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Charge Transfer and Thermal Decomposition of NH_4ClO_4 Crystals*

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On the basis of previous work on the determination of transport numbers the following mechanism has been proposed for the formation and migration of the conduction proton in the NH_4ClO_4 (AP) lattice.

1. Transfer of the proton from cation to anion

$$NH_4^+ + ClO_4^- \rightarrow NH_3 + HClO_4.$$

2. Reorientation of the protonated anion

$$HClO_4 \rightarrow ClO_4H.$$

3. Proton jump to a neighboring anion

$$ClO_4H + ClO_4^- \rightarrow ClO_4^- + HClO_4.$$

The conductivity of AP crystals is increased proportionally to the concentration of added proton donor impurity HSO_4^- ion. Analysis of the impurity conductivity allows one to write for the mobility of protons in the AP lattice the expression $\mu = 20\exp(-0.81\ \mathrm{eV}/kT)\ \mathrm{cm^2/V\ sec}$. The dielectric relaxation of AP crystals has been investigated. Agreement has been shown of the time of dielectric relaxation with the correlation time of the diffusion process as determined by the Nernst–Einstein relation from the magnitude of the mobility. Values of the activation energy for the mobility and for the time of dielectric relaxation are also close to each other. These data are considered in the nature of experimental evidence for use of the proposed mechanism of conductivity in AP.

The influence of the indicated impurity on formation rate V_n and growth rate V_g of nuclei on thermal decomposition of AP has been investigated and corresponding activation energies E_n and E_g calculated.

For pure AP, $E_n = 70 \pm 4$ kcal/mole; whereas for doped AP, 50 ± 4 kcal/mole. Significant differences between pure and doped AP with respect to corresponding values of V_g and E_g were not detected.

Attention is directed to the closeness of the values of the activation energy for the overall rate of low temperature decomposition $E_{lt} = 33.9 \pm 1.6$ kcal/mole and $E_g = 35 \pm 5$ kcal/mole. Consequently, just the processes of nuclear growth determine the total rate of thermal decomposition of AP.

Arguments are presented in favor of a proton-donating character for the effect of adding HSO_4^- on the thermal decomposition of AP. It is predicted that addition of proton acceptors, among them $(NH_4)_2HPO_4$, will significantly decrease the value of V_n in AP.

As has been shown earlier ammonium perchlorate (AP) appears to be a proton conductor (*1*, *2*). The mechanism of formation and transfer of the conduction proton in the AP lattice, in analogy with corresponding mechanisms proposed earlier (*3*) for other ammonium salts, can be represented in the form of the following three steps.

1. Transfer of a proton from cation to anion;

$$NH_4^+ + ClO_4^- \rightarrow NH_3 + HClO_4.$$

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* Original manuscript received in Russian. A copy is available on written request to the editors.

2. Reorientation of the protonated anion:

$$HClO_4 \rightarrow ClO_4H.$$

3. Jump of the proton to a neighboring anion:

$$ClO_4H + ClO_4^- \rightarrow ClO_4^- + HClO_4.$$

The first step corresponds to a process of forming free current carriers, the second and third to their transfer. In accordance with the stated mechanism, it can be expected that introduction of a proton-donating impurity into the AP lattice should lead to a rise in conductivity and to a decrease in its activation energy. In the role of proton-donating impurity, we have used HSO_4^-, having the same size, charge, and geometry as the perchlorate ion, consequently cocrystallizing well with AP. The cocrystallization was carried out with slow (0.5 deg/day) cooling of saturated aqueous solutions of AP from 40°C to room temperature. Measurement of the conductivity and chemical analysis of the content of added impurity was carried out as described earlier (*3*).

As can be seen from Fig. 1, introduction of the impurity indeed leads to the anticipated effect. In accord with the theory of impurity conduction, proposed by Koch and Wagner (*4*), from these data one can determine the magnitude and activation energy of the mobility of the protons in the AP lattice:

$$\mu = 20 \exp(-0.81 \text{ eV}/kT) \text{ cm}^2/\text{V sec}. \qquad (1)$$

In analogy with results that are well known for other ammonium salts (*3*), one can suppose that also in the case of AP the activation stage of the proton mobility seems to be the reorientation of the protonated anion. In fact, as follows from the graph of the thermal dependence of the time of dielectric relaxation (Fig. 2), the values of the activation energy of the time of dielectric relaxation E_d and of the mobility E_m satisfactorily coincide.

This stage, the reorientation of the protonated anion, appears limiting in the process of proton transport. This conclusion follows from comparison of the value of the time of dielectric relaxation τ_d and the correlation time of the proton diffusion process τ_c. The latter quantity is determined from the value of the mobility at the given temperature by the Nernst–Einstein relation, written in the form

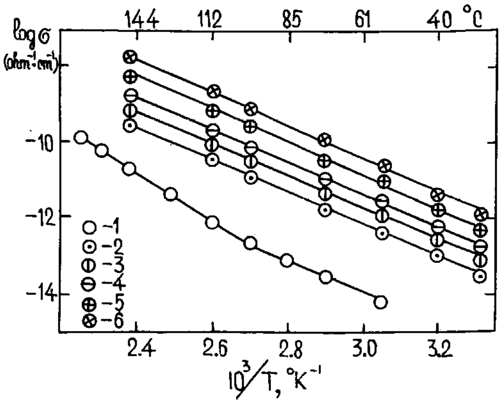

FIG. 1. Temperature dependence of the volume conductivity of crystals of ammonium perchlorate: (1) pure, (2) 8×10^{-4}, (3) 1.4×10^{-3}, (4) 3.5×10^{-3}, (5) 1.31×10^{-2}, and (6) 3.9×10^{-2} mole% NH_4HSO_4.

$$\tau_c = (e\gamma\alpha^2/\mu kT), \qquad (2)$$

where e is the elementary charge, γ is a geometric factor defined by the symmetry of the lattice, α is the unit cell parameter, k is the Boltzmann constant, and T is the absolute temperature. Actually, as is evident from Table I, for AP as well as for the other ammonium salts investigated earlier (*3*), $\tau_c \simeq \tau_d$.

Identity of the first elementary steps in the

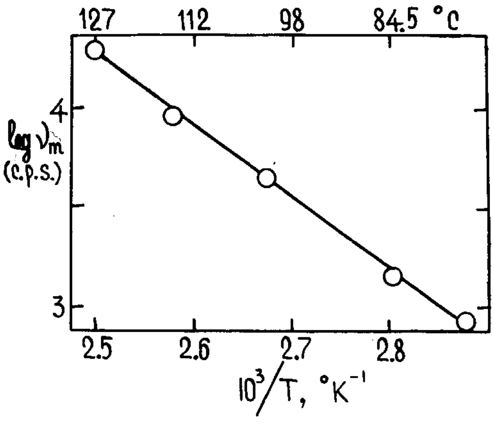

FIG. 2. Temperature dependence of the time of dielectric relaxation in crystals of ammonium perchlorate containing 10^{-1} mole% of NH_4HSO_4.

TABLE I

VALUES OF τ_c AND τ_d FOR CRYSTALS OF THREE AMMONIUM SALTS AT 23°C

Substance	E_m (eV)	E_d (eV)	γ	$\alpha \times 10^8$ (cm)	$\tau_d \times 10^5$ (sec)	$\tau_c \times 10^5$ (sec)
NH_4ClO_4	0.81 ± 0.05	0.76 ± 0.06	$\frac{1}{4}$	5.8	6.7×10^3	3.0×10^3
$NH_4H_2PO_4$	0.54 ± 0.03	0.50 ± 0.04	$\frac{1}{4}$	7.4	4.6	8.3
$(NH_4)_2SO_4$	0.49 ± 0.03	0.51 ± 0.04	$\frac{1}{6}$	6.0	5.5	3.3

conductivity and thermal decomposition, attention to which was given in Ref. (*2*), allows one to believe that not only the conductivity but also the rate of thermal decomposition will change with indicated doping of AP. It was interesting to examine how a proton-donating impurity influences the rate of formation and growth of nuclei produced in the thermal decomposition of AP.

Microscopic investigations were carried out by standard methods (*5*). At each temperature no fewer than 10 crystals containing the same amount of impurity were examined; the data obtained were processed on computer Nairi-2 by the method of least squares analysis. Results of the refining are summarized in Fig. 3. As can be seen from the data presented, the nucleation rate V_n is increased with dopant addition almost over the entire temperature interval, whereas the rate of growth of nuclei V_g is practically unchanged. The activation energy of the nucleation process corresponds to 70 ± 4 kcal/mole for the pure crystals and to 50 ± 4 kcal/mole for the doped specimens, whereas the activation energy for the process of growth of the nuclei, computed from these data, amounts to 35 ± 5 kcal/mole. Needless to say these numbers are effective values of the activation energy, since the processes of formation and growth of nuclei are certainly multistepped.

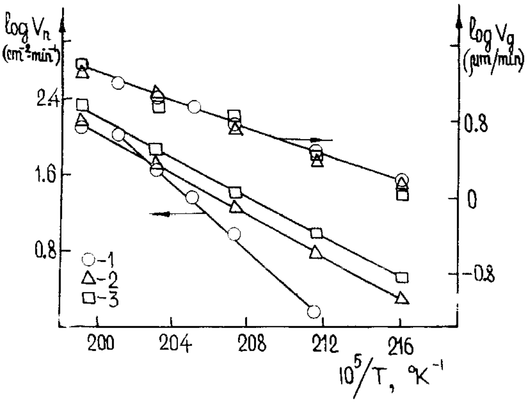

FIG. 3. Temperature dependence of V_n and V_g for crystals of ammonium perchlorate: (1) pure; (2) with $10^{-2}\%$ HSO_4^-; (3) with $10^{-1}\%$ HSO_4^-.

Comparison of these values with the magnitude of E_{lt}—the activation energy derived from analysis of the data on the gross kinetics of the low-temperature decomposition of AP (*6*)—shows that $E_g \simeq E_{lt}$. One can assert, therefore, that the overall rate of low-temperature decomposition of AP is determined basically by the processes of the growth of the nuclei. Indeed it appears that, even at extent of decomposition $\alpha = 0.1$, practically the whole crystal is covered with nuclei that run into each other and further decomposition proceeds only at the expense of their intergrowth into the volume of the crystal.

The significant difference in the values of E_n and E_g shows that the mechanisms of the processes of formation and growth of the nuclei are different. This conclusion is strengthened by the dissimilar character of the influence of proton-donating impurity on the rate of formation and growth of the nuclei. Evidently, generation and disintegration of $HClO_4$ seem to be the first steps responsible for appearance of the nuclei, consequently addition of proton-donating impurity leads to increase in V_n.

The indicated increase of V_n is undoubtedly dependent on the proton-donating action of the impurity. Actually adding such amounts of SO_4^{2-} (in the form of ammonium sulfate) to

AP does not lead to an increase in V_n (and even somewhat decreases it). One can anticipate further that introduction of proton acceptors will result in a decrease in the value of V_n, consequently inhibiting thermal decomposition of AP in its initial stages. Evidently, precisely in this lies the mechanism of action of such widely used practical stabilizers of low-temperature decomposition of AP as $(NH_4)_2HPO_4$ (*7*).

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