Thermal decomposition of transition metal carboxylates
2.* Role of evolution of microstresses in the kinetics of decomposition of anhydrous copper(II) formate

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Dynamics of changes in microstresses during thermal decomposition of $Cu(HCOO)_2$ crystals and their effect on the thermal decomposition kinetics were studied by IR spectroscopy at 105 to 120 °C. The formation of solid intermediate HCOOCu was observed, and the dynamics of its accumulation was followed. Kinetic regularities of transformation of HCOO groups were compared with those for gas evolution.

Key words: copper(II) formate, thermal decomposition; IR spectroscopy; microstresses.

Topochemical peculiarities of thermal decomposition of copper(II) formate (**1**) (see Ref. 1) point to a substantial effect of microstresses on the transformation kinetics. Compound **1** decomposes in parallel *via* homogeneous and heterogeneous mechanisms, resulting in dispergation of crystals and an increase in the thermal decomposition rate due to an increase in the specific surface.

It has also been found that the rate of tranformation of **1** at low degrees of decomposition decreases sharply due to the consumption of the most reactive defect region of crystals of **1** at the initial stage, elimination of microstresses due to cracking of crystals, and other reasons. In order to reveal relative contributions of these factors to the thermal decomposition kinetics, a change in lattice microstresses during the thermal decomposition of **1** was studied in this work by the previously developed IR spectral method.[2]

Experimental

IR spectra were recorded on a Specord 75 IR spectrophotometer in the frequency range from 400 to 4000 cm^{-1} with a spectral gap of 0.8 to 6.0 cm^{-1} (gap program 1—3) and maximum times of recording in order to minimize the signal to noise ratio.

Samples for studying kinetic and spectral parameters were prepared by molding in pellets (at 0.5 to 1.0 MPa) the powder of compound **1** with excess KBr. This method for preparation of samples makes it possible to follow simultaneously the reaction kinetics and changes in the IR spectrum during transformation reducing to minimum random errors of measurements. The use of KBr as an immersion medium almost completely eliminates distortions of the shape of spectral bands caused by IR radiation scattering. In addition, stresses of the crystal lattice of the initial substance can be eliminated by high-pressure molding.[20] No distortions of the shape and no new absorption bands were observed in the IR spectra at prolonged exposure of the pellet at the temperature lower than the reaction temperature. Since the activation barrier of diffusion processes is low and no liquid (aqueous) phase exists at the reaction temperatures, the reaction of KBr with **1** during the decomposition seems highly improbable.

Results and Discussion

Correlation between the rate of solid-phase decomposition and local stresses. The kinetics of solid-phase reactions is determined by chemical and physical factors (local defects and dislocations, interphase boundaries, mechanical stresses, *etc.*). Of the latter, microstresses appearing in the solid phase during chemical transformations are the least studied, which is related to methodical difficulties of their quantitative registration. Nevertheless, the significance of microstresses in topochemical reactions was repeatedly demonstrated, for example, in polymer destruction,[3] oxidation of stretched polymeric films,[4] mechanical initiation of chain reactions in matrices,[5] and retardation of reactions in the stress front in crystals.[6]

In uniformly deformed systems (for example, under conditions of hydrostatic compression of solid species), the effect of deformation on the thermal transformation rate constant in many cases can be described by activation volume $\Delta V^{\neq}$[7] by analogy with liquid-phase reactions that occur at high pressure p:

$$k = k_0 \exp[-(E_a{}^0 + p\Delta V^{\neq})/RT], \qquad (1)$$

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where E_a^0/kcal mol^{-1} is the activation energy in the unstressed lattice.

In nonuniformly stressed crystal lattices, in particular, when stresses are generated by growing nuclei of the new phase, the spatial stress distribution (σ) with density $\rho(\sigma)$ is realized. In this case (see Ref. 8), Eq. (1) can be generalized by the introduction of the local rate constant that depends on the component of stress tensor, which affects to the greatest extent the reaction coordinate

$$k(\sigma) = k_0\exp[-(E_a^0 + \alpha\sigma)/RT], \tag{2}$$

where α is the constant meaning the activation volume (α...0) and $E_a = E_a^0 + \alpha\sigma$ is the local activation energy.

Measurement of stress distribution. A linear correlation between the pressure and the shift of bands in the IR absorption spectrum of solids (see, *e.g.*, Ref. 9) observed in the absence of phase transitions at pressures of several tens kbar is presented in numerous works for hydrostatic compression conditions. Linear correlations between shifts of spectral bands and stress under macroloading conditions were observed for polymers and glasses.[10,11] Discrete bands for different positions of the absorbing center relative to the stress source of the lattice were recorded by FTIR spectroscopy.[12] Asymmetric shapes of bands in solid solutions under assumption of localized modes can be described quantitatively using the hypothesis about the linear character of the correlation between the vibration frequency (ν) and local stress.[13] The resulting contour of the band $I(\nu)$ can be described as a superposition of the initial contour of the band, whose shape, as a rule, is close to the Lorentz shape, $I_L(\nu)$, and asymmetric contour $I_{as}(\Delta\nu)$ with sharply descending wings (Fig. 1). Similar shapes are characteristic of spectral bands of stressed crystal lattices.[12] In the case when stress gradients result in the localization of lattice vibrations,[14] contour $I_{as}(\Delta\nu)$ can be presented as the convolution

$$I_{as}(\Delta\nu) = \int_{\nu_1}^{\nu_2} \rho(\nu_0 - z)I_0(z)dz\,, \tag{3}$$

where $\Delta\nu$ is the frequency shift compared to that of the undisturbed band, $I_0(z)$ is the symmetric contour of the band of the isolated absorbing center, $\rho(\Delta\nu)$ is the density of local frequency distribution appeared at the stress distribution in crystal, and z is the current integration variable with a sense of vibration frequency.

Function $\rho(\nu)$ for local vibrations is similar to the density of lattice stress distribution in the absence of the vibration resonance in the region of elastic deformations.[13] The density of lattice stress distribution depends on a particular spatial model determined by anisotropy of the crystal lattice, sizes and forms of species and stressing centers. For example, local stressing centers distributed stochastically in the weakly anisotropic lattice (model M_1) produce density $\rho(\sigma)$ described by the asymmetrically cut Lorentz function:[13]

$$\rho(\nu) = \begin{cases} A/(1 + B(\sigma - \sigma_0)^2), & \sigma_0 - 2\Delta\sigma \le \sigma \le \sigma_0 + \Delta\sigma \\ 0, & \sigma < \sigma_0 - 2\Delta\sigma,\ \sigma > \sigma_0 + \Delta\sigma \end{cases}, \tag{4}$$

where A and B are the constants, $\Delta\sigma$ is the stress at the boundary of the stressing defect, and σ_0 is the uniform component of stresses. In the absence of substantial overlapping of stress fields created by different centers (either no more than one stressing center in one species or when the distance between stressing centers is much greater than their size — models M_2 and M_3, respectively), the density of distribution of frequencies of local vibrations has the form:

$$\rho(\nu) = \begin{cases} P(\nu - \nu)^{-1}, & \nu_1 \le \nu \le \nu_2 \\ 0, & \nu < \nu_1,\ \nu > \nu_2 \end{cases}, \tag{5}$$

where parameters ν_1 and ν_2 correspond to the frequencies of local vibrations at the boundaries of the stressed region and stressing center. For example, in the case of cylindrical symmetry, the contribution of the layer dr in

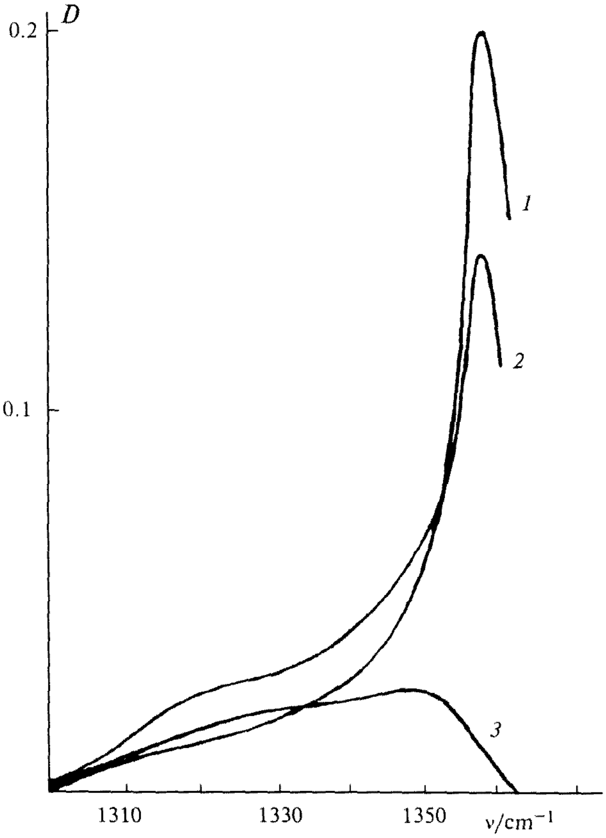

Fig. 1. IR spectra in the range of symmetric stretching vibrations of the COO^- groups: initial compound **1** (*1*), compound **1** after thermostating at 120 °C for 60 min (*2*), and difference in spectral curves $\Delta D(\nu) = D_2(\nu) - (1 - \eta)D_1(\nu)$ (*3*), where η = 0.3 is the extent of transformation of the HCOO groups.

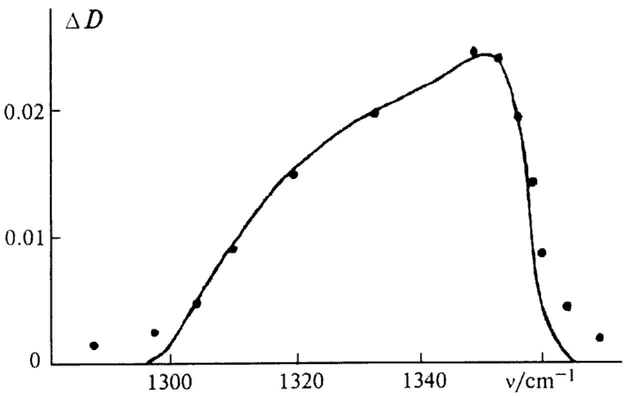

Fig. 2. The dependence $\Delta D(\nu)$ (curve) and its best description by hyperbolic convolution with the Lorentz function (points).

width to the absorption is the following: $dI \sim r dr$; the frequency as the stress decreases according to the law $\Delta\nu \sim r^{-2}$, whence it follows that $I \sim \Delta\nu^{-1}$, where $\Delta\nu = \nu - \nu_0$. By analogy, in the case of spherical symmetry, $dI \sim r^2 dr$, $\nu \sim r^{-3}$, and $I \sim \Delta\nu^{-1}$.

In the case of compound **1**, function (5) (see Fig. 2) satisfies the integral form of Eq. (3), *i.e.*,

$$I_{as}(\Delta\nu) = \mathrm{P}\int_{\nu_1}^{\nu_2} \rho(\nu - \nu_0 - z)^{-1} I_0(z)dz\,. \qquad (3^*)$$

In the case of spherical or cylindrical symmetry, the ν_2/ν_1 value characterizes the ratio of average particle size R to average radius r of the stressing center. The fraction of the stressed substance (β) (in our case, compound **1**) can be estimated as the ratio of the surface area under the spectral envelope of the stressed region of the substance to the surface area under the whole spectral envelope

$$\beta = \rho_0 \int_0^{\infty} d\nu \left[\int_{\nu_1}^{\nu_2} (\nu - \nu_0 - z)^{-1} I_0(z)dz\right] \Big/ \int_0^{\infty} I(\nu)d\nu\,. \qquad (6)$$

Thus, in terms of the suppositions made above, distribution densities $\rho(E_a)$, $\rho(\sigma)$, and $\rho(\nu)$ are mutually similar due to the linear correlation between E_a, σ, and ν. It should be mentioned that the substitution of the stress tensor for the scalar parameter is justified only in the case when the direction of the coordinate of normal vibrations at the frequency is close to that of the reaction coordinate.

Change in the IR absorption spectrum during decomposition of compound 1. In the range of symmetric stretching vibrations of COO^- groups, the IR spectrum of initial compound **1** contains four bands with absorption maxima at 1360, 1370, 1383, and 1405 cm^{-1}. The transformation was followed by a decrease in the absorption intensity at 1360 cm^{-1} after exposure of the KBr pellet with compound **1** under isothermal conditions for a specified time at the experimental temperature T_{exp} = 100 to 120 °C. The same pellet was used for kinetic experiments at T_{exp} = const. The changes in absorption intensity were examinated as the function of the time of exposure. The extent of transformation for the HCOO groups were determined as the ratio $\eta = (D_{0,1360} - D_{t,1360})/D_{0,1360}$, where t is time, $D_{0,1360}$ and $D_{t,1360}$ are the optical densities of the absorption band at 1360 cm^{-1} at the beginning of the experiment and at the t time, respectively.

At the constant temperature of the experiment, dependence $\eta(t)$ is S-like (Fig. 3, curves *1* and *2*) similar to that for the degree of gas evolution upon decomposition of crystals of **1**.[1] The dependence of the consumption rate of the HCOO groups in compound **1** is described by the equation that coincides with the rate equation for autocatalysis

$$W = k(1 - \eta)^2(\eta + \xi_0), \qquad (7)$$

where k and ξ_0 are the constants depending on T_{exp}, $k = 9.2 \cdot 10^6 \exp[-(18500\pm2000)/RT]$ s^{-1}, and $\xi_0 = 3.6 \cdot 10^3 \exp[-(9300\pm1500)/RT]$. Therefore, $W_0 = k\xi_0 = 3.3 \cdot 10^{10} \exp(-27800/RT)$ s^{-1}. It is noteworthy that the kinetic parameters of the consumption rate of HCOO groups differ from those of the rate of gas evolution from crystalline powders of **1** in the region of autoacceleration of the transformation.[1] For example, when the ξ_0 values are close (in the case when $\xi_0 = 1.2 \cdot 10^3 \exp(-8500/RT)$),[1] the k values for the consumption rate of the HCOO groups are higher by almost an order of magnitude than the corresponding k values for the rate of gas evolution ($k = 3.5 \cdot 10^2 \exp(-12000/RT)$ s^{-1}).[1] It is likely that this difference is due to the fact that gas evolution is the result of subsequent processes involving diffusion of gaseous products formed to the interface and their desorption from the interface to the gas phase along with the interaction of the HCOO groups (the consumption of the HCOO groups does not limit the rate of gas evolution).

The IR spectroscopic study of solid-phase transformations of compound **1** allowed us to detect an intermediate decomposition product, which absorbs at 1417 and 1430 cm^{-1} and is present in low concentration (see Fig. 3, curves *3* and *4*). The concentration of this intermediate product reaches a maximum at the degrees of formate transformation of η = 0.25 to 0.30. The maximum concentration of the intermediate product increases as T_{exp} increases. At 110 °C its concentration reaches a constant level, which is maintained almost to the end of transformation, and this concentration can be considered as quasi-stationary (see Fig. 3, curve *4*). The absorption at 1417 and 1430 cm^{-1} can be associated with both vibrations of the $HCOO^-$ ion and stretching vibrations of the carbonate ion, $\nu_{as}(CO_3{}^{2-})$.[15] However, the intermediate character of the absorption and its disappearance at such low temperatures allow one to consider

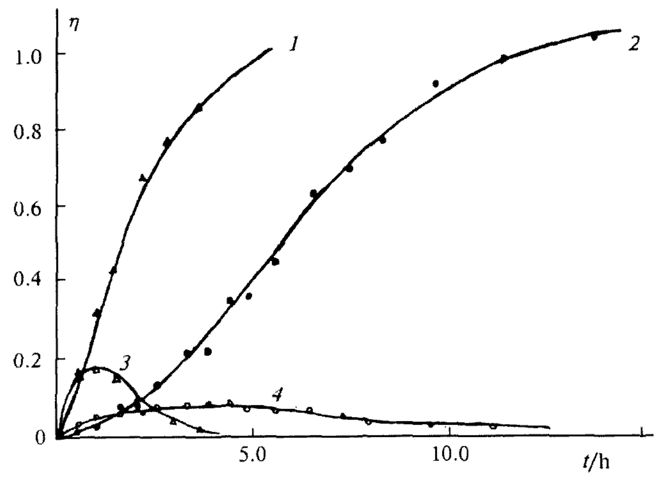

Fig. 3. Time dependences of the degree of transformation of the HCOO groups $\eta(t)$ at 120 °C (*1*) and 110 °C (*2*) and kinetics of accumulation of the intermediate product at 120 °C (*3*) and 110 °C (*4*).

that the assignment of the frequencies at 1417 and 1430 cm^{-1} to $\nu(CO_3^{2-})$ of copper(II) carbonate is highly improbable, because $CuCO_3$ is rather stable at these temperatures. An alternative can be the formation of intermediate copper(I) formate HCOOCu (**2**). The possibility of the formation of compound **2** upon thermal transformation of compound **1** has been supposed previously.[16–18] The upfield shift of the absorption of stretching vibrations of the COO group in compound **2** compared to that of compound **1** is likely related to a change in the polarization action of the cation and relative strengthening of the C—O bonds in the HCOO$^-$ ion. The reduction of Cu^{II} to Cu^{I} at these temperatures can be caused by a sufficiently low redox potential of Cu^{II}/Cu^{I} (E^0 = +0.158 V[19]). Compound **2** formed is probably less stable than compound **1** and decomposes rather rapidly to give copper metal. Thus, it is likely that the solid-phase decomposition of compound **1** is the stepwise process

$$Cu(HCOO)_2(s.) \rightarrow CuHCOO(s.) \rightarrow Cu(s.)$$

Dynamics of changes in microstresses during decomposition of compound 1. During transformation of compound **1**, the low-frequency component of the band of symmetric stretching vibrations of COO$^-$ at ν_0 = 1360 cm^{-1}, whose shape in the spectrum of initial compound **1** is close to the Lorentz shape, undergoes the strongest changes. At degrees of transformation η = 0 to 0.3 the intensity of the long-wave shoulder of the band increases (see Fig. 1). As mentioned above, a similar shape of the absorption band contour is characteristic of spectral bands of stressed crystal lattices with predominating stretching stresses. Parameters ν_1 and ν_2 in Eq. (3*) remain nearly unchanged during decomposition, which testifies that the R/r ratio is constant (this ratio is close to 4 in the most stressed decomposing species). It is likely that this value allows one to rule out model M_3 (see above). If the species are considered to be spherical, their average radius R is ~1000 nm[1] on the basis of the data on the specific surface of the initial powder of **1**. Then in terms of model M_2 (not more than one stressing center per species), the average radius of the stressing center $\bar{r} \approx 250$ nm. If one supposes that the stressing center is copper metal (the final decomposition product) and its specific density corresponds to the density of copper metal, then the number of copper atoms in the stressing center can be estimated as 10^9 to 10^{10}.

The fraction of stressed substance **1** (β) increases continuously as η increases to 0.30. At $\eta > 0.30$, the β value decreases, which can be associated with the fast relaxation of stresses due to cracking crystals of **1** and a decrease in particle size, which has previously been observed[1] by optical microscopic studies. A decrease in the β parameter is accompanied by a decrease in the rate of transformation of compound **1** (see Fig. 3).

These observations allow one to propose that microstresses play a role of specific catalyst in decomposition of compound **1**, and the effective rate constant determined from the instant decomposition rate is a superposition of local rate constants related to different regions of the decomposing substance with different extents of stress[2]:

$$k(T) = k_0\int_0^\infty \rho(E_a)\exp(-E_a/RT)\,dE_a\,, \qquad (8)$$

where $\rho(E_a)$ is the density distribution of local activation energy appeared upon the stress distribution. As shown previously,[2] at the power character of distribution $\rho(E_a)$ the Arrhenius form of dependence $k(T)$ is retained with the effective activation energy ($E_{a,eff}$) related to the portion of the substance that introduces the maximum contribution to the overall transformation rate. The regions of the decomposing substance with the E_a values, which are considerably higher than ($E_{a,eff}$), introduce no noticeable contribution to the overall decomposition rate due to low values of the corresponding rate constants. The regions, for which local E_a values are considerably lower than $E_{a,eff}$, comprise a small fraction of the substance and also exert no substantial effect on the overall transformation rate. An increase in stresses of the lattice, in particular, due to an increase in the number of stressing centers results in the positive correlation between $E_{a,eff}$ and the logarithm of effective pre-exponential $\log k_{0,eff}$ in the range of low concentrations of stressing centers.

Thus, if local stresses result in a decrease in $E_{a,eff}$, low values of $k_{0,eff}$ should also be observed. It is likely that the difference in effective rate constants describing the consumption rate of the HCOO groups upon thermal decomposition of compound **1** should be considered just from this point of view:

$$W(\eta) = d\eta/dt = k_1(1-\eta)^2 + k_2(1-\eta)^2\eta, \qquad (7^*)$$

where η is the degree of transformation of the HCOO groups; k_1 and k_2 are the effective rate constants, $k_1 = 3.3 \cdot 10^{10} \exp(-27800/RT)$ s^{-1}, $k_2 = 9.2 \cdot 10^6 \exp(-18500/RT)$ s^{-1}; Eq. (7*) is another form of Eq. (7).

It is noteworthy that establishment of the nature of stress sources is substantial for revealing the mechanism of decomposition of compound **1**. It is likely that the decomposition of compound **1** is the subsequent process with intermediate formation of HCOOCu and copper metal, the final transformation product. It can be supposed that stresses in the crystal lattice of compound **1** upon decomposition are caused by reaction products (gaseous products or nuclei of the forming new phase). Since HCOOCu decomposes rather rapidly (which is testified by low stationary concentrations during decomposition), the assumption about its effect on the appearance of stresses seems highly improbable. The source of stresses can be forming nuclei of the final product of decomposition of compound **1**, copper metal, whose specific volume is considerably lower than that of compound **1**. Gaseous products of transformation of compound **1** cannot serve as the source of stresses of the crystal lattice, because the studies of the effect of m_0/V (m_0 is the initial mass of compound **1** and V is the volume of the reaction vessel) on the gas evolution kinetics showed[1] the absence of substantial diffusion difficulties for yielding gaseous products from the matrix of decomposing compound **1**.

References

1. A. S. Rozenberg and E. I. Aleksandrova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, **45**, 71 [*Russ. Chem. Bull.*, 1996, **45**, 64 (Engl. Transl.)].
2. N. V. Chukanov, L. V. Berlyand, B. L. Korsunskii, and V. A. Dubovitskii, *Zh. Fiz. Khim.*, 1990, **64**, 1824 [*Russ. J. Phys. Chem.*, 1990, **64** (Engl. Transl.)].
3. E. V. Deyun, G. B. Manelis, E. B. Polianchik, and L. P. Smirnov, *Usp. Khim.*, 1980, **49**, 1574 [*Russ. Chem. Rev.*, 1980, **49** (Engl. Transl.)].
4. B. E. Krisyuk, A. A. Popov, and G. E. Zaikov, *Vysokomol. Soedin., Ser. A*, 1980, **22**, 329 [*Polym. Sci. USSR*, 1980, **22** (Engl. Transl.)].
5. V. A. Benderskii, V. M. Beskrovnyi, E. Ya. Misochko, and P. G. Filippov, *Dokl. Akad. Nauk SSSR*, 1983, **273**, 364 [*Dokl. Chem.*, 1983, **273** (Engl. Transl.)].
6. A. A. Sidel'nikov, A. P. Chupakhin, and V. V. Boldyrev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* [*Bull. Sib. Branch Acad. Sci. USSR, Div. Chem. Sci.*], 1985, **17**, 49 (in Russian).
7. N. N. Sirota, in *Kinetika i mekhanizm kristallizatsii* [*Kinetics and Mechanism of Crystallization*], Nauka i Tekhnika, Minsk, 1973, 41 (in Russian).
8. S. N. Zhurkov, *J. Fract. Mater.*, 1965, **4**, 311.
9. D. M. Adams and T.-K. Tan, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1711.
10. S. N. Zhurkov, V. I. Vittegren', V. E. Korsunkov, and I. I. Novak, *Fiz.. Tverd. Tela* [*Solid State Phys.*], 1969, **11**, 290 (in Russian).
11. V. V. Baptizmanskii and I. I. Novak, *Fiz.. Tverd. Tela* [*Solid State Phys.*], 1975, **17**, 1989 (in Russian); K. N. Kuksenko, I. I. Novak, and V. P. Pukh, *Zh. Prikl. Spektrosk.* [*Zh. Appl. Spectrosc.*], 1975, **22**, 1048 (in Russian).
12. J. McBride and J. Michael, *Acc. Chem. Res.*, 1983, **16**, 304.
13. L. V. Berlyand, N. V. Chukanov, and V. A. Dubovitsky, *Chem. Phys. Lett.*, 1991, **181**, 450.
14. N. V. Chukanov, D. Sci. (Chem.) Thesis, Chernogolovka, 1991 (in Russian).
15. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
16. S. Schuffenecker, Y. Trambouze, and M. Prette, *Ann. Chim. (Paris)*, 1962, **7**, 133.
17. A. K. Galway, D. M. Jamirson, and M. S. Brown, *J. Phys. Chem.*, 1974, **78**, 2664.
18. V. V. Aleksandrov, V. V. Boldyrev, V. A. Bocharnikov, and V. G. Morozov, in *Tezisy soveshch. po kinetike i mekhanizmu khim. reaktsii v tverdom tele* [*Proc. Meeting on Kinetics and Mechanism of Solid-Phase Chemical Reactions*], Part 1, Novosibirsk, 1977, 133 (in Russian).
19. R. A. Lidin, L. L. Andreev, and V. A. Molochko, *Sprav. po neorganicheskoi khimii. Konstanty neorganicheskikh veshchestv* [*Manual on Inorganic Chemistry. Constants of Inorganic Substances*], Khimiya, Moscow, 1987, 210 (in Russian).
20. A. W. Baker, *J. Phys. Chem.*, 1957, **61**, 450.

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