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Nitrosobenzene Dimerizations as a Model System for Studying Solid-State Reaction Mechanisms

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Thermal dimerization of nitroso compounds in the solid state was investigated by using para-substituted nitrosobenzenes as model compounds. A mechanism that includes the interplay of topochemical reaction trajectories and phase transfer was proposed on the basis of FT-IR spectroscopic kinetics, time-resolved powder diffraction, and low-temperature X-ray structure determination. From shapes of the kinetic curves analyzed on the basis of the Avrami model, it was found that phase transfer could be triggered by a dimerization reaction of para-substituted nitrosobenzene to azodioxide, which, in turn, can be caused by different packing factors such as disorder in the starting nitroso monomer crystals. Since the represented model can be extended to a broad series of compounds, we propose it as a general method for investigations of solid-state reaction mechanisms.

Introduction

A search for new thermochromic and/or photochromic systems is of great importance in the design of intelligent materials and molecular electronic devices.[1] However, only a limited number of *reaction types* are known to afford efficient photochromism[2] or thermochromism in the solid state.

In our recent paper, we reported a new, very simple chemical system, the solid-state nitroso dimer–monomer interconversion, which is based on low-temperature photodissociation of azodioxides to nitroso compounds and their thermal dimerization above 170 K.[3] The advantage of this novel photochromic system is the formation and/or breaking of the one-atom-to-one-atom chemical bond, i.e., the chemical “off–on switch”, because most of the previously described photochromic reactions included formation or breaking of more than two bonds between reactive atoms (for instance, cycloadditions or cyclizations, etc.).

The large difference in color between the monomer (blue, absorbs near 660 nm) and the dimer (colorless, absorbs in 290 nm region) satisfies the main condition required for photochromism by which the reactant and product should absorb at as different as possible wavelengths.[2] Because coloration of the dissolved nitroso compounds has been routinely used even as a visual indication of the equilibrium, the photodissociation can be easily followed.[4] However, thermal dimerization that starts after photolysis by warming the sample above 170 K proceeds too fast to be measured accurately, perhaps because monomers obtained by photolysis remain the mode of packing of dimeric precursors. For that reason it was necessary to find another way to measure dimerization reaction rates. The best approach must be based on finding such a crystal phase in which monomers survive long enough that reaction rates could be measured. As can be seen later in this paper, such phases can be obtained simply by sublimation.

Although most of the nitroso compounds appear as dimers in the solid state, compounds such as 4-iodonitrosobenzene (**1**), 4-bromonitrosobenzene (**2**), and 4-methylniytrosobenzene (**3**) are also known as more or less stable crystalline monomers.[5] However, while 4-iodonitrosobenzene immediately after its sublimation exists as a long-living monomer crystalline species,[5e] solid 4-bromonitrosobenzene and 4-methylnitrosobenzene monomers are unstable under the similar conditions. After sublimation, **2** and **3** form crystals of nitroso *monomers*,

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[1] Irie, M., Ed. Photochromism. Memories and Switches. *Chem. Rev.* **2000**, *100* (No. 5).

[2] (a) Dürr, H. A*ngew. Chem., Int. Ed. Engl.* **1989**, *28*, 413. (b) Dürr, H. *Pure Appl. Chem.* **1990**, *62*, 1477. (c) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871. (d) Becker, H. G. O.; Böttcher, H.; Dietz, F.; Rehorek, D.; Roewer, G.; Schiller, K.; Timpe, H.-J. *Einführung in die Photochemie*; Deutscher Verlag der Wissenschaft: Berlin, 1991; p 419. (e) Keating, A. E.; Garcia-Garibay, M. A. In *Photochemical Solid-to-Solid Reactions. Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1998; Vol. 2, pp 195–248.

[3] (a) Vancik, H.; Simunic-Meznaric, V.; Caleta, I.; Mestrovic, E.; Milovac, S.; Mlinaric Majerski, K.; Veljkovic, J. *J. Phys. Chem. B* **2002**, *106*, 1576–1580. (b) Orrell, G.; Stephenson, D.; Velarque, J. H. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1297.

[4] (a) Wajer, Th. A. J.; De Boer, Th. J. *Recueil* **1972**, *91*, 565. (b) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409. (c) Greer, M. L.; Sarker, H.; Medicino, M. E.; Blackstock, S. C. *J. Am. Chem. Soc.* **1995**, *117*, 10460.

[5] (a) Gowenlock, B. G.; Lütke, W.; *Quart. Rev.* **1958**, *12*, 321. (b) Snyder, J. P.; Heyman, M. H.; Suciu, E. *J. Org. Chem.* **1975**, *40*, 1395. (c) Singh, P. *J. Org. Chem.* **1975**, *40*, 1405. (d) Fletcher, D. A.; Gowenlock, B. G.; Orrell, K. G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 797. (e) Fletscher, D. A.; Gowenlock, B. G.; Orrell, K. G.; Sik, V.; Hibbs, D. E.; Hursthouse, M. B.; Malik, A. K. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 191.

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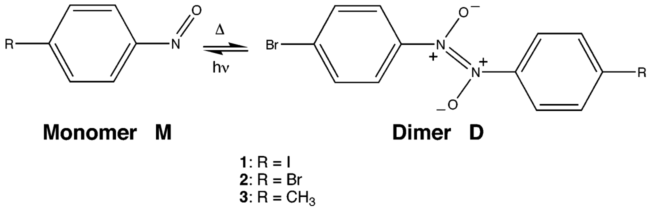
SCHEME 1



which survive at room temperature for a couple of minutes before their dimerization to azodioxides. This rate of transformation (Scheme 1) is experimentally convenient for measurements and affords good opportunity for the study of kinetics of dimerization in the solid state as well as the study some of general principles of solid-state reaction mechanisms.

Chemical reactions in the solid state are in different ways more or less accompanied and coupled with phase changes in the crystal lattice.[6] Since both processes, i.e., the change in covalent topology (chemical reaction) and conversion of supramolecular self-organization (e.g., phase transfer) occur in the more or less rigid condensed systems, our concept of the reaction mechanism could be extended in such a way that it includes both processes.

To find out how these two processes (chemical reaction and phase conversion) are coupled, it is appropriate to measure the chemical process and the corresponding phase changes by different and independent experimental methods. While the rate of chemical reaction can be best determined by spectroscopy, the solid-state phase transition kinetics can well be studied by time-resolved X-ray powder diffraction methods.[7]

Results and Discussion

Our experimental method is based on findings that freshly sublimed nitroso compounds appear in monomer forms. The process of thermally induced dimerization that affords a new phase was followed by time-resolved powder X-ray diffraction and by FT-IR spectroscopy. Typical ON=NO stretching signals appear in the 1250 cm^{-1} spectral region[5,8] as very intensive absorbance, and the change in its intensity can serve as accurate method for reaction rate measuring.

4-Bromonitrosobenzene. Dimerization kinetics of the chemical reaction $\mathbf{M} \rightarrow \mathbf{D}$ (Scheme 1) was measured for the freshly sublimed **2** by following the change in intensity of the IR absorption assigned to azodioxide ONNO asymmetric stretching at 1260 cm^{-1}. The reaction can be visually observed as a disappearance of the blue color of the starting monomer. The reaction affords first-order kinetics with the rate constant $k_1 = 3.48 \times 10^{-3}$ s^{-1} (25 °C), which corresponds to $t_{1/2} = 3.32$ min (Figure 1). By application of the Arrhenius plot based on measurements at three different temperatures, we have estimated the activation energy 35 kcal mol^{-1} (145 kJ mol^{-1}), which is higher than for similar reactions in solution.[4a] This reaction is relatively slow in comparison with the same reaction observed earlier with monomers obtained after the photolysis of the dimer at cryogenic temperatures. At 180 K, this reaction was so fast that under these experimental conditions we were unable to measure the reaction rate accurately. This difference in the dimerization rates is evidently topochemically controlled because the dimers in two experiments (produced by sublimation and cryogenic photolysis, respectively) were self-organized in different phases.

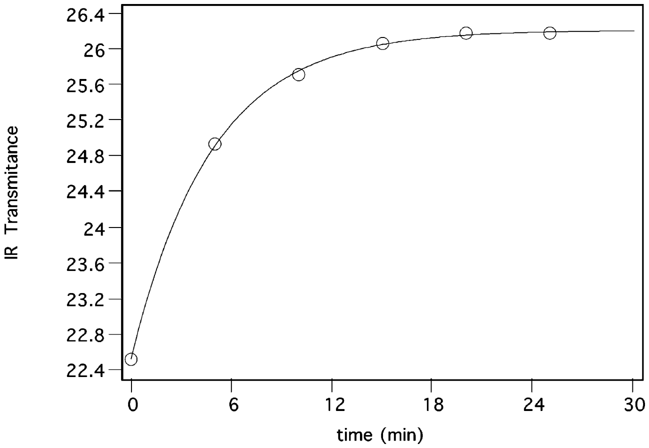


FIGURE 1. Kinetics of the solid-state dimerization if **2** measured in IR at 25 °C.

To follow crystal packing reorganization triggered by dimerization, we have measured the kinetics of the phase transfer of sublimed **2** by time-resolved X-ray powder diffraction at 15 °C (Figure 2). Another advantage of this experiment is that the sublimed sample of monomer was not exposed to high pressure, as has been the case for preparation of a KBr pellet for IR spectroscopy. Consequently, the possible pressure- induced reaction (and/or phase transformation) is excluded in this experiment. On the suggestion of a reviewer, we made kinetic measurements by using reflectance IR spectroscopy (see the Supporting Information). The rate constant that was obtained ($k = 3.17 \times 10^{-3}$ s^{-1}) is in principle the same as in the measurements on the basis transmittance spectra. In time resolved X-ray diffraction kinetics we found that different reflections change their intensity following different kinetic laws. However, satisfactory accuracy of measurement was obtained only for two most intensive peaks. The signal at $\Theta = 27.5°$ that belong to the reactant monomer phase disappears during the reaction and follows the first-order kinetics (Figure 3) with the "*phase change rate constant*" $k_2 = 1.31 \times 10^{-3}$ (15 °C). Because k_2 is very similar to the spectroscopically measured *chemical reaction rate constant* k_1, the disappearing crystal plane at $\Theta = 27.5°$ can tentatively be identified as the *critical crystal plane* for the dimerization reaction trajectory, i.e., the plane that intersects the reactive nitroso groups! If these nitroso groups dimerize to azodioxides, positions of N and O atoms are changed, and the crystal plane in which these atoms were positioned must disappear.

To confirm this assertion, we have determined the crystal structure of the sublimed monomer **2**. The obtained monomer crystals are blue and must be selected very quickly by catching them directly from the sublimator coldfinger. By standing at room temperature, crystals change their color and shape. After nearly 1 h, only white polycrystalline powder of nitroso dimers

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[6] Schmidt, G. M. J., et al. *Solid State Photochemistry*; Ginsburg, D., Ed.; Verlag Chemie, Weinheim, New York, 1976; p 80.

[7] Kim, J. H.; Hubig, S. M.; Lindeman, S. U.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 87–95.

[8] Fletscher, D. A.; Gowenlock, B. G.; Orrell, K. G. *Ibid.* **1997**, 2201.

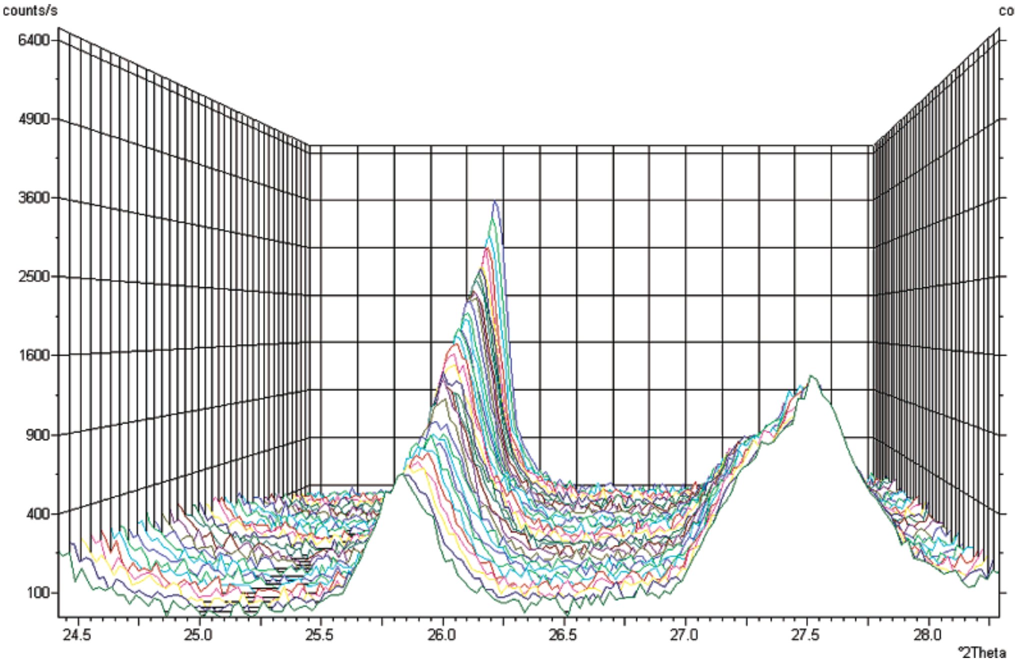

FIGURE 2. Time-resolved X-ray diffractogram for the A → B phase transfer of the nitroso dimer of **2**. Characteristic signals for the first-order kinetics at $\Theta = 27.5°$ and for the sigmoid phase transition kinetics at $\Theta = 25.8°$.

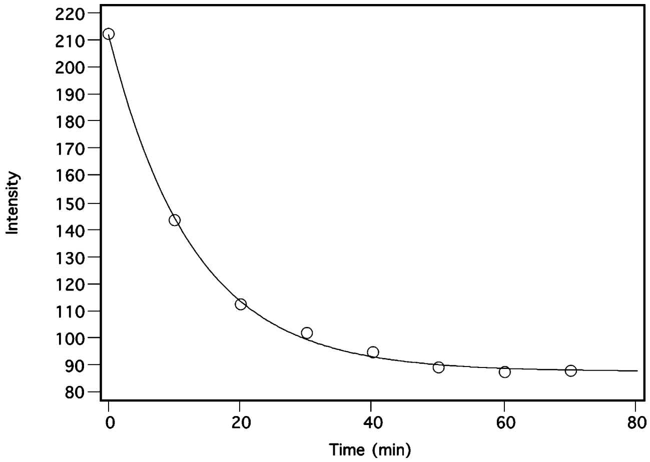

FIGURE 3. Disappearance of the reflection at $\Theta = 27.5°$ that affords the first-order kinetics.

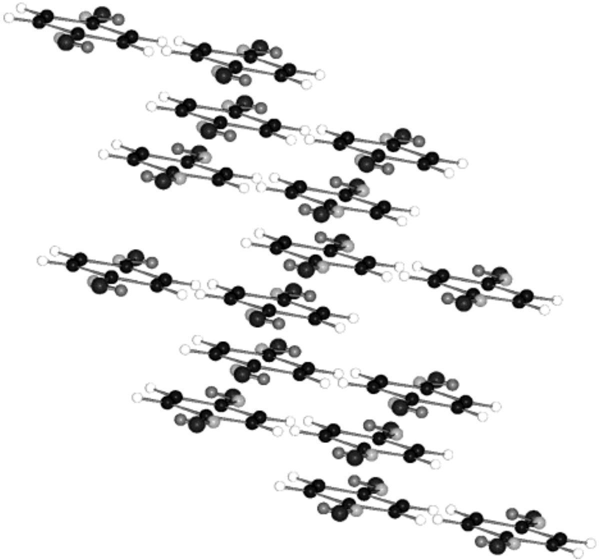

FIGURE 4. Crystal packing of **2**. 50% of nitroso groups are reactive for dimerization; i.e., they are close to each other.

remained. Consequently, this reaction is unfortunately not a *single-crystal-to-single-crystal* transformation. The compound crystallizes in space group *P*-1 as monomer with one molecule in an asymmetric cell. Molecules are packed within normal van der Waals distances but with 50% disorder in respect to in-plane orientation of Br and NO groups (Figure 4). The observed N═O distance [N═O 1.124(3)Å and N*═O* 1.124(3) Å] is slightly shorter than in other reported structures of nitroso compounds (1.22 Å).[9] The geometry of benzene ring is in the expected frame for this class of structures (Figure 5).

Two structural features are important for considering the mechanism of dimerization. First, as can be seen from Figure 4, since the monomer molecules are statistically 50% disordered, maximally half of monomer pairs are oriented so that nitroso groups are close enough to enable dimerization. Second, as we have predicted, the *critical crystal plane*, which is from the single-crystal diffraction identified as 2.0.0. plane (with powder X-ray reflection at 27.5°) really intersects reactive nitroso groups (Figure 6). Since these topochemically well-oriented pairs of nitroso groups that are candidates for dimerization are distributed randomly, the phase *transfer* (measured as disappearance of this critical 2.0.0. X-ray reflection) must follow the same first-order kinetics as the chemical reaction (measured by IR spectroscopy). In other words, first-order kinetics of both, chemical reaction (k_1) and the loss of the [200] diffraction signal (k_2) indicates that the dimerization within the crystal lattice proceeds in a statistical fashion and forms a metastable phase.

On the other hand, the reflection at $\Theta = 25.8°$ follows quite a different kinetic law (Figure 7) and starts to change its intensity only when the chemical reaction is

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[9] (a) Webster, M. S. *J. Chem. Soc.* **1956**, 2841. (b) Talberg, H. J. *Acta Chem. Scand. A* **1979**, *33*, 289.

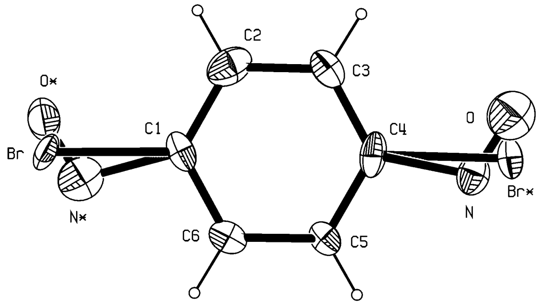

FIGURE 5. Molecular structure of *p*-bromnitrosobenzene **2** showing 50% probability displacement ellipsoids and the disorder of atoms O, N, and Br.

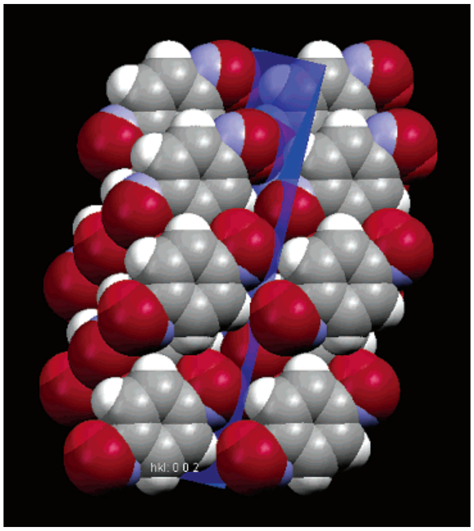

FIGURE 6. Crystal packing of **2**. The extra labeled *critical plane* 2.2.0 at Θ = 27.5° (blue), which disappears during the dimerization following the first-order kinetics. The plane intersects reactive nitroso groups (red) of monomers.

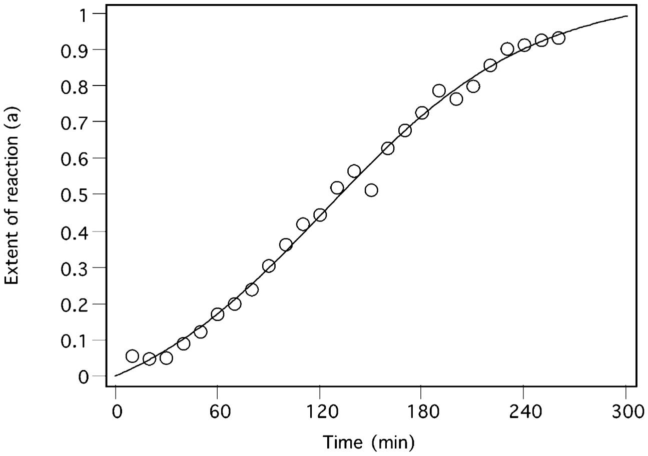

FIGURE 7. Sigmoid kinetics of the phase transition in **2** observed for the reflection at Θ = 25.8°.

almost complete. Its sigmoid shape is typical for an autocatalytic type phase transition. In the diagram in Figure 7 the degree of the transformation (*a*) is shown as function of time. The value *a* is defined[10] as intensity normalized relative to the maximal intensity obtained when the overall process is complete.

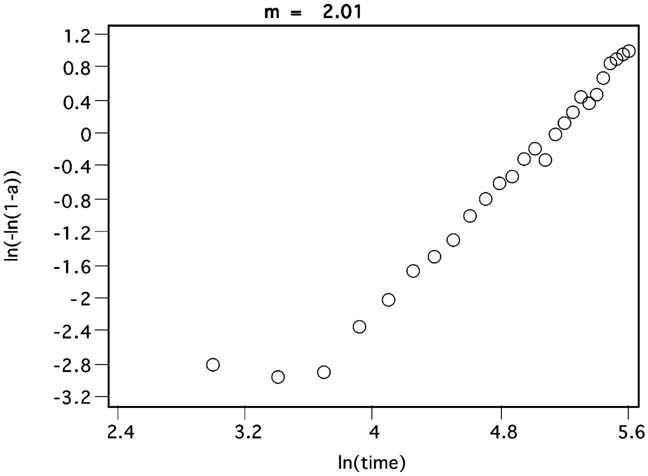

FIGURE 8. Logarithmic "Sharp−Hanock plot" for the sigmoid-type kinetics obtained for the crystal plane at Θ = 25.8°.

$$a(t) = I_{\Theta}(t)/I_{\Theta}\ (t = \infty)$$

In solid-state kinetics based on the Avrami−Erofeyev[11] equations it is also convenient to convert the sigmoid curve to the logarithmic function (Figure 8) to obtain the so-called "Sharp−Hancock plot".[12] The slope of the line, the gradient *m*, can be used as an indication for the mechanism of the phase transfer. A series of *m* values associated to corresponding mechanism of phase transformations were tabulated systematically on the basis of their solid-state kinetics models.[13] In our case, the best line fitting was obtained for *m* = 2.01, the value that is proposed to be the characteristics of the one-dimensional phase transfer (lineal growth). Avrami also proposed an another convenient representative index for estimating the type of phase growth. It is the ratio of times for 75% and 25% of extent of transformation.[11] In our case this ratio is 2.25, and it represents the limiting value between platelike growth and lineal growth.

Comparing the kinetics in Figures 3 and 7, it could be concluded that changes of different crystal planes during and after chemical reaction belong to different phase transformations. There is one crystal plane, which follows the chemical reaction by its first order kinetics, but there is also another crystal plane that develops quite independently and affords the slow "autocatalytic" sigmoid phase transfer. The most important observation is that this second transition does not begin before the chemical reaction is almost complete (after 40 min). Consequently, dimerization of the sublimed **2** proceeds by forming the metastable phase within the starting monomer crystal lattice. After all, it seems to be very difficult to answer the "chicken or egg problem" question, i.e., what is first event, chemical reaction that triggers observed phase transition, or packing arrangements such as disorder of

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[10] Evans, J. S. O.; Price, S. J.; Wong, H.-W.; O'Hare, D. *J. Am. Chem. Soc.* **1998**, *120*, 10837−10846.

[11] (a) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103−1112. (b) Avrami, M. *J. Chem. Phys.* **1940**, *8*, 212−224. (c) Avrami, M. *J. Chem. Phys.* **1941**, *9*, 177−184. (d) Erofeev, B. V. *Compt. Rend. Acad. Sci. U.S.S.R.* **1946**, *52*, 511−514.

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[13] Hulbert, S. F. *J. Brit. Ceram. Soc.* **1969**, *6*, 11−20.

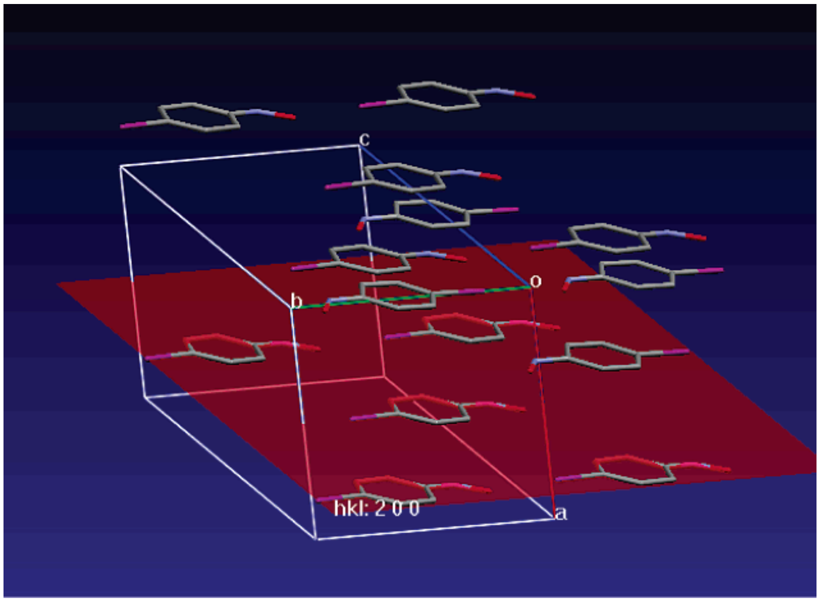

FIGURE 9. Crystal packing of **1**.[9] Nitroso groups are close to the iodine atom and not to each other, and their dimerization is impossible.

monomer, which is responsible for instability that leads to dimerization. This system is much more complex than for example the previously observed mechanism of solid-state Diels–Alder reaction where chemical reaction and phase transition occur simultaneously.[7]

The Case of 4-Iodo- and 4-Methylnitrosobenzene (1 and 3). As can be seen from the structure and packing of 4-iodonitrosobenzene monomer **1** (Figure 9, based on literature diffraction data[9]), the in-plane molecules are arranged without any disorder, and they are oriented so that the nitroso group lies always close to the iodine atom, and there are no neighboring pairs of nitroso groups, which could react with each other. Consequently, in such regular packing, dimerization is topochemically impossible, and the compound remains in form of stable monomers in the crystal. From exactly the same reason, *p*-methoxynitrosobenzene survives as stable monomer in the crystal because its nitroso groups are far from each other and close to the methoxy groups.[9b]

It could be speculated that halogen–nitrogen nonbonding interactions[14b] play more important role in stabilization of crystals of **1** than in stabilization of crystals of **2**, where disorder has been observed.

We were also able to measure solid-state dimerization kinetics of 4-methylnitrosobenzene **3** starting with the freshly sublimed monomer. The best kinetics we found for the signal at $\Theta = 11.4°$ (Figure 10). From its typical sigmoid shape we estimated the time for the complete transformation 13 min, i.e., faster than in the case of 4-bromonitrosobenzene (nearly 40 min). A logarithmic “Sharp–Hanock plot” for this sigmoid (Figure 11) provides much higher slope $m = 3.04$, the value that can be characterized for the three-dimensional growth. Therefore, such phase transfer is different than in 4-bromonitrosobenzerne ($m = 2.01$) because of different topochemical conditions. While molecules of **1** and **2** are packed with stack structure, for the unit cell of **3** we have preliminary indications that it has different structure.[14] Unfortunately, we were not able to solve the structure of monomer **3** completely, mainly because of thermal instability of its single crystal, but work on this is in progress.

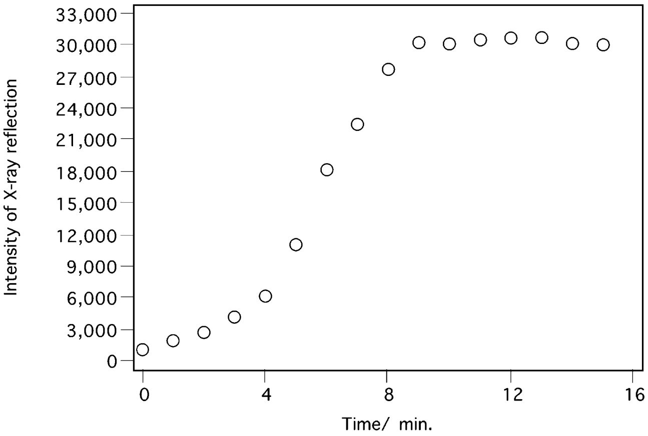

FIGURE 10. Sigmoid kinetics of the phase transition in **3** observed for the reflection at $\Theta = 11.4°$.

Conclusion

We have demonstrated that 4-substituted nitrosobenzenes form crystalline monomers after their sublimation. Stability of obtained monomer in the solid state is such that it spontaneously dimerizes at room temperature with the reaction rate that can be accurately measured either by spectroscopy or by time resolved powder X-ray diffraction. This property of nitrosobenzenes gives opportunity for using the described procedure as a more general method for detailed experimental study of solid-state reaction mechanisms, simply by variation of the group R in *para* or *meta* position (Scheme 1). In such a way, correlation between molecular structure, packing, and reactivity can be established.

From the comparison of the dimerization rate and corresponding phase transition rate with the way on

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[14] (a) Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids;* Elsevier: Amsterdam, 1989; pp 92. (b) Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids;* Elsevier: Amsterdam, 1989; p 197.

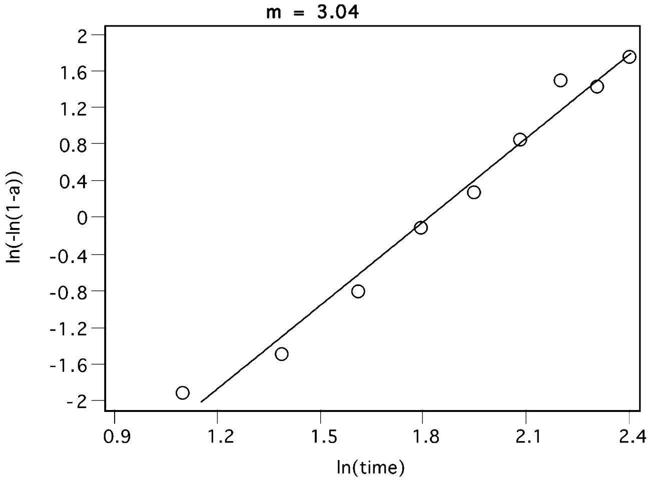

FIGURE 11. Logarithmic "Sharp−Hanock plot" for the sigmoid type kinetics for dimerization of **3**, measured as decrease in the intensity of the reflection assigned to the crystal plane at $\Theta = 11.4°$.

which monomer molecules were packed in crystal lattice, it becomes evident that topochemical environment is an important factor, which can trigger the dimerization reaction. Moreover, in the case of 4-bromonitrosobenzene (**2**), the *critical* crystal plane, which intersects the reactive center (nitroso groups) responsible for dimerization was located on the basis of powder diffraction kinetics combined with the single-crystal structure analysis.

Experimental Section

Nitrosobenzenes were prepared by standard methods.[3a,b]

FT-IR Kinetics. The solid-state dimerization rate was measured by following the temporal change in transmittance of the ONNO asymmetric stretching signal at 1260 cm^{-1}. This signal obeys Lambert−Beer's law. Bruker FT-IR spectrometer was used for this measurement. The freshly sublimed sample was prepared as standard KBr pellet.

Single-Crystal X-ray Diffraction. A single crystal of monomer for diffraction experiment was prepared by sublimation of dimers precursor under 10^{-2} Torr pressure at 60 °C. The sublimed monomer is unstable at room temperature because it dimerizes within few minutes, and this transformation destroys the single crystal. Consequently, the crystal must be mounted in diffractometer very quickly, and the measurement must be performed at 100 K. For better handling with so unstable sample, the temperature of cooling water for sublimator was never above 10 °C. The crystal of satisfactory quality has been selected directly from the coldfinger, but after many repetitions of the experiment. An Oxford Diffraction Xcaliburg Kappa CCD X-ray diffractometer with graphite-monochromated Mo K_{α} radiation was used to collect diffraction data.[15] The data sets were collected using the ω scan mode over the 2θ range of 4−60°.

The structures were solved (direct methods) and refined (difference Fourier synthesis) using the SHELXS[16] and SHELXTL[17] packages. The structural refinement was performed on F^2 using all data. The carbons of the benzene rings were refined anisotropically without any restriction. Br, N, and O atoms were refined anisotropically with some restrictions on thermal and geometrical parameters. After determination of all position of non-hydrogen atoms the hydrogen atoms were placed geometrically, with C−H distance in the range 0.98−0.99 Å and allowed to refine using $U_{\text{iso}}\text{H} = 1.2U_{\text{eq}}(\text{C})$. All calculations were performed using WINGX[18] crystallographic software package. Crystal data and details of data collection and structure analysis are summarized in Table 1 (Supporting Information). The ORTEP[19] diagram of the molecular structure are present in Figure 5, and the unit cell packing diagrams prepared by SHACAL[20] are present in Figures 4 and 6.

Powder X-ray Diffraction. Data were collected on Philips PW 1700 automated diffractometer with control unit PW3710 using the scanning method with the following parameters: monochromatic Cu $K\alpha 1$ radiation ($\lambda = 1.5406$ Å), observation range 5°−2θ−35°, continuous scan mode, step scan with 0.025°, counting time per step 0.5 s. With this choice of parameters one circle lasts 10 min. We collect data in period of 4 h. The data collection was performed by Expert Software suite 1.2 (*Program package for measuring and analysis diffraction data on Philips X-ray diffraction equipment*; Analytical, Lamely: The Netherlands, 1999). For background correcting, $K\alpha 2$ striping and integration of intensity were performed using X'Pert Plus 1.0 (*Program for Crystallography and Rietveld Analysis*; Panalytical, Almelo: The Netherlands 1999).

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Supporting Information Available: Change in reflectance IR spectra of **2** with time and details of low-temperature single-crystal experiments and summary of crystallographic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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