Fast self-propagating chemical processes in inorganic solids induced by an elastic wave pulse*

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Fast self-propagating chemical processes in solids initiated by an elastic wave pulse were studied in relation to ammonium dichromate. A possible mechanism for these processes was proposed.

Key words: elastic wave pulse; ammonium dichromate; ESR spectroscopy.

Previously,[1] it was found in relation to pressed polycrystalline ammonium dichromate $(NH_4)_2Cr_2O_7$ that an elastic wave pulse (EWP) can cause fast self-propagating chemical processes in solids; the front of these processes in $(NH_4)_2Cr_2O_7$ propagates at the velocity $V_f = (1.3\pm0.2)\cdot10^3$ m s^{-1}, which differs from the velocity of propagation of the EWP in pressed ammonium dichromate ($V_{EWP} = (2.2\pm0.2)\cdot10^3$ m s^{-1}), and the sample of $(NH_4)_2Cr_2O_7$ warms up by no more than $\Delta T = 300$ °C. This allowed the authors[1] to claim that some of the energy of the exothermic reaction (1)

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4\,H_2O + 298\ \text{kJ mol}^{-1} \qquad (1)$$

is spent *via* non-thermal channels, because in the case of thermal decomposition, a sample of $(NH_4)_2Cr_2O_7$ warms up to 1300 °C. However, in the study cited,[1] the V_f, V_{EWP}, and ΔT values were measured separately. In addition, later[2,3] it has been shown that solid-phase chemical processes initiated by an EWP have a threshold, *i.e.*, they are excited by an elastic wave, whose power is greater than a certain critical value (or is equal to it), and that early stages of these processes involve formation of active electrons and cations.

The purpose of this work was (a) to find out whether fast self-propagating processes in $(NH_4)_2Cr_2O_7$ have a threshold; (b) to carry out measurements of the onset of the chemical transformations and the temperature changes in $(NH_4)_2Cr_2O_7$, synchronized with the instant of the EWP; (c) to study the products arising in pressed $(NH_4)_2Cr_2O_7$ under the action of EWPs with different intensities by ESR spectroscopy.

Experimental

The experiments were carried out using the setup shown in Fig. 1. Elastic wave pulses were excited in a steel waveguide (*2*, see Fig. 1) by rheological explosion occurring upon uniaxial compression of polymeric (polystyrene, polypropylene) plates. Then the EWPs advanced to the sample under study, which was subjected simultaneously to the EWP and to uniaxial compression in a closed steel jacket between steel waveguides (*2* and *3*). The setup permitted time-synchronized recording of the acting EWPs and the electric and temperature changes in the sample using piezoelectric transducers (*4* and *5*), contact pickups (*6* and *7*), and planar thermocouple (*8*) linked to two S9-8 double-beam oscillographs, connected to a personal computer (see Fig. 1). The accuracies of synchronization of the measurements with respect to the indication of transducer *5* (after switching on of the oscillographs by the signal from transducer *4*) amounted to −1.6, +5.4, and +13 μs for transducers *6* and *7* and thermocouple *8*, respectively. The heights of waveguides *2* and *3* were 1.8 cm, and that of the steel jacket with the $(NH_4)_2Cr_2O_7$ sample was 3 cm. It is known[4] that if one of contacting bodies is heated to temperature T_1 and the other occurs at temperature $T_2 < T_1$, then the temperature in the plane of their contact is $(T_1 + T_2)/2$. The transit-time effects in planar thermocouples during fixation of fast processes can decrease the electric signal no more than twofold.[4] Thus, the indication of thermocouple *8* can differ from the actual temperature of the $(NH_4)_2Cr_2O_7$ sample after the chemical reactions by a factor of 4.

Results and Discussion

The diagram for the increase in the pressure acting on the sample, whose pattern is determined by the elastic properties of the polymer plates, consists of several sections (Fig. 2): reflecting non-steady-state creep of the polymer, steady-state creep, accelerated creep and destruction, and, finally, explosion under pressure

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* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

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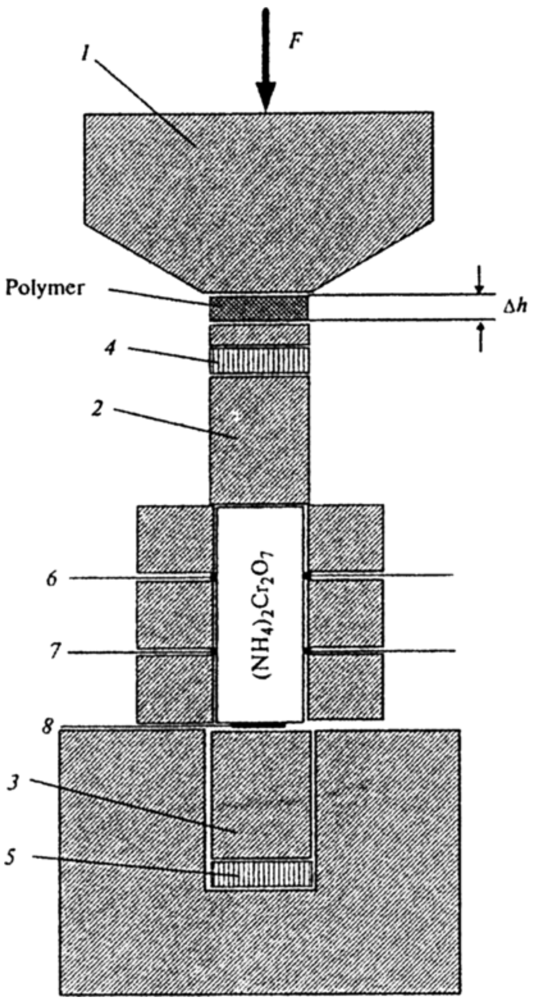

Fig. 1. Scheme of the experimental setup: Bridgman anvil (*1*); steel waveguides (*2*, *3*); piezoelectric transducers (*4*, *5*); contact pickups (*6* and *7*); planar thermocouple (*8*).

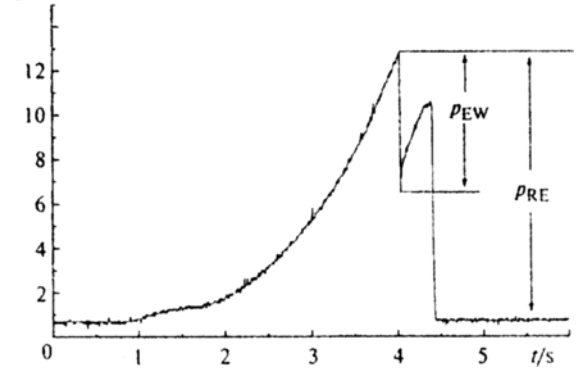

Fig. 2. Diagram for the pressure build-up and appearance of EWPs acting on the $(NH_4)_2Cr_2O_7$ sample.

referred to as rheological explosion. The pressure at which rheological explosion occurs (p_{RE}) is related to the thickness of the polymer plate (Δh) by the expression $p_{RE} \sim 1/\Delta h$.[5] By changing the Δh value and the type of polymer (polystyrene, polypropylene), p_{RE} can be varied over wide limits (5—20 kbar and even more). The first three stages take 4—7 s, while the fourth one (rheological explosion) occurs within tens of microseconds. As this takes place, an elastic wave is excited in the steel waveguide. Its oscillogram obtained by virtue of piezoelectric transducer *5* (see Fig. 1) is shown in Fig. 3, *a*. It can be seen that the first wave front with the amplitude p_{EW} is fast discharge, and this is followed by an oscillation process of the elastic wave action. Fourier analysis of the frequency parameters of this wave showed that the frequencies of the elastic waves excited in waveguide *2* (see Fig. 1) by the rheological explosion in the polymer at p_{RE} = 5 to 18 kbar range from 100 to 900 kHz. From this it follows that the upper plane of the $(NH_4)_2Cr_2O_7$ sample occurs under pressure $p = p_{RE} - \Sigma p_{a_i}\cos(2\pi f_i t)$. It is known[3] that $p_{a_i} = k_i p_{RE}$ and $\Sigma k_i < 1$; hence, $p = p_{RE}[1 - \Sigma k_i \cos(2\pi f_i t)]$.

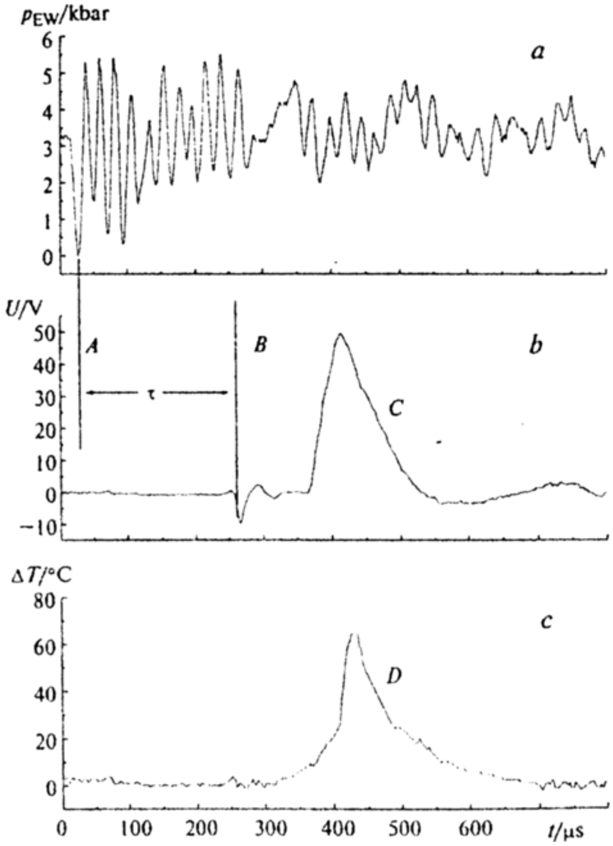

Fig. 3. *a*. Oscillogram for the EW acting on the $(NH_4)_2Cr_2O_7$ sample. *b*. Oscillogram for the variation of the voltage on contact pickup *6* (see Fig. 1). *c*. Oscillogram for the temperature variation on the planar thermocouple.

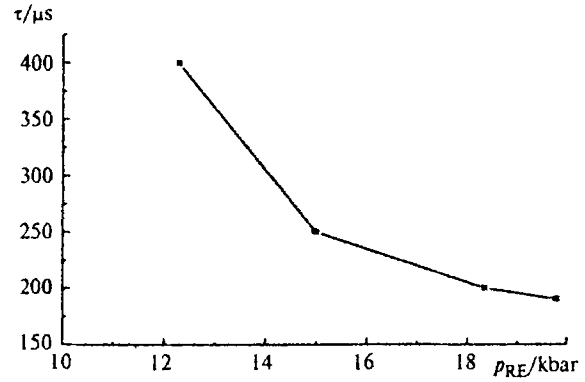

Fig. 4. Dependence of the time delay (τ) before the onset of chemical transformations in $(NH_4)_2Cr_2O_7$ on the pressure of rheological explosion (p_{RE}).

The generation of a fast self-propagating chemical process in $(NH_4)_2Cr_2O_7$ is always associated with the appearance of a short electric signal (*B*, see Fig. 3, *b*) caused by the formation of charge carriers and by the onset of redox reactions.[1] In our experiments, this electric signal appeared only at p_{RE} = 9 to 10 kbar, and at higher p_{RE} values it was permanently detected. Therefore, it can be concluded that chemical transformations in $(NH_4)_2Cr_2O_7$ have a threshold. In addition, it can be seen from Fig. 3, *a*, *b* that signal *B* lags behind the first discharge pulse of the elastic wave (*A*) by time τ. The determined τ values lie in the (170—400)±10 μs range. The observed dependence of τ on p_{RE} (Fig. 4) is straightened in the $\tau^{-1} = \alpha p^2_{RE} + \beta p_{RE} + C$ coordinates ($\alpha = -4.48 \cdot 10^{-5}$; $\beta = 1.78 \cdot 10^{-3}$; $C = -1.26 \cdot 10^{-2}$) and contains both quadratic and linear terms with respect to p_{RE}, *i.e.*, τ depends both on the static pressure on the sample (p_{RE}) and on the flow of energy delivered by the elastic wave.

The signal for temperature changes (*D* in Fig. 3, *c*) coincides in time with the broad low-frequency electric signal (*C*, see Fig. 3, *b*) generated in the $(NH_4)_2Cr_2O_7$ sample by the primary front of chemical reactions, which passes through the sample after it has already been affected by the front of primary ionization processes.

When a sample of $(NH_4)_2Cr_2O_7$ is treated with an EWP with $p_{RE} < 10$ kbar, it exhibits ESR signals with $g_{\perp} = 1.991$ and $g_{\parallel} = 1.933$ (Fig. 5), typical of Cr^{5+} ions,[6] whose intensity increases to $p_{RE} \approx 10$ kbar and then sharply decreases (Fig. 6). Simultaneously, pressed $(NH_4)_2Cr_2O_7$ samples with $p_{RE} \approx 10$ kbar started to exhibit broad ESR signals with $g_{aver} \approx 2.00$ and $\Delta H \approx$ 50 mT (see Fig. 5), characteristic of ultradisperse Cr_2O_3.[7] The plots for the accumulation of Cr^{5+} and Cr^{3+} (see Fig. 6, curves *1* and *2*, respectively) for p_{RE} = 10—11 kbar follow antiparallel patterns, which indicates that Cr^{5+} is reduced to Cr^{3+}. Treatment of the $(NH_4)_2Cr_2O_7$ sample with portions of elastic energy (*i.e.*, with several pulses at $p_{RE} < 10$ kbar), whose total amount is equal to the critical energy at p_{RE} = 10 kbar, does not induce self-propagating processes. The character of accumulation of Cr^{5+} ions (see Fig. 6, curve *3*) indicates that several time-separated pulses with $p_{RE} < 10$ kbar (the pulses are separated by at least 30 s) do not create conditions for a self-propagating chemical process, *i.e.*, these processes have clear-cut power character.

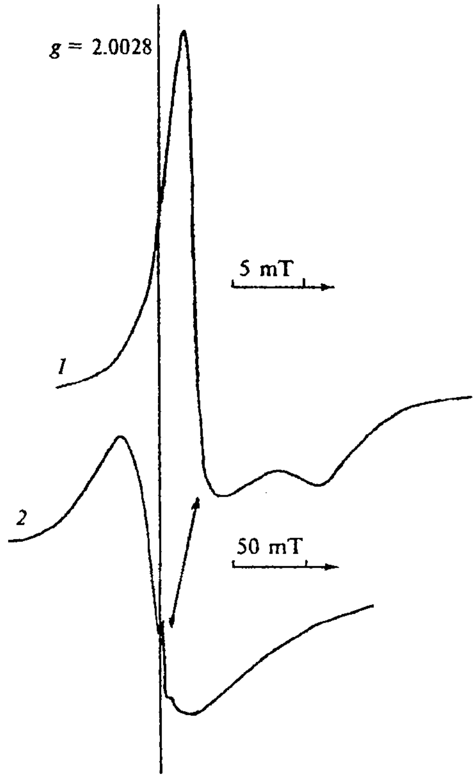

Fig. 5. ESR spectra of Cr^{5+} ions (*1*) and ultradispersed Cr_2O_3 (*2*) arising in $(NH_4)_2Cr_2O_7$ under the action EWP (p_{RE} = 6 and 10.3 kbar, respectively).

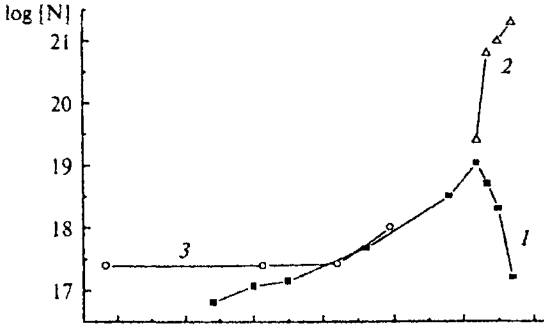

Fig. 6. Dependences of the concentrations of Cr^{5+} (*1*) and ultradispersed Cr_2O_3 (*2*) in the $(NH_4)_2Cr_2O_7$ sample on p_{RE} for separate EWPs and dependence of the concentration of Cr^{5+} on the action of several EWPs (*3*) at different p_{RE} introducing into the sample equal quantities of elastic energy, equivalent to the energy at $p_{RE} \approx 10$ kbar ([N] = [PMC]/g).

Based on the results of our experiments together with published data,[1] the following mechanism for the observed processes can be proposed.

Since the front of the chemical reactions arises only upon introduction of an EWP with a critical power and after time delay τ at the junction of waveguide *2* (see Fig. 1) and the $(NH_4)_2Cr_2O_7$ sample, it can be assumed that it is in the upper narrow layer of the sample that crystal lattice defects, vacancies, and dislocations start to appear. This process is characterized by a certain threshold energy and results in extensive amorphization of the substance. In terms of the band theory of solids,[8] amorphization is associated with smearing of the edges of the conduction and valence bands and also with the formation of a set of sub-bands in the forbidden gap, which correspond to ensembles of defects of different dimensionalities and are negatively (D^-) and positively (D^+) charged. The scheme for this hypothesized process is shown in Fig. 7, *a*. The appearance of smeared sub-bands facilitates free transfer of charge density over the amorphous polycrystalline material. From the chemical viewpoint, this is accompanied by excitation (activation) of $(NH_4)_2Cr_2O_7$ molecules and by formation of free electrons, protons, Cr^{5+} ions, and charge dipoles on individual $(NH_4)_2Cr_2O_7$ molecules and clusters consisting of these molecules, due to the non-neutralized charges; deactivation of $(NH_4)_2Cr_2O_7$ molecules is also accompanied by evolution of electromagnetic radiation quanta. The presence of dipole structures ensures the connection between mechanical and electromagnetic vibrations, *i.e.*, leads to overlap (coalescence) of the acoustical and optical phonon modes with the appearance of the so-called soft mode (Fig. 7, *b*). This phenomenon can be observed for a broad range of inorganic compounds.[9]

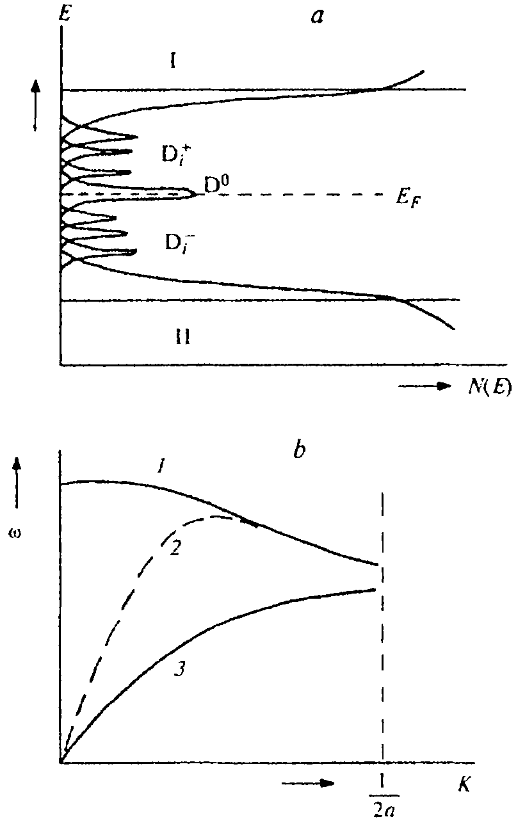

Fig. 7. *a*. Scheme of the density of defect states ($N(E)$/eV^{-1} cm^{-3}) generated in amorphous $(NH_4)_2Cr_2O_7$ by EWP depending on their energy (E/eV): D_i^+, D_i^- are sets of charged defect states, D^0 are metastable molecules; I is conduction band, II is valence band. *b*. Typical disperse curves for optical (*1*), soft (*2*), and acoustical (*3*) branches of the spectrum of vibrations when they overlap (ω is frequency, *a* is the lattice parameter, *K* is the wavenumber).

Thus, the upper narrow layer of the sample acquires the properties of a source of elastic and electromagnetic waves, which act on the underlying layers of the substance. The arising quasi-particles, for example, polarons $\bar{e}_p$, are related to these vibrations.[10,11] When (after time τ) the concentrations of dipoles and quasi-particles in the upper narrow layer of $(NH_4)_2Cr_2O_7$ reach a critical value, self-induced correlation between the dipole moments should occur, which is in good agreement with the processes of super-radiation at optical and hyperacoustic frequencies.[12] All this results in the initiation of chemical reactions in the underlying layers and in the propagation of the chemical reaction front over the $(NH_4)_2Cr_2O_7$ sample. The scheme proposed here is in good agreement with the concepts of phonon[13] and exciton-dislocation[14] fracture of solids and ionic crystals and with the views on the relationship between the fronts of solid-phase reactions and internal mechanical stresses[15] or non-linear waves.[16]

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