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Crystal disordering and organic solid-state reactions

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Abstract

This work is the extension of our preliminary communication[1] about the relationship between the change in the solid-state structure and the chemical reaction in the crystal. The investigation is a case study about the nature of the adiabatic organic solid-state reactions by kinetic measurements of the processes that occur during the dimerization of aromatic nitroso compounds (*p*-bromo- and *p*-iodonitrosobenzenes, respectively) in crystals. From the reaction rates at different temperatures we have calculated the activation energy. Since dimerization is induced by the appearance of crystal deformations on the surface caused by sublimation[1], we study here the relationship between the rate of sublimation and the rate of dimerization. There are indications that the sublimation of molecules from the surface serves only for activation of chemical solid-state reaction. Dimerization is studied also under three different topochemical environments: strong topochemistry in the cryogenic conditions where the starting monomers were obtained by photolysis of crystals of the corresponding dimer at 14 K, looser topochemistry in the freshly sublimed crystals of monomers, and randomly

distributed monomer molecules in thin layers prepared by cryogenic deposition. It is demonstrated that the change in topochemistry drastically modifies the reaction rate.

Introduction

Interest in the reactions occurring in the solid phase increases rapidly because of their application in the development of solvent-free synthetic methods, and in the designing of new intelligent materials. While studies of the photochemically induced processes and their mechanisms are available from the vast literature, the mechanisms of the thermal organic solid-state reactions are still an open question. Although Paul and Curtin[2] have established the theoretical basis of the solid-state reactions forty years ago, the detailed and quantitative descriptions of these processes, especially in the organic chemistry, is still missing. The fundamental problem is how the two processes, chemical reaction and changes in the molecular arrangements (phase transition), are interrelated. The necessary condition for initiating the solid-state reaction is the "loosening of molecules at the reaction site".[2] In our previous papers we have proposed the molecular model (dimerization of aromatic nitroso compounds) for the kinetics and structural studies of the reactions in crystal environments.[3] By simultaneous measurement of the rate of chemical reaction and the rate of phase transformation by time-resolved FTIR and time-resolved XRPD, we have found that two processes could afford different types of kinetic curves. It seemed that the sigmoid kinetic curve indicates the phase transformation as the predominant process. In cryogenic studies of dimerization of photochemically prepared nitrosobenzene monomers in the crystal,[4] it has been demonstrated that the re-dimerization is very fast reaction guided by strong topochemical principle.

From the literature it is known that the most of *p*-substituted aromatic nitroso compounds appear in the crystal in the form of dimers, azodioxides.[5] However, after sublimation only monomers deposit on the cold finger of the sublimer. When these crystals of monomers are warmed to room temperature, the dimerization followed with the phase transformation starts immediately.[3] Microscopy studies of the change in the morphology of monomer crystals during the reaction have shown that the solid state dimerization is noticeably enhanced by off-sublimation of the molecules from the surface, the process that induces the formation of vacancies-deformations in the crystal lattice.[1] For instance, if the crystals of monomers are immersed into glycerol, the reaction is difficult to register within the reasonable time, or, the reaction is markedly slower in the sealed ampoules where the vapor pressure prevents the sublimation. The rate of the "loosening of the molecules at the reaction site"[2] in our example is proportional to the rate of loss of mass caused by sublimation, the process that can be easily measured by isothermal TGA.

Another factor that influences the efficacy of the solid-state reaction is the topochemical effect.[6] By studying the reactions under different topochemical environments, we propose the possible theoretical explanation of the thermal organic reaction mechanisms in the solid state.

Experimental

Preparation of nitrosobenzenes

Halonitrosobenzene, *p*-bromo- and *p*-iodo- dimers were prepared by oxidation of corresponding anilines with Oxone$^®$ ($K_2SO_5 \times K_2SO_4 \times KHSO_4$) analogously to the method previously described in the literature.[3,7] Monomer crystals of the halonitrosobenzenes were

prepared from dimers by sublimation under reduced pressure of around 10 mbar. The temperature of cooling water was around 10 °C.

Kinetic measurements

The monomer samples were prepared as a standard KBr pellets (m(monomer)~1,5 mg, m(KBr)=200 mg, p(press)=10 t, thickness(KBr pellet)=1.2 mm). Fourier transform spectra were recorded on a PerkinElmer Spectrum Two spectrometer, equipped with a Bruker Eurotherm 2216 thermoblock. The background spectrum was obtained by observing ambient air. The spectra were recorded at different temperatures (293–313 K) in the spectral range between 4000 and 400 cm^{-1} at the resolution of 4 cm^{-1}. Normally, 32 scans were averaged for a spectrum. The spectra were recorded every 2 min and the data were collected in a period of 2 h. The solid-state dimerization rate was measured by following the temporal change in transmittance of the ONNO asymmetric stretching signal at 1260 cm^{-1} and the NO stretching signal of monomer at 1489 cm^{-1}. The data collection and analysis were performed using the program package Perkin Elmer Spectrum V10.[8]

Kinetic measurments under the cryogenic conditions

Monomer crystals of the halonitrosobenzenes were prepared by photolysis of the dimers prepared as a standard KBr pellet and also by cryogenic deposition of the monomers cooled at 14 K by Leybold-Heraeus ROK 10–300 cyclic helium cryostat. A high-pressure Hg lamp 250 W was used for the photolysis. The same photolytical reaction occurs if the 253.7 nm low-pressure Hg lamp is used. The solid-state dimerization rate is measured after warming the sample to 170 K analogously to the method described in the previous section.

Thermal and Spectroscopic Analysis

Thermal analysis was carried out on Mettler Toledo TGA/SDTA 851 and DSC823 modules in opened aluminium pans (40 μL), heated in flowing nitrogen (50 mL min^{-1}) in the temperature range between 298 K and 333 K over a period of 2 h. The samples were placed in a preheated TGA instrument Mettler Toledo TGA/SDTA 851. The data collection and analysis were performed using the program package STARe Software 9.01.[9]

Results and discussion

Reaction rates and topochemical condition

For the detailed kinetic studies of the solid-state reaction we have used *p*-bromo- and *p*-iodonitrosobenzene as molecular models, because their rates of dimerization can be measured under the "room" experimental conditions (Scheme 1).
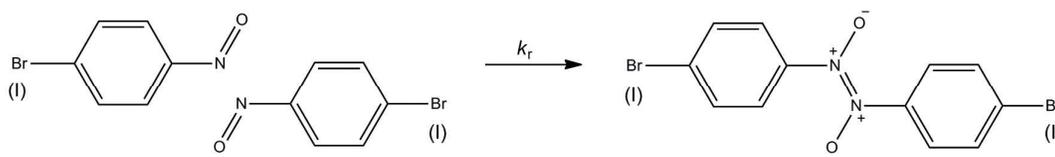
Scheme 1

The reaction rate constant, k_r, is measured by time-resolved FTIR by following the decrease of the intensity of the N=O stretching signal at 1489 cm^{-1}, or by following the growth of the peak associated to the asymmetric stretching of the ON=NO group at 1260 cm^{-1}. It must be commented that even though the rate constant strongly depends on the individual

experimental conditions (the size of crystals, and the area of surfaces), in earlier experiments we have found that the grinding and pressing the sample to a KBr pellet does not induce dimerization.[3c] In our previous paper[3c] samples were sublimed and directly transferred to ATR sampling accessory (without grinding and pressing). In this study, the obtained value of the rate constant for dimerization of *p*-bromonitrosobenzene falls in the range of the values measured in this work.

From the rates observed at different temperatures (Table 1), the activation energy 59.27 ± 0.44 kJmol^{-1} is calculated by using the Arrhenius plot (Fig. 1).

Table 1. The solid-state dimerization rate constants (k_r) of the *p*-bromonitrosobenzene in the crystal at different temperatures (*T*)

T / K	$10^4 \, k_r$ / s^{-1}
293	1.78 ± 0.37^a
298	3.33 ± 0.15
303	4.41 ± 0.10
308	7.51 ± 0.63
313	8.21 ± 0.31

[a]Standard deviation.
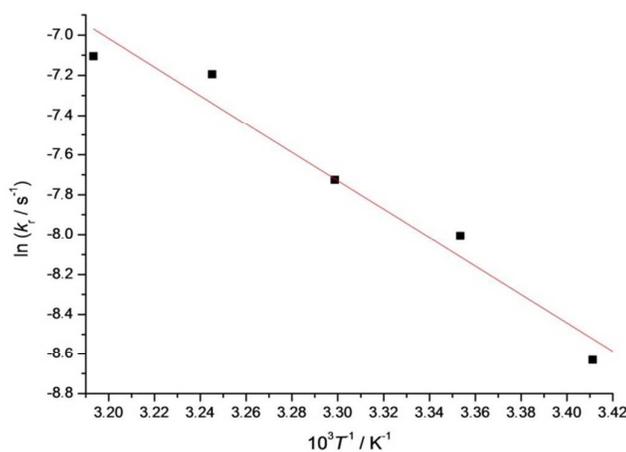
Fig. 1 The $\ln(k_r)$ *vs.* $1/T$ plot for the dimerization of the *p*-bromonitrosobenzene in the crystal.

The observed activation energy is not very different from the value previously measured for analogous reactions in solution.[5] From the variable temperature NMR measurements, the activation enthalpy for the dimerization of nitrosobenzene is estimated to be 51.9 kJmol^{-1}.[5b] Appearance of vacancies after removing the molecules from the crystal enables the rest of the molecules to move in the preferred direction for the formation of the new (O)N=N(O) bond. As we know from previous studies, the molecular arrangement in the crystal of *p*-bromonitrosobenzene is in the orientational disorder[3] in which large number of monomer molecules are oriented such that the high percentage of the reacting nitroso groups are close enough to each other that the "soft" topochemical condition is satisfied for the formation of the new chemical bond. Oppositely, the *p*-iodo analogs, although isostructural, are packed with much higher regularity, and most of the nitroso groups are closer to iodine atoms rather than to each other, and the topochemical condition does not exist. In the solid monomeric phase each molecule thus, according to the topochemical principle[6b], may or may not have the neighboring molecule oriented suitably for dimerization. For molecules which do not have a suitably oriented neighbor (*p*-iodonitrosobenzene), dimerization is thus expected only if large scale molecular movement during the reaction is possible.[6b] Accordingly, the dimerization of the freshly sublimed *p*-iodonitrosobenzene, $k_r = 4.15 \times 10^{-4}$ s^{-1} (at 333 K), is for order of magnitude slower (ten times slower) relative to the bromo [k_r (extrapolated for 333 K) $= 3.69 \times 10^{-3}$ s^{-1}] at the same temperature, **and the reaction ends in the early stage**, leaving the most of the monomeric material unreacted.

The impact of topochemical effect is more evident by measuring the reaction rate under the cryogenic conditions. In this case the *p*-bromonitrosobenzene monomers were obtained by photolysis of the crystals of dimer cooled in the KBr pellet to 14 K. Dimerization kinetics were measured after warming the sample to 170 K and the rate constant k_r was found to be 2.24×10^{-4} s^{-1}. Starting with the value of the activation energy obtained from the previous room temperature experiment (59.27 kJmol^{-1}), the extrapolated rate constant of the sublimed monomer would at the temperature of 170 K be $k_r = 4.44 \times 10^{-12}$ s^{-1}, *i.e.* for eight orders of magnitude lower. Such drastic difference in the reactivity is the consequence of the strong topochemical condition in the photolyzed crystal in contrast to the "soft" topochemical arrangement in the sublimation-affected samples. The strong topochemical condition follows from the observation that the N···N distance in the crystal of monomers obtained by photolysis is for 23 % shorter than the sum of the van der Waals radii of nitrogens.[3b] The complete model could be regarded as a three minima system. Besides the covalently bounded azodioxide in the solid state could exist also two nonbonding minima depending on the way how the nitroso monomers were obtained. The concept is represented in Fig. 2.
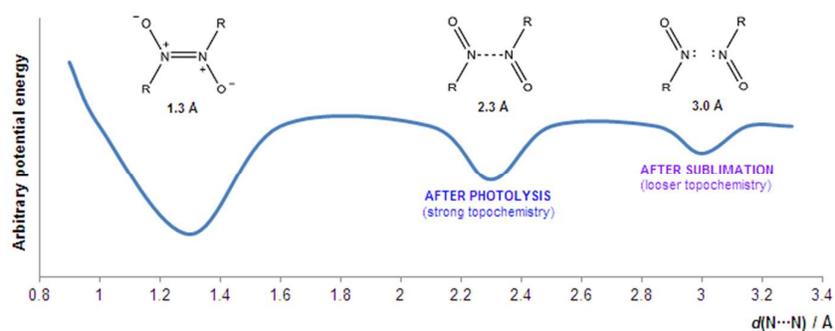
Fig. 2 The nitrogen-nitrogen atom distances in three different potential energy minima corresponding to covalent bond (azodioxide), closed packed monomers in photolysed sample,

and van der Waals interaction in sublimed crystal. Potential energy is represented only schematically.

On the other extreme, topochemical condition does not exist if the molecules are randomly distributed. Such chaotic molecular distribution was obtained by cryogenic deposition of *p*-bromonitrosobenzene monomers on the CsI surface cooled to 14 K. It must be noted that within the presented experimental set-up, which is based on the equipment generally used for matrix deposition we are not able to determine the detailed structure of the deposited sample. Warming this sample to 170 K caused only negligible dimerization, and most of the reactant molecules disappeared in the high vacuum chamber before the reaction has started.

Relation of the reaction rate and the phase transformation

Let us return to the kinetics of the sublimed monomers. To confirm our previous interpretation that the off-sublimation of molecules from the surface triggers the reaction, we have compared the reaction rate constants (k_r) with the rates of the loss of masses measured at the same temperatures (k_s). The isothermal TGA curves (Fig. 3) show that, after the short incubation period, almost linear loss of mass of the reactant becomes faster at the higher temperatures.
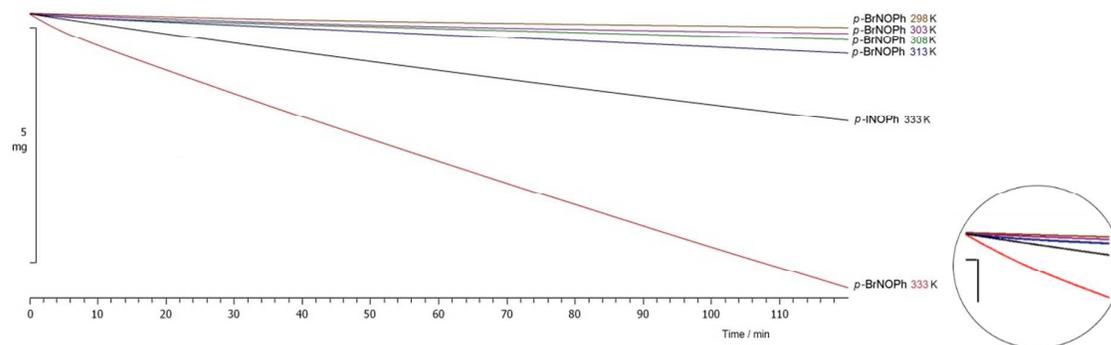
Fig. 3 Isothermal TGA diagrams for *p*-bromo- and *p*-iodinitrosobenzene crystals. The loss of mass is caused by removing the material by sublimation. The first ten minutes are extrapolated in the circle on the right. The y-axis shows the relative weight scale (only in 5 mg range).

From the zero-order kinetic curves obtained at different temperatures, we have calculated the activation energy for the sublimation as 72.89 ± 5.34 kJmol^{-1}. Since this value is larger than the activation energy of the chemical reaction, and since the observed exponential kinetics is typical of chemical reactions, the two processes must be parallel. The loss of mass of the iodo- derivative is similar to that of the bromo- compound. However, in spite of that the iodonitrosobenzene dimerization ends immediately after initialization.

Interesting observation is that the dimerization of the sublimed monomer does not start immediately after warming the crystals to room temperature, but only after some short incubation period which is manifested by the growth of the monomer signal (the NO stretching) (Fig. 4). This incubation period is shorter as the reaction temperature is higher.
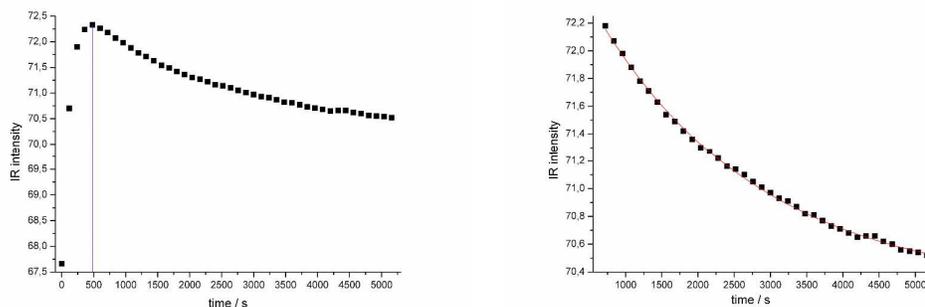
Fig. 4 Change in intensities of the monomer (v(NO)=1489 cm^{-1}) during solid-state dimerization of the *p*-bromonitrosobenzene at 25 °C measured by time-resolved FTIR. Intensity change during incubation period (left) and reaction period (right)

Almost the same incubation time has also been observed from the initial curvature of TGA lines (Fig. 3, fragment within the circle on the right side, Table 2). The linear dependence of such preincubation period on the temperature (Fig. 5) indicates that the reaction can start only when some initial critical number of vacancies (i.e. critical loss of mass) on the crystal surface is formed. This critical initial disorder is temperature independent and corresponds to the loss of 1.0 ± 0.5% of mass (see the value X / % in Table 2). This observation indicates that the damage of the surface caused by sublimation is required for the initiation of the reaction rather than for its progress.

Table 2. Mass reduction of *p*-bromonitrosobenzene after the incubation period at different temperatures (m_o is starting mass, m_{inc} is the mass increment within the Incubation period)

Temperature / K	Incubation period	m_o / mg	m_{inc} / mg	X / %

	/ min			
298	16	6.746	6.678	1.01
303	8	6.700	6.646	0.81
308	3	3.931	3.890	1.04
313	2	4.000	3.972	0.70
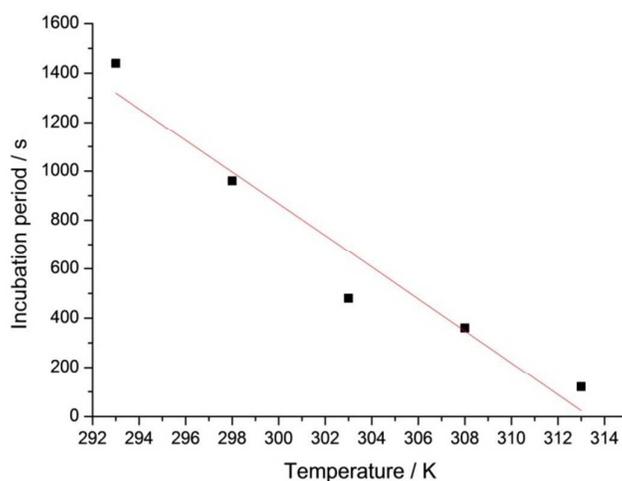
Fig. 5 Dependence of the incubation period for the solid-state dimerization on the temperature.

Conclusions

1. The solid-state dimerization of nitrosobenzene derivatives in crystals is triggered by formation of vacancies caused by off-sublimation of molecules from the crystal surface. Findings that the reaction starts only after the corresponding incubation period, and that the dimerization of the *p*-iodonitrosobenzene ends shortly after activation (with the bulk of the

crystal remaining unreacted) indicate that the damage of the surface caused by sublimation serves only for the activation of the chemical reaction rather than for its progressing.

2. Since the activation energy of this solid-state reaction is similar as in solution, it could be supposed that the movements of molecules exist also in the crystal (or on its surface). The only limitation is that in the crystal the molecules can move anisotropically, as it has been long time ago proposed by Paul and Curtin.[2] Anisotropy of translation is also demonstrated by observation of the low reactivity of *p*-iodinitrosobenzene. Regular molecular rearrangement without the orientational disorder in the crystal lattice of *p*-iodinitrosobenzene with nitroso groups distant from each other is conserved even after the formation of vacancies. From that we conclude that in spite to the relaxation of the crystal lattice, the molecules of *p*-iodinitrosobenzene cannot be reoriented in the proper position for the chemical reaction. Although its sublimation continues, the dimerization ends in the early phase of the process.

3. Our experiments in principle represent different topochemical conditions. a) Under the cryogenic conditions the reactants are in perfect topochemical configuration where the reaction is very fast and does not require any additional molecular relaxation. b) In the sublimed crystals of *p*-bromonitrosobenzene the topochemical effect is only partially fulfilled as a consequence of the orientational disorder, and the reaction is drastically slower (predicted for 8 orders of magnitude) than in the previous case. c) After the low-temperature cryogenic deposition the topochemical condition does not exist, and under these conditions, which are inconvenient for the reaction, the reaction has not been registered. Only the sublimation of monomer molecules in the surrounding vacuum chamber occurred. d) The example of the dimerization of *p*-iodinitrosobenzene represents the case of the "anti-

topochemical effect" where the molecular orientations are improper for the chemical reaction.

Acknowledgements

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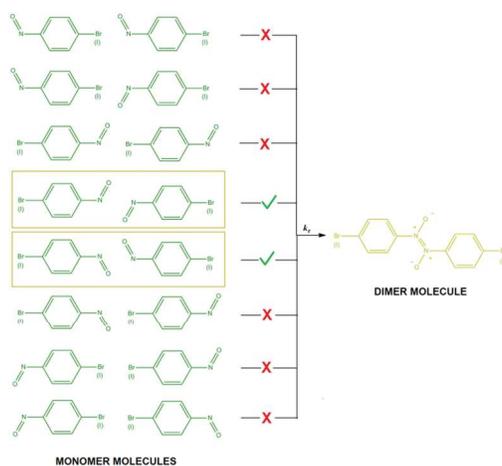
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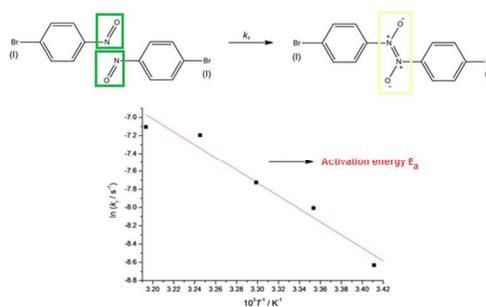
The investigation is a case study about the nature of the adiabatic organic solid-state reactions by **kinetic measurements** of the processes that occur during the **dimerization of aromatic nitroso compounds under three different topochemical environments in crystals.**