacting SU is the physical basis for excluding from the analysis of the potential surface all variables except those that describe the association of N-activated SU undergoing transformation. Justification for this lies in the fact that the formation of a configuration of the environment of the activated SU favorable for ECS and the transformation of these SU are viewed as independent processes.

For crystals composed of "saturated" SU (molecular and ionic crystals), a comparatively small adiabatic change of electron distribution takes place in passing from the ground state of the corresponding free particles to the ground condition of the SU of the crystal. In the case of "unsaturated" SU (valence crystals and metals) the analogous change is large so that it can turn out to be suitable for studying the corresponding free particles in an excited state. One should bear in mind that in the case of crystals with "unsaturated" SU, a transition of SU into electron excited states such that essential restructuring of the electron clouds accompanied by "isolation" of the electronically excited SU can take place.

The proposal introduced results in the problem of nonempirical evaluation of E_a with the need to examine the potential surfaces only for the N-reacting SU. Formally, the problem is reduced to the usual molecular one. The model proposed thus allows us in analyzing the ECS in crystals to use concepts and methods appropriately worked out for consideration of the usual molecular problems. This indicates the similarity of problems and methods between the theory of the chemical bond in solids and molecular quantum chemistry (*8*). Nevertheless, let us turn our attention to the fact that the simplification proposed does not assume that the reacting SU are free. The electron terms have to be viewed as approximations of the electron terms of the crystal. This applies both to ground and electronically excited states (in the latter case, formation of an essentially band structure for the energy levels corresponding to collective excitation of the crystal as a whole is possible).

2.3. A Rough Estimate of the Speed of the Elementary Transition in Crystals

Based on the determinate role of E_a, we limit ourselves in the present work only to a comparison of E_a and do not carry out an evaluation of the speed of the ECS. We only note that for a crude estimate of the speed of various realizations of ECS in crystals one can use a simplification, according to which, with ECS molecularity equal to 1 or 2, Eq. (1) can be roughly approximated in the following relation for the speed of an elementary chemical act:

$$v = \kappa\nu \exp(-E_a/kT)C_a, \quad (2)$$

where C_a is the concentration of SU undergoing the transformation. In the event of a monomolecular ECS in crystals, Eq. (2) is an acceptable approximation in which $\nu \sim 10^{12}$ to 10^{13} sec^{-1} (see, for example, Ref. (*6*), pp. 45 and 126), i.e., ν can be interpreted as an effective frequency of oscillation of the lattice nodes. The absence of free moving of the SU of the crystal leads to the fact that in the expression for the speed of a bimolecular transformation the first power of the concentration C_a is preserved. In Eq. (2) there arises at the same time time a factor (within the limits of order) which is determined by the number of possible interactions of SU with other particles of the same type in the closest environment (in a complex crystal containing SU of different types, e.g., cations and anions in an ionic crystal). The statistical sums in Eq. (1) do not include the contribution of progressive degrees of freedom. Variation in the statistical sums conditioned by degrees of freedom in oscillating and rotational movements is found within the limits of 1 or 2 orders of magnitude. Possible variations of the numerical values in the pre-exponential factor of Eq. (2), including cases of mono- and bimolecular transformations in the SU of a certain type, are thus found within the limits of 2 or 3 orders of magnitude so that a small change in E_a, which is important for fixing the exponent, corresponds to them.

On the strength of a preeminent concentration of heat energy as well as a result of the localization of the energy of photo and radiation effects on the crystal in the region of structural defects, the elementary acts of chemical transformation occur in these areas. As was already noted, the elemental acts of chemical transition are realized only in a favorable configuration of the environment. At the same time, from the diversity of the various defects in a crystal for the case of a specific reaction, the ones whose configurations favor transformation are selected. Consequently, it is necessary to calculate the concentration of defects in estimating the speed of the ECS, and one should bear in mind the configuration of defects in modeling the AC. In a cruder sense, as a first approximation, one may consider the geometry of the AC without considering the configuration of the defect and assume that it can be calculated on refinement of the model, leading to a decrease in E_a. With such an approach, it is desirable to evaluate the magnitude of the possible decrease in E_a.

2.4. *Correlation Diagram Method for Evaluating the Energy of Activation*

For defining the most probable path of ECS realization, the absolute values of E_a do not actually interest us as much as the possibility of comparing E_a for a series of various permitted paths of the elementary chemical transition. This simplifies the task by decreasing the need for accuracy in the quantitative evaluation of E_a. However, in spite of this and in spite of the fact that the basic simplifying hypothesis formulated above in its most essential form simplifies the task of nonempirical evaluation of E_a, it does not follow that one must calculate the solution of this problem using quantum chemical methods. Actually, at the present time, quantum chemical calculations of electron terms are either practically nonexistent or (in the simplest case) demand very great efforts (*2*). Therefore, using the rather simple method of a rough estimate of activation energy is advisable.

For comparison of E_a in a series and also for rough quantitative evaluation of the magnitude of E_a, use of the correlation diagram (CD) method is suggested. A method for correlating orbitals and states developed in the fundamental studies of Woodward and Hoffmann (*9*) gained wide acceptance, but primarily in organic systems and only for certain adiabatic paths of transformation. The model proposed for the ECS in crystals makes possible the application of the CD method for analysis of chemical transformations in inorganic crystals as well. Moreover, use of CD for evaluating the magnitude of E_a is suggested. Including the CD approach as a method for evaluating E_a completes the model and makes it principally applicable to analysis of chemical elementary acts in cases of rather complex solid phase reactions.

In the process of establishing a correlation of the orbitals in the model under discussion, one must begin with the electronic structure (*A*O or *M*O) of the free particles that are formed adiabatically from the SU of the crystal. At the same time, possible perturbation of the electronic structure of the particles on passage from the free state to the state of SU in the crystal should be analyzed and calculated. It is desirable to fix the position of the energy levels from experimental data, filling this out with calculated data.

In analyzing the movement along the reaction coordinates in the CD method, it is customary to use the simplest linear approximation of the electronic terms. In an adiabatic chemical transformation, E_a can be determined as the difference of enthalpies of the initial reagents and of the products (ΔH) if the electron term along the path of transformation changes monotonically and does not contain "potential peaks." In such a case, the details of the change of electron energy are not important and the CD method leads directly to the goal. If the "potential peaks" on the transformation path are related to steric difficulties, the CD method will not reveal them. The CD method reveals "potential peaks" that are effected by lack of correlation of the ground states of the products and the reactants of the ECS. At the same time, transformation can be adiabatic, nonadiabatic, or diabatic, but is necessarily related to the "quasi-intersection" (*10*) of the terms.

Nonadiabatic reactions have a smaller probability compared with "adiabatic reactions" which correspond to movement along a specific term of "zero approximation." In Eqs. (1) and (2) this is expressed by having $\kappa < 1$ for "nonadiabatic reactions." Nonadiabatic reactions should play no less an important role in the realization of ECS in crystals than has been established in the case of gas phase reactions; however, in applying them to chemical transformations in inorganic crystals, this question apparently has never been examined specifically.

Both the electronic terms and the CD can be tested in various approximations, depending on the capability of the computation methods used and the goal of the analysis. Following the classification of Ref. (*10*), we suggest three possible approximations for testing the CD. To determine the correlation of the terms of systems consisting of light atoms, it is possible to test orbital symmetry and the spin part of the wavefunction separately. At the same time, generally speaking, a wavefunction for the entire system of valence electrons is proposed. A test is possible even in cruder approximation —in *M*O approximation, where the effects of electron correlation are not considered. At the same time, the CD are used for individual *M*O; indeed, the rules of Woodward and Hoffmann (*9*) are formulated in this approximation. Finally, the valence bond method may be used and the correlation of states may be viewed in an adiabatic separation of molecules into fragments.

The preceding discussion has focused attention on the fact that the elementary acts of solid state chemical transitions are realized in defect areas of the crystal. If, then, a review of the elementary act includes an analysis of the states of the SU of the regular (ideal) crystal, then one should consider for SU of the ideal crystal that correlation "prohibitions" in the orbital moment (*11*) are always absent. In this case, probably only prohibitions fostered by spin or during a change in the number of electrons in the system undergoing transformation take place.

The change in energy from the value corresponding to the initial state of the system to the value corresponding to the peak of the "potential barrier" fixed by the intersection of the linear terms is a measure of E_a when examining CD. The values obtained for E_a apparently are too high; however, it is difficult to evaluate the error occurring in the general case. In order to prove the CD method in a quantitative evaluation of E_a, we compared the graphically determined values of E_a with experimental values for the thermal decomposition of molecules (in the gas phase). The possibilities for such a comparison are rather limited for lack of either sufficiently reliable experimental data or thermodynamic and spectroscopic data for the construction of the CD.[1] However, the test revealed that E_a determined from the CD corresponds well with experimental values of E_a. We illustrate this conclusion with two examples.

Consider a monomolecular thermal decomposition of a molecule of N_2O, isoelectronic with N_3^- (azides are the subject of our examination in Part II):

$$N_2O(^1\Sigma_g^+) \rightarrow N_2(^1\Sigma_g^+) + O(^3P),$$
$$\Delta H \approx 40 \text{ kcal/mole.} \qquad (3)$$

The decomposition expressed in Eq. (3) is "forbidden" both by spin and by orbital symmetry. The CD can be examined in an approximation of disregarding the spin–orbit interaction. Figure 1 shows approximately calculated sections along the reaction coordinates of the potential surfaces corresponding to electronic terms which are of interest (*2*). The same figure also shows the CD corresponding to the decomposition expressed in Eq. (3). The E_a resulting from the CD practically coincides with the E_a determined at the point of intersection of the "real" surfaces and also with the experimental value (~60 kcal/mole) according to (*14*). In Fig. 1, however, it is seen that such close agreement of values is, in fact, coincidental and one should speak only of an agreement of orders of magnitude.

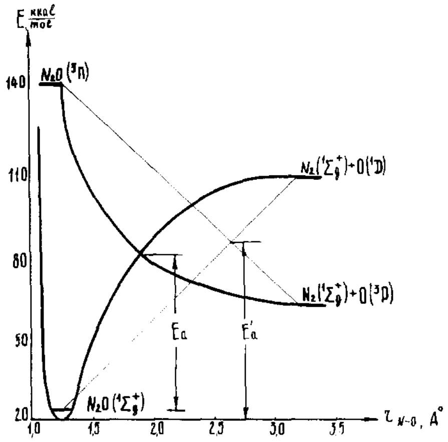

FIG. 1. Cross section of the potential energy surfaces and the CD of the thermal decomposition of N_2O.

As a second example, we examine the bimolecular transformation:

$$N_2O(^1\Sigma_g^+) + O(^3P) \rightarrow N_2(^1\Sigma_g^+) +$$
$$O_2(^3\Sigma_g^-) \qquad \Delta H = 79.5 \text{ kcal/mole.} \qquad (4)$$

In analyzing it, it is necessary to make a rough adiabatic approximation using the valence bond method. At the same time, lack of correlation between the ground states of the reagents and of the products appears. The lack of correlation of ground states is conditioned by the fact that the oxygen atom detached from the $N_2O(^1\Sigma_g^+)$ turns out to be not in the ground state (^3P) but in the excited state (^1D). In conformity with this, the ground state of the reagents correlates with the excited state of the $O_2(^3\Sigma_u^-)$ + $N_2(^1\Sigma_g^+)$. At the same time, the ground state of the products $O_2(^3\Sigma_g^-)$ + $N_2(^1\Sigma_g^+)$ corresponds with the excited state of the reagent $N_2O(^3\pi)$ + $O(^3P)$, since in breaking the bond in the $O_2(^3\Sigma_g^-)$, oxygen atoms in the ground state (^3P) are obtained. The E_a determined from construction of the CD equals 36.6 kcal/mole in experimental analyses, over a range from 14 to 25 kcal/mole (*14*). Thus, the CD method produces an overly high value, but the order of magnitude of E_a is correct.

In allowing the possibility of a rough qualitative evaluation of E_a from the CD, we should not lose sight of the fact that even in the

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[1] In constructing the CD, thermodynamic and spectroscopic data were taken from Refs. (*12*, *13*).

case of very simple changes in system configuration (only in such case can we hope to obtain reasonable estimates of E_a within the framework of the CD method), the method should be used with care, primarily for comparison within a series. The CD method does not allow for the splitting of interacting adiabatic terms but it can be exceedingly valuable. Moreover, the CD method can overlook important individual peculiarities of the structure of the potential surfaces. It is not applicable to cases where the potential surfaces along the reaction coordinate have extrema in the interval between the states of the reagents and products. Thus, the reaction of a thermal monomolecular decomposition

$$\begin{gathered} CO_2(^1\Sigma_g^+) \rightarrow CO(^1\Sigma_g^+) + O(^3P) \\ \Delta H \approx 125 \text{ kcal/mole} \end{gathered} \tag{5}$$

can be viewed just like the reaction given in Eq. (3). However, the CD method applied to the reaction expressed by Eq. (5) leads to an incorrect value of E_a. This is caused by the fact that the adiabatic surface corresponding to the ground state of the products and to the excited state of the reagents $CO_2(^3\pi_g)$ has, in the region between the states of products and reagents, a deep minimum (*15*). The barrier determined in the CD turns out to be false; in that case, the E_a coincides with the ΔH of the reaction.

As evidence in favor of the validity of the conclusion for evaluating E_a, one may consider the possibility of a conclusion on the basis of the CD of empirical relations of chemical kinetics. For example, the CD method in determining the E_a permits us to give a simple interpretation to the well-known Poliani–Semionov correlation

$$E_a = C - \alpha|q| \tag{6}$$

(C and α are constants, where C is an invariant constant within the limits of a specific homologous series and $0 < \alpha < 1$). Actually, it is easy to determine E_a (see Fig. 2) as the value of the energy at the point of intersection of two linear terms given by the equations:

$$E_1 = \frac{\varepsilon_a}{l} x; \quad E_2 = \Delta H - \frac{\varepsilon_b}{l}(x - l). \tag{7}$$

Here we have

$$E_a = \frac{\varepsilon_a(\Delta H + \varepsilon_b)}{(\varepsilon_a + \varepsilon_b)} = \frac{1}{\left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_b}\right)} + \frac{\Delta H}{\left(1 + \frac{\varepsilon_b}{\varepsilon_a}\right)}. \tag{8}$$

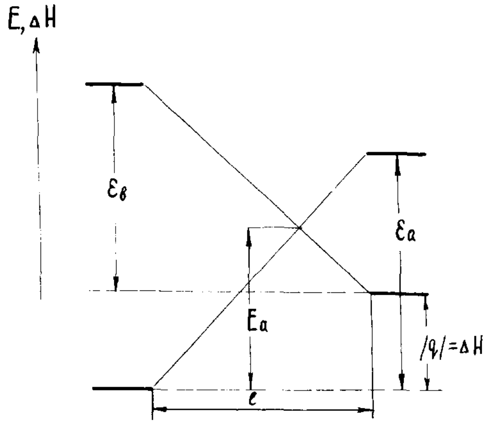

FIG. 2. On determining parameters of the Poliani–Semionov correlation.

An examination of the CD for finding the E_a of a series of reactions conforming to Eq. (6) confirms the applicability of the method (the reactions Na + RCl → NaCl + R where R = aliphatic radical).

Since, within the framework of the hypotheses formed above, a correlation analysis for solid state ECS is formally indistinguishable from an analysis of molecular transformations, it is possible to admit a rough estimate of E_a in the case of ECS in crystals, taking into account the remarks made about the limited possibilities of the method.

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