The transition of spontaneous polymerization of acrylamide to "explosive" regime

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Experimental results related to the transition of spontaneous polymerization of acrylamide complexes with metal nitrates to the "explosive" regime at room temperature are presented. It is suggested that the "explosion" has a thermal nature.

Key words: polymerization, acrylamide, metal nitrates, thermal explosion.

The study of spontaneous polymerization (SP) of the acrylamide (AAm)—$Ca(NO_3)_2 \cdot 4H_2O$ system at room temperature showed[1] that when the mixture that began to polymerize was transferred from a porcelain cup in which it was prepared to a object with a lower thermal capacity, the system solidifed following intense warming up of the mixture with induction period, vapor evolution, and an increase in volume.

Similar self-warming of systems during their polymerization at room temperature are documented. For example, it has been reported[2] that the introduction of the inhibitor of radical reactions, 2,2,4,4-tetramethylpiperidine-1-oxyl, in an AAm—$Cr(NO_3)_3 \cdot 9H_2O$ mixture resulted in a noticeable increase in heat evolution and sometimes even in the ignition of the reaction mixture. The spontaneous explosive decomposition of complexes has been observed[3] in the polymerization at 20—60 °C of butyl vinyl sulfoxide in the presence of Fe^{III}, Cr^{III}, and Co^{III} nitrates.

This report presents the experimental results of the study of the transition of polymerization of the AAm complexes with metal nitrates to the "explosive" regime.

Experimental

Acrylamide (pure grade, Reanal, Hungary) and Ca^{II}, Ni^{II}, Pb^{II}, Mn^{II}, UO_2^{II}, Bi^{III}, Cr^{III}, Nd^{III}, Y^{III}, and Er^{III} nitrates (chemical pure grade) were used. Mixtures were prepared by a known method[4] for different molar ratios of AAm and metal nitrates (water was added when anhydrous $Pb(NO_3)_2$ was used), and the total weight of the mixture was 1.8—2.0 g. When the mixture became thick (did not spread) due to the structure formation[5] and polymerization, it was applied onto a Dacron film (~1.5 μm thick) that was placed on a dense paper (for heat insulation). Then a copper—constantan couple was introduced into the mixture, and the change in the temperature of the reaction mixture was monitored using a V2-36 d.c. voltmeter. The samples were weighed before and after the reaction on a VLR-200 balance. Following liberation of water of crystallization (~1 min after the beginning of mixing), the pH of the system was measured on an EV-74 ionometer. The duration of the pH measurement was ~10 s.

Results and Discussion

The temperature of the mixture placed on the heat insulating support increases slightly within several min. Then a sharp increase in temperature (>100 °C) in ~5—10 s occurred, and the system immediately cooled down (Fig. 1). The results of the observations of this "explo-

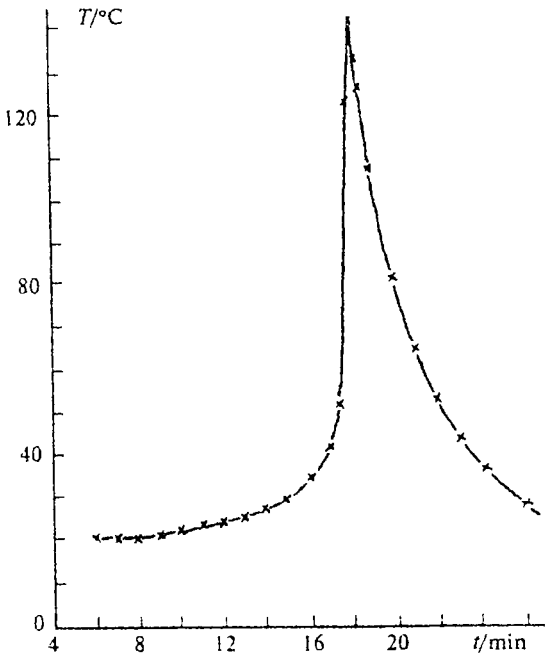

Fig. 1. Time (t) dependence of the temperature of the AAm—$Ca(NO_3)_2 \cdot 4H_2O$ mixture (molar ratio 4 : 1) after mixing of the components.

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sive" regime of the SP reaction for different mixture compositions and concentrations (x = 3—40, where x = [AAm] : [metal nitrate]) can be summarized as follows:

1. The maximum temperature T_{max} detected in the "explosion" depends on both the composition of the mixture and the content of AAm. Salts of bivalent metals induce "explosive" reactions mainly at the molar ratios $x < 10$ and trivalent metal salts, at $x > 5$. The maximum temperature of the sample reaches ~120—140 °C in the first case and ~150—250 °C in the second case.

2. The time t_{expl}, in which T_{max} is achieved, varies within ~6—30 min depending on the type of metal nitrate and its content in the mixture. The shortest time t_{expl} is observed for the mixtures with bismuth nitrate. However, the t_{expl} value is not characteristic and can differ several fold depending on the batch of acrylamide, which is likely related to the different content of undetectable admixtures. If an inhibitor (phenothiazine) is introduced, a linear dependence between its concentration and the time t_{expl} is observed.

3. Before the sharp temperature increase, the thickened system begins to melt, then crackling can be heard, and gaseous products evolve. The volume of the reaction mixture increases abruptly (3—60-fold) and 2—40% of the weight is lost. The system becomes solid, porous, looking like pumice (specific density up to ~0.015 g cm^{-3}). All the samples with $T_{max} > 100$ °C are almost insoluble in water. The ESR signal of the samples was similar to that obtained upon heating of AAm up to the temperature of its decomposition, but differed in a lower value of the g factor.

4. The estimations (due to the low content of water (viscosity) of the solutions obtained[6]) of pH of the systems show that at pH > 3.3 (mixtures with manganese and neodymium salts) "explosive" reactions do not occur. For the mixtures with pH < 3.3, the lower the pH, the more regular the "explosive" SP reactions (mixtures with bismuth and chromium salts had pH ~0.5 and 0.7, respectively). However, no unambiguous relation between pH, temperature T_{max}, and the existence of the "explosion" itself is observed in the range of pH < 3.3.

5. The transition of the SP reaction to the "explosive" regime does not take place if the mixture is in a porcelain cup or a glass capillary with an inner diameter of ~1.5—4 mm (the temperature of the system increases insignificantly (by 1—10 °C) as the capillary diameter increases).

Additional experiments showed the absence of the transition of the SP reaction to the "explosive" regime for the AAm—HNO_3 system down to pH ≈ 0.3, which indicates that metal ions have a substantial influence on the effect observed. In the case of the system with HNO_3, the maximum temperature of warming did not exceed 10 °C.

The facts presented can be rationalized as follows. After the components are mixed and water of crystallization is released, the salt is partially hydrolyzed to yield free-radical NO_2 species that initiate SP as described previously.[7] During the structure formation of the system,[5] the monomer molecules coordinate around the metal ion, thus facilitating the reaction, the polymerization rate increases, and, when the heat removal is insufficient, heating of the mass results in attaining the temperature at which the salt begins to decompose, yielding nitrogen oxides. This coordination is important for the realization of the "explosive" character of the polymerization process, which likely follows from its absence if polymerization is initiated by nitric acid. Nitrogen oxides initiate further polymerization up to the "explosive" character with a partial oxidation of the material. Therefore, "explosive" reactions are better reproduced at lower pH values, which is characteristic of the mixtures with bismuth and chromium nitrates. This results in the formation of cross-linked structures[8] above 100 °C, due to which the material obtained is almost insoluble in water. The estimations performed, without taking into account melting of the system and heat removal, show (for the mixtures with nickel(II) and chromium(III) nitrates) that the heat released due to SP is sufficient for heating the sample to a temperature 2—4 times higher than that observed (if the heat of polymerization of the AAm complex is taken as 81 kJ mol^{-1}).[2] It is likely that the kinetics of decomposition of the salt, in addition to the pH value, affect the induction time. Therefore, in particular for the mixtures with yttrium(III) and erbium(III) nitrates ("explosion" occurs at $x > 8$), a greater amount of heat is required (due to an increase in the fraction of AAm) for decomposition of the salt with the formation of nitrogen oxides.

This phenomenon probably can be related to the thermal "explosion"[9] caused by the spontaneous polymerization of the AAm complexes with metal nitrates at room temperature. The estimation of the effective activation energy of the process $E_{eff} \approx 35$—40 kJ mol^{-1} found from the pre-explosive warming up of the sample gives the "quality" parameters[10] of the thermal explosion: $\beta = RT_0/E_{eff} \approx 0.07$ and $\gamma = cRT_0^2/(QE_{eff}) \approx 0.03$ (R is the gas constant, T_0 is the ambient temperature, E_{eff} is the effective activation energy, c is the specific heat capacity, and Q is the heat effect of the polymerization reaction). The small values of these parameters are prerequisites for the thermal explosion.[9,10]

The analysis presented is preliminary, and the phenomenon discussed should be further studied.

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1-(1-Adamantyl)diaziridine

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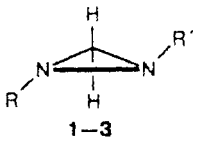
The reaction of 1-aminoadamantane with CH_2O and H_2NOSO_3H in the presence of K_2CO_3 under phase-transfer conditions leads to hitherto unknown 1-(1-adamantyl)diaziridine and (1-adamantyl)aminoacetonitrile, characterized by spectral data.

Key words: 1-(1-adamantyl)diaziridine, (1-adamantyl)aminoacetonitrile, ^1H and ^{13}C NMR spectra.

Recently, we demonstrated the possibility of synthesis of 1,2-di-*tert*-alkyldiaziridines **1** [1] and **2**,[2] which opens the way to study the sterically hindered inversion of nitrogen atoms.



R = R′ = Bu^t (**1**), Ad (**2**)
R = H, R′ = Bu^t (**3**)

1—3

One line of investigation is to introduce a second bulky substituent into diaziridines of type **3** (for example, the addition of β-substituted acrylates), separate the diastereomers, and determine the inversion barriers of nitrogen atoms by studying the kinetics of epimerization. Another line is to introduce a bulky achiral substituent (for example, β,β-dimethylacrylates) and separate the enantiomers using their carboxyl derivatives. In the past,[1,3,4] diaziridine **3** has been obtained in yields no higher than 15% and characterized by spectral data.[1] In the present work, crystalline diaziridine **4** was synthesized for the first time, which is more convenient for the above-mentioned studies (Scheme 1). The structure of this diaziridine was unambiguously confirmed by the spectral data.

Similar values of spin-spin coupling constants $^3J_{H_a,H_c}$ and $^3J_{H_b,H_c}$ typical of analog **3** [1] and the high-field position of the ^{13}C signal of the diaziridine ring, which is characteristic of sterically hindered diaziridines **1**—**3**,[1,2] are observed in the NMR spectra of diaziridine **4**. In the mass spectrum (electron impact, 70 eV) of

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