Kinetics and mechanism of thermal decomposition of hydroxylammonium nitrate

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The kinetics of thermal decomposition of melted hydroxylammonium nitrate have been investigated by the rate of heat production in the temperature range 84.8—120.9°C. The decomposition proceeds with autocatalysis and up to 60 % of conversion the rate of the process increases proportionally to the square of the degree of decomposition. The initial rate is proportional to the square of the concentration of HNO_3 formed due to dissociation of the salt. The activation energy of this process is 15.3±1.8 kcal/mol. It is suggested that the initial stage the process proceeds via interaction between N_2O_5 and NH_3OH^+, whereas the subsequent acceleration is due to oxidation of NH_3OH^+ by nitrogen oxides formed as well as by nitrous acid.

Key words: hydroxylammonium nitrate, preparation, thermal decomposition, kinetics, mechanism.

Hydroxylammonium nitrate $NHOH \cdot HNO_3$ (HAN) belongs to the class of onium salts whose specific feature is the equilibrium character of their formation and, as a consequence, the presence in the salts of the molecular forms of the initial salt-forming compounds.[1] Hydroxylamine and nitric acid, with pronounced reducing and oxidizing properties, respectively, are capable of independent thermal transformations even at room temperature. For these reasons, HAN is of interest as an object capable of several routes of conversion: thermolysis of the NH_2OH and HNO_3 formed by dissociation and interaction between acid and salt. The kinetic regularities of the thermal decomposition of HAN in the individual state have not been studied. There are only qualitative observations of changes in the Raman spectra of an 11 *M* aqueous solution of HAN and of its decomposition products at pressures of several kilobars.[2]

Experimental

The initial compound was prepared by an exchange reaction between $NaNO_3$ (pure grade) and hydroxylammonium sulfate $2NH_2OH \cdot H_2SO_4$ (HAS) (analytically pure grade) according to a specially developed procedure. About 8 moles of distilled water was added to a mixture of fine crystalline salts containing 2 moles of $NaNO_3$ and 1.05 mole of HAS. The viscous mass was heated with constant stirring on a water bath (92°) until complete dissolution of the salts. The flask with the solution was kept for 1—1.5 h at ~20°C. The viscous mass formed in the dry chamber was washed with ~50 ml of abs. ethanol divided into 4—5 portions. The alcohol solution of HAN was filtered from the solid residue on a ceramic filter. About 30 ml of dry diethyl ether was added to the obtained solution, following which the mixture was allowed to settle for 15—20 min. After the alcohol-ether solution of HAN was filtered off from the residue under reduced pressure on a water bath (30°C), most of the solvent was carefully removed from it. The remainder of the solvent was frozen into an entrainment separator cooled with liquid nitrogen. HAN was considered dry when the vapor pressure in the system became less than 10^{-2} Torr at a water bath temperature of 60—65°C. The pressure was measured with a VIT-2 vacuum gauge. The obtained preparation was repeatedly recrystallized and dried as described above. Specially prepared solvents were used for the synthesis. Rectified alcohol was treated with $KMnO_4$ (the solution of 0.5 g of $KMnO_4$ in 200 ml of alcohol was kept for 12 h, the precipitate of MnO_2 formed was removed by decanting), dehydrated by refluxing with CaO, and then distilled. Ether was preliminarily purified from peroxides by treating with Na_2SO_3 solution, then with solutions of $KMnO_4$ and NaOH,[3] dried for 1 day with $CaCl_2$, and distilled. The thermal stability of HAN became considerably worse when unpurified solvents were used.

The concentration of NH_2OH was measured by iodometric titration in a weakly basic medium of HAN. It turned out to be 34.24 %, which corresponds to a purity of 99.6 % for the preparation. The content of Na^+ in HAN determined on a flame photometer (Flame Photometer, Model "A", EEL, England) was 0.1—0.05 %, the qualitative reaction of SO_4^{2-} to barium chloride indicated the absence of this ion in the obtained salt.

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Results and Discussion

Acording to the IR spectroscopy data, the gaseous final products of HAN decomposition are NO_2, NO, N_2O, and H_2O. The kinetics of thermal decomposition were studied by the rate of heat release[4] under isothermal conditions in completely thermostatted preliminarily evacuated glass ampules in the temperature range 84.8 to 120.9°C, which is higher than the melting point T_m (43—44°C) at filling degrees m/V of $1 \cdot 10^{-3} \div 27 \cdot 10^{-3}$ g cm^{-3}. The decomposition of HAN is characterized by a strong acceleration; the maximum rate is 200—500-fold greater than the initial one, and this ratio noticeably increases with the increase in m/V. Typical kinetic curves of the salt decomposition are presented in Fig. 1.

The decomposition of ~60% of HAN is described by the following kinetic law

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

where $\eta < 0.6$.

At higher conversions autoacceleration of the reaction depends more strongly on η (Fig. 1). The value of k_1 essentially decreases as the ratio m/V increases (Fig. 2). The values of the initial rate at different m/V and temperatures are presented in Table 1.

The estimate of the average value of the full heat effect of HAN decomposition at ~100°C and $m/V = 2 \cdot 10^{-3} \pm 3 \cdot 10^{-3}$ g cm^{-3} is 380 cal g^{-1}. The values of k_1 at $m/V = 2.5 \cdot 10^{-3}$ g cm^{-3} are found by interpolation from the experimental data in Fig. 2. Their temperature dependence is

$$k_1 = 4.2 \cdot 10^4 \exp\left(-\frac{16450 \pm 450}{RT}\right) \qquad (2)$$

The introduction of ammonia at 110.4°C and $m/V = 2.75 \cdot 10^{-3}$ g cm^{-3} noticeably increases $(dQ/dt)|_{t=0}$; the time at which the sharp acceleration of the reaction occurs simultaneously increases as well (Fig. 1). Additions of 5—20 molar per cent of 100% HNO_3 result in vigorous decomposition of the salt even at ~20°C, therefore the study was performed in dilute HNO_3 solutions. For this purpose, the dependence of the decomposition rate of a mixture containing 1/3 mol. fractions of HAS and 2/3 mol. fractions of $NaNO_3$ has been studied. This mixture models HAN in HNO_3 solutions of different concentrations. The characteristic kinetic curves of decomposition of these systems are presented in Fig. 3.

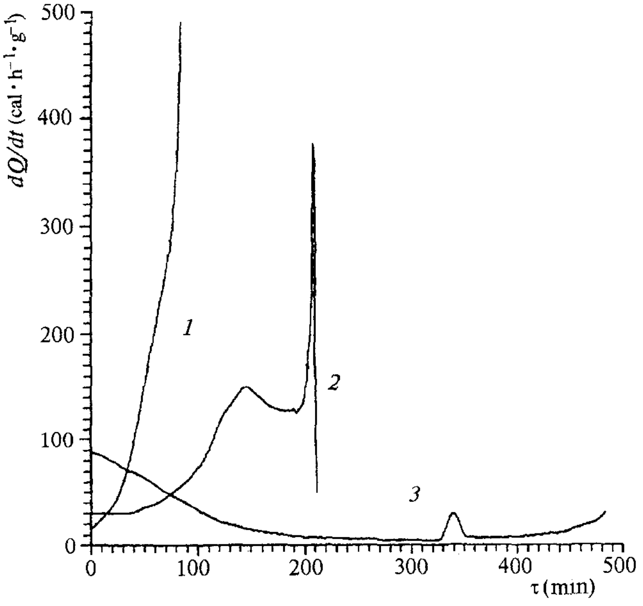

Fig. 1. Kinetic curves of HAN decomposition in the melt at 101.5 (*1, 2*) and 110.4°C (*3*), m/V (g cm^{-1}): $2.56 \cdot 10^{-3}$ (*1*), $0.68 \cdot 10^{-3}$ (*2*), $2.75 \cdot 10^{-3}$ g cm^{-1} (*3*) (+7.7 mol.% of NH_3).

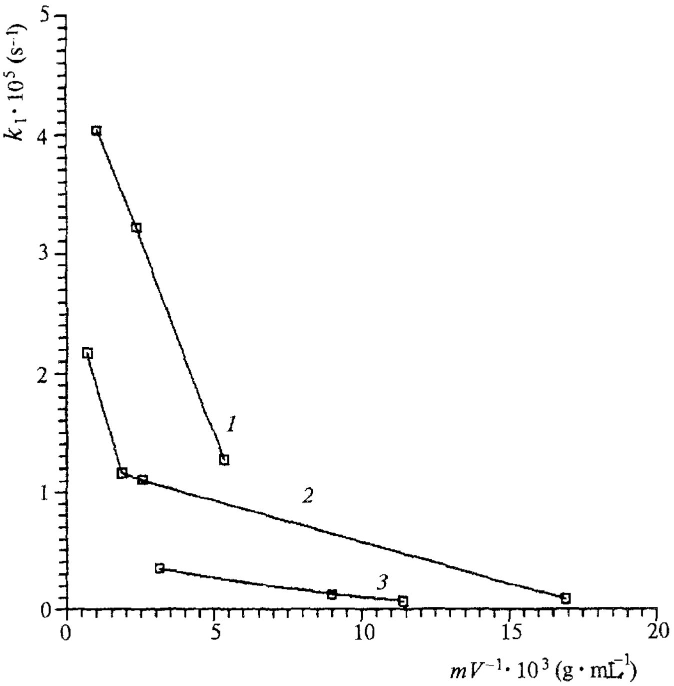

Fig. 2. Dependence of k_1 on the ratio m/V at HAN decomposition: 120.9 (*1*); 101.5 (*2*); 84.8°C (*3*).

Table 1. Initial rates of decomposition of $NH_2OH{\cdot}HNO_3$ in the melt under different conditions

T / °C	$m/V \cdot 10^3$ / g cm^{-3}	$\left.\frac{dQ}{dt}\right\|_{t=0}$ / cal (h g)$^{-1}$	$\left.\frac{d\eta}{dt}\right\|_{t=0} \cdot 10^5$ / s^{-1}	$k_{ef} \cdot 10^8$ / s^{-1}
84.8	3.13	4.75	0.35	0.74
	9.0	1.64	0.12	0.73
	11.4	0.95	0.069	0.53
101.5	0.68	29.7	2.17	1.15
	1.85	15.8	1.16	1.51
	2.56	15.2	1.11	1.98
	16.9	1.2	0.088	1.00
110.4	8.36	9.87	0.72	4.10
110.4*	2.75	88.4	6.46	
120.9	1.03	55.2	4.04	3.30
	2.34	44.1	3.22	5.46
	5.35	17.3	1.27	4.68

* NH_3, 7.8 mol.%.

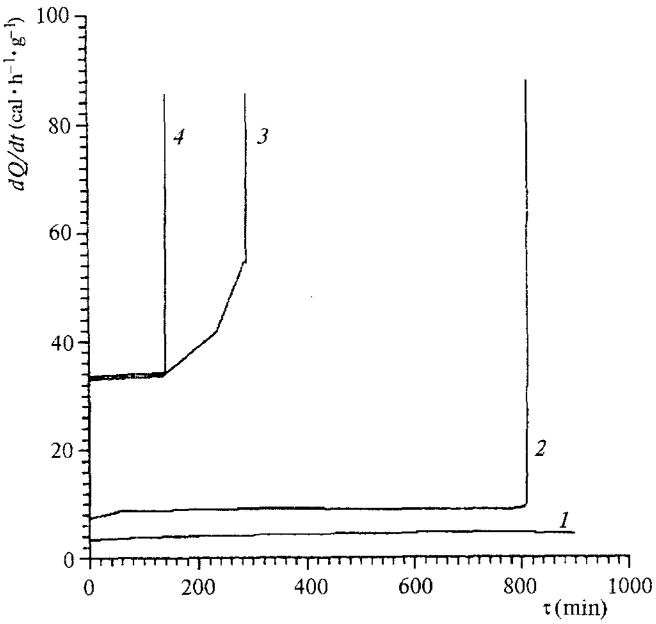

Fig. 3. Kinetic curves of decomposition of mixtures of HAS (1/3 mol. fractions) with $NaNO_3$ (2/3 mol. fractions) in solutions of HNO_3 at 122.1°C:
$[NH_3OH^+]$ = 1.41 *M*, $[HNO_3]$ = 0 (*1*);
$[NH_3OH^+]$ = 1.43 *M*, $[HNO_3]$ = 1.55 *M* (*2*);
$[NH_3OH^+]$ = 1.42 *M*, $[HNO_3]$ = 2.42 *M* (*3*);
$[NH_3OH^+]$ = 1.42 *M*, $[HNO_3]$ = 2.76 *M* (*4*).

Table 2. Initial rates of decompositions of mixtures of $2NH_2OH{\cdot}H_2SO_4$ with $NaNO_3$ in solutions of HNO_3 at 122.2°C

$[NH_3OH^+]_0$ / *M*	$[HNO_3]_0$ / *M*	$\left.\frac{dQ}{dt}\right\|_{t=0}$ / cal (h g)$^{-1}$
1.41	—	3.42
1.43	1.55	7.45
1.42	2.42	33.5
1.42	2.76	33.0

The initial decomposition rates of these mixtures are tabulated in Table 2 ($(dQ/dt)|_{t=0}$ relates to 1 g of HAN).

The decomposition was also studied in more concentrated HNO_3 solutions up to 9 *M*, but when the concentration of acid was more than ~2.8 *M* the reaction managed to develop while the ampule was being heated, and most of the initial NH_3OH^+ ions underwent transformations during this period. The release of NO_2 is observed in ampules containing mixtures with 2.8 *M* (and more) HNO_3 immediately after the heating period, and the free volume of the ampule becomes dark grayish-brown, which does not occur before the sharp autoacceleration of the reaction when the concentration of HNO_3 is lower. According to literature data,[5,6] thermal decomposition of HAN at 25°C occurs with autoacceleration only in HNO_3 solutions with concentrations greater than 2.5 mol/l.

The obtained data about the essential influence of the addition of HNO_3 and NH_3 on the initial rates of HAN decomposition attest that the process occurs via the molecular forms of the initial acid and base formed as the result of the dissociation of the salt (Eq. (3)) and not through decomposition of the ionic form of NH_3OH^+, because thermal decomposition of some salts of hydroxylammonium, for example, perchlorate (HAP),[7] occurs more slowly (by more than ten times) in the initial stages at the temperatures studied.

$$\begin{array}{ccccc} NH_3OH^+ + NO_3^- & \overset{K_{d1}}{\rightleftharpoons} & NH_2OH^l & + & HNO_3^l \\ l\text{ — liquid,} & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ g\text{ — gas} & & NH_2OH^g & + & HNO_3^g \end{array} \qquad (3)$$

The addition of anhydrous HNO_3, as compared with NH_3, has a greater effect on the rate of HAN decomposition. This indicates that HNO_3 plays a determining role in the initial stages of the interaction between HNO_3 and the ionic or molecular form of NH_2OH. In order to estimate the value of the initial HNO_3 concentration in the melt, one should take into account that the equilibrium

$$NH_3OH^+ + NH_2OH \overset{K_{d2}}{\rightleftharpoons} [NH_3OH^+ \cdot NH_2OH] \quad (4)$$

is essentially shifted to the right, and in HAP at 108.5°C, K_{d2} is close to 7 liters/mol.[7] From equilibria (3), (4) using concentrations instead of activities, and assuming equimolarity of the HNO_3 formed and the sum of NH_2OH and $NH_3OH^+ \cdot NH_2OH$, and that $C_0 >> [HNO_3]_{0,l}$, $C_0 >> [NH_2OH]_{0,l}$, one can obtain for the initial time:

$$[HNO_3]_{0,l} = K_{d1}^{1/2} C_0 \left(\frac{\frac{V_l}{V_g} + K_{d2}C_0 + \frac{P_{0,h}}{2RTC_0}}{\frac{V_l}{V_g} + \frac{P_{0,n}}{2RTC_0}} \right)^{1/2} \quad (5)$$

$$[NH_2OH]_{0,l} = K_{d1}^{1/2} C_0 \left(\frac{\frac{V_l}{V_g} + \frac{P_{0,n}}{2RTC_0}}{\frac{V_l}{V_g} + K_{d2}C_0 + \frac{P_{0,h}}{2RTC_0}} \right)^{1/2} \quad (6)$$

where C_0 is the initial concentration of HAN in the melt; V_l, V_g are volumes of the liquid and gaseous phases in the ampule; $P_{0,h}$ and $P_{0,n}$ are pressures of NH_2OH and HNO_3 above the pure components at the corresponding temperature.

The dependences (5), (6) are obtained with the assumption that the pressures of the HNO_3 and NH_2OH vapor are proportional to their molar fractions in the melt of HAN and to the vapor pressures above the pure components. It follows from dependences (5), (6) that the initial rate of HAN decomposition must not depend on the ratio m/V, if the interaction of the molecular forms of NH_2OH and HNO_3 in the melt plays a key role. The drop in the initial rate with the increase in m/V can be explained by the fact that the interaction between NH_3OH^+ and HNO_3 is limiting in the decomposition process. The experimental results obtained are satisfactorily described by a kinetic law suggesting that the reaction is second order with respect to the acid (Eq. (7)).

$$\left. \frac{d[NH_3OH^+]}{dt} \right|_{t=0} = -k[NH_3OH^+]_0 \cdot [HNO_3]^2_{0,l} \quad (7)$$

In this case, proceeding from Eq. (5) and taking into account that the value $K_{d2}C_0$ in the numerator of this dependence is considerably greater than the other terms, the initial decomposition rate of the pure salt can be presented in the form of Eq. (8).

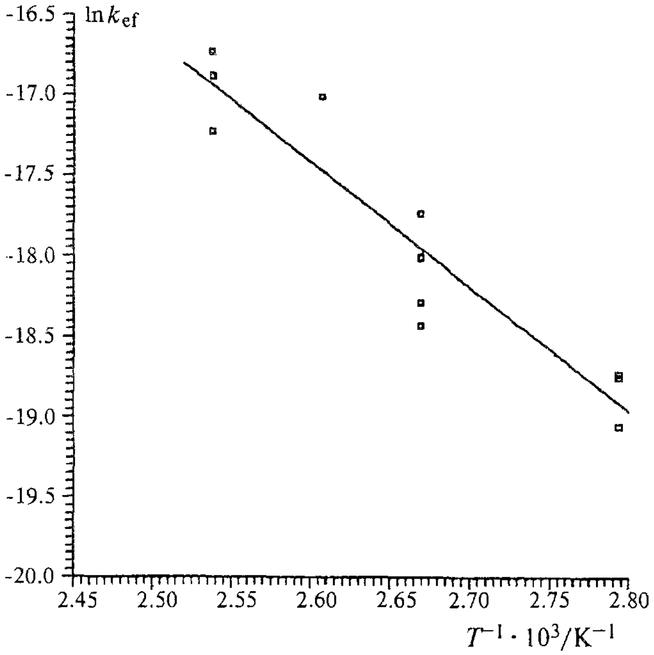

Fig. 4. Dependence of the natural logarithm of the effective constant of HAN decomposition on temperature.

$$\left. \frac{d\eta}{dt} \right|_{t=0} = kK_{d1}K_{d2}C_0^3 \frac{1}{\frac{V_l}{V_g} + \frac{P_{0,n}}{2RTC_0}} \quad (8)$$

According to dependence (8), the initial rate of HAN decomposition decreases as m/V increases because $V_l/V_g = m_{HAN}/(V_g \rho_{HAN})$. The values $k_{ef} = kK_{d1}K_{d2}C_0^3$ (Table 1) calculated from correlation (8) are independent of m/V, differing by not more than 40 % from the average value at a fixed temperature, and are described by an exponential dependence on temperature (Fig. 4).

$$k_{ef} = 13.73 \cdot \exp(-15300 \pm 1800/RT), \text{ s}^{-1} \quad (9)$$

For the calculation of k_{ef}, values of $P_{0,n}$ estimated from the literature data[8] were used; the value of ρ_{HAN} was taken to be equal to 1500 g/l.

The fact that the reaction is second order with respect to HNO_3 at the initial stages of decomposition of the pure salt probably means that there is interaction between NH_3OH^+ and nitrogen(V) oxide or the nitronium cation formed as the result of the following equilibrium reactions:

$$HNO_3 + HNO_3 \overset{-H_2O}{\rightleftharpoons} N_2O_5 \rightleftharpoons NO_3^- + NO_2^+ \quad (10)$$

Owing to Coulomb repulsion forces, the mechanism that includes an uncharged attacking agent is preferable (Eq. (11)).

$$NH_3OH^+ + N_2O_5 \longrightarrow \begin{array}{c} HNO_3 + NH_3^+ONO_2 \\ \downarrow \\ HNO + H_2^+NO_2 \end{array} \qquad (11)$$

Further transformations can occur by reactions established for the transformations of HAN in aqueous solutions of HNO_3[5,6] (reactions (12)—(16)).

$$H_2^+NO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O \qquad (12)$$

$$N_2O_4 + NH_2OH \longrightarrow HNO + N_2O_3 + H_2O \qquad (13)$$

$$N_2O_4 + HNO \longrightarrow HNO_2 + N_2O_3 \qquad (14)$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad (15)$$

$$HNO_2 + NH_3OH^+ \longrightarrow H_3O^+ + H_2O + N_2O \qquad (16)$$

In the melt of the salt, dissociation of N_2O_3 can occur to an essential extent:

$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad (17)$$

with the subsequent equilibrium dimerization of NO_2. NO found in the decomposition products likely does not participate in the HAN transformations, because it reacts at noticeable rates with NH_2OH only in an alkaline medium, and N_2, which is one of the reaction products,[9] is not found in the products of HAN decomposition.

For aqueous solutions HAN decomposition according to the scheme of reactions (12)—(16) is confirmed by studies of labeled nitrogen in $NH^+{}_3OH$. The concentrations of N_2O with a label and the change in the concentration of HNO_2 in the system calculated using known reaction rate constants for (12)—(16) agree well with the experiment.[10]

In the case of the addition of ammonia to the system, which considerably increases the equilibrium concentration of NH_2OH, the decomposition of NH_2OH, which occurs without autocatalysis under such conditions, begins to play a limiting role (Fig. 1). At the decomposition of the pure salt the effective rate constant of the limiting stage is the product $kK_{d1}K_{d2}C_0{}^3$ (Eq. (8)). Hence, the effective activation energy can be presented as follows:

$$E_{ef} = E + \Delta H_1 + \Delta H_2, \qquad (18)$$

where E is the activation energy of the reaction between HNO_3 and $NH^+{}_3OH$; ΔH_1 is the enthalpy of HAN dissociation, Eq. (3); ΔH_2 is the enthalpy of complexation, Eq. (4).

Proceeding from the values of enthalpies of formation of HAN (−87 kcal/mol), NH_2OH and HNO_3 available in literature[8] (−27.5 and −41.3 kcal/mol, respectively), and assuming that heat of formation of the complex between NH_2OH and HAN is close to the enthalpy of complexation of NH_2OH with HAN (−10 kcal/mol[7]) and equals (−10)÷(−15) kcal/mol, one can estimate that in the melt of HAN the activation energy of the reaction between HNO_3 and $NH^+{}_3OH$ is 7—12 kcal/mol. In aqueous solutions it is 25 kcal/mol.[6]

The scheme of reactions considered describes the experimentally observed drop in the initial decomposition rate with the increase in the ratio m/V, explains the increase in the degree of autoacceleration and also describes the composition of the products of HAN decomposition.

References

1. Yu. I. Rubtsov and A. I. Kazakov, *Gorenie i vzryv. Materialy IV Vses. Simpoziuma po goreniyu i vzryvu (Combustion and Explosion. Materials of IV All-Union Symposium on Flame and Combustion),* Nauka, Moscow, 1977, 600.
2. C. A. Van Dijk and R. G. Priest, *Combust. and Flame,* 1984, **57**, 15.
3. Yu. K. Yur'ev, *Prakticheskie raboty po organicheskoi khimii (Practical Works on Organic Chemistry),* Vols. I and II, MGU, Moscow, 1964 (in Russian).
4. O. S. Galyuk, Yu. I. Rubtsov, G. F. Malinovskaya, and G. B. Manelis, *Zh. Fiz. Khimii,* 1965, **39**, 2319 [*J. Phys. Chem.,* 1965, **39** (Engl. Transl.)].
5. J. R. Rembridge and G. Stedman, *J. Chem. Soc., Dalton Trans.,* 1979, 1657.
6. R. J. Gowland and G. Stedman, *J. Inorg. Nucl. Chem.,* 1981, **43**, 2859.
7. Yu. I. Rubtsov, E. S. Rumyantsev, L. P. Andrienko, V. A. Rafeev, L. N. Lyubimova, and G. B. Manelis, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1980, 1463 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.,* 1980, 1011 (Engl. Transl.)].
8. V. A. Rabinovich and Z. Ya. Khavin, *Kratkii khimicheskii spravochnik (Short Chemical Hand-Book),* Khimiya, Leningrad, 1978 (in Russian).
9. J. N. Cooper, J. E. Chilton, Jr., and R. E. Powell, *Inorg. Chem.,* 1970, **9**, 2303.
10. M. S. Garley, K. G. Phelan, and G. Stedman, *J. Chem. Soc., Dalton Trans.,* 1984, 2835.

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