Photochemical transformations of dinitrogen tetraoxide in a frozen glassy matrix

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The presence of minima on the potential energy surface was shown by semiempirical calculations. These minima correspond to five isomers of dinitrogen tetraoxide: two symmetrical structures of the $O_2N—NO_2$ type, two nonsymmetrical structures of the $O_2N—ONO$ type, and nitrosonium nitrate $NO^+NO_3^-$. Quantum yields of photochemical reactions of dinitrogen tetraoxide in a matrix of glassy methylcyclohexane (at 77 K) were determined experimentally to be equal to ~1, ~0.15, and $\sim 10^{-5}$ for photoisomerization of symmetrical N_2O_4 into the nonsymmetrical isomer, reverse photoisomerization, and photodissociation to form the stabilized pair of NO_2 fragments, respectively. Measurements of the degree of orientation of the products of photochemical transformations performed by photolysis with polarized light show that the photoisomerization occurs *via* the intramolecular mechanism in a matrix cage, and the photodissociation is associated with considerable migration of the molecular fragments formed.

Key words: dinitrogen tetraoxide, isomers, photoisomerization, photodissociation, quantum yield, photoselection.

The reactivity of nitrogen oxides and, in particular, their photochemical behavior, are presently intensely studied in connection with the problems of the chemistry of atmosphere. These studies are also of interest from the viewpoint of the theory of reactivity, because nitrogen oxides, on the one hand, are rather simple model objects and, on the other hand, demonstrate a rich and diverse set of chemical transformations. It is known[1] that the planar symmetrical structure is the most stable form of dinitrogen tetraoxide. Deposition of gaseous NO_2 on a cooled (4—77 K) surface results in the formation of the dinitrogen tetraoxide molecules with another, less stable structure: nonsymmetrical isomer O_2NONO and nitrosonium nitrate $NO^+NO_3^-$ (see Refs. 2 and 3).

It was assumed that heating of N_2O_4 deposited onto the cooled surface results in the spontaneous autoionization of the N_2O_4 molecules to form nitrosonium nitrate, which is stable below 180 K.[3] However, detailed studies showed[4,5] that planar N_2O_4 is stable in the crystalline phase obtained by slow depositing. Nitrosonium nitrate is formed upon heating of the unstable nonsymmetric isomer O_2NONO, which is contained in multicomponent films including several crystalline and one amorphous phases. These films are obtained upon fast deposition. Thus, it is shown that the following order of stability of isomers is valid for the low-temperature solid phases of dinitrogen tetraoxide:

$$N_2O_4 > NO^+NO_3^- > O_2NONO.$$

It is known that the isomerization of N_2O_4 in the deposited solid films is stimulated by UV irradiation.[5—8] However, no systematic study of the photochemical activity of dinitrogen tetraoxide was performed.

In the present work, photochemical reactions of N_2O_4 in methylcyclohexane (MCH) solutions frozen at 77 K were studied. Concentrations of N_2O_4 that are sufficiently low to isolate the molecules in a matrix cage can be created in such solutions. Since MCH forms transparent glasses upon freezing, optical absorption spectra of the system studied can be recorded. Photodissociation of N_2O_4 was recorded by ESR from accumulation of stabilized fragments of the molecule, NO_2 radicals.

Experimental

Semiempirical calculations of the geometry of N_2O_4 isomers were performed by the PM3 method, using the MOPAC 6.1 program package on an IBM PC 486 DX2.

Gaseous NO_2 was obtained by thermal decomposition of lead nitrate and dried by passing over P_2O_5. Glassy samples were prepared by dissolution of gaseous NO_2 in liquid MCH directly in 3-mm quartz tubes followed by freezing in liquid nitrogen. ESR spectra were recorded on a Varian E-3 spectrometer. Optical absorption spectra at 77 K were recorded on a Specord M-40 spectrophotometer at liquid-nitrogen temperature. Since spectra of different isomers overlap, the optical density at the maximum of the absorption band of the initial N_2O_4 was determined by the basic line method. Photolysis was

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carried out by light from a high-pressure mercury lamp (500 W) attached to a quartz optical system for obtaining a parallel beam and standard glass filters to isolate lines of the mercury lamp. Glan prisms were used for photolysis and recording of spectra in polarized light.

The intensity of incident light was determined by ferrioxalate actinometry.[9] The measurements were carried out in a working tube at room temperature under the same conditions as the photolysis of samples.

The number of paramagnetic centers was determined by comparison of the areas under the absorption curves of the sample and the standard (weighted single crystal of $CuCl_2 \cdot 2H_2O$). Surface areas were calculated by numerical double integration of the ESR spectra.

Results and Discussion

Structure of isomers. Semiempirical calculations with optimization of the molecular geometry were performed to establish whether the existence of isomers of dinitrogen tetraoxide is possible. Several minima were observed on the potential energy surface. These minima can be assigned to the isomers and rotamers of the N_2O_4 molecule (Fig. 1). The results obtained for the planar symmetrical structure of N_2O_4 (structure **1** in Fig. 1) agree well with the bond lengths and angles in the molecule determined experimentally and with the results of nonempirical calculations.[1,10] Another minimum on the potential energy surface corresponds to a structure with perpendicular arrangement of the planes of two NO_2 fragments (**2**, see Fig. 1). Previously, in the analysis of IR spectra of solid deposited films the existence of two isomers of nonsymmetrical N_2O_4, designated as *D*- and *D'*-isomers, was assumed.[11,12] These isomers were considered to be planar. The results of our calculations show that in isomer *D'* (structure **3**, see Fig. 1) the NO_2 and ONO fragments are perpendicular. The energy of the *D*-isomer (**4**, see Fig. 1) depends very little on the angle between the planes in which two fragments of the molecule are arranged, *i.e.*, the calculation predicts free rotation around the bond connecting the NO_2 and ONO fragments. However, it should be mentioned that the reliability of semiempirical methods of calculation of molecules is low. Therefore, the question about the geometry of nonsymmetrical isomers of N_2O_4 requires more detailed consideration.

In structures **1**—**4** presented in Fig. 1, the bond connecting two NO_2 fragments is the longest. The dipole moment of symmetrical N_2O_4 is equal to zero and those of the O_2NONO isomers range from 1.0 to 1.3 D. In the planar molecule of compound **5** (Fig. 1), the NO_3 and NO fragments are linked by a long chemical bond. The calculation shows that this structure is characterized by a significant negative charge on the NO_3 fragment and positive charge on the NO fragment. The dipole moment of nitrosonium nitrate is equal to 4.8 D.

Thus, the calculations show the possibility of existence of isomeric forms of dinitrogen tetraoxide, whose energies of formation differ from one another by not more than 5 kcal mol^{-1}.

Photochemical reactions of N_2O_4. The absorption spectra of frozen glassy solutions of N_2O_4 in MCH exhibit an absorption band at λ_{max} = 339 nm (in liquid solutions λ_{max} = 442 nm). The extinction coefficient at the maximum of the absorption band remains almost unchanged upon freezing of the sample (ε = 233 L mol^{-1} cm^{-1}). Frozen samples do not contain monomeric NO_2 molecules.

Absorption spectra obtained upon photolysis of solutions of N_2O_4 in MCH by light with λ 365 and 313 nm differ significantly and contain no isobestic points (Fig. 2, *a*,*b*). This allows one to suppose that several subsequent photochemical transformations occur rather

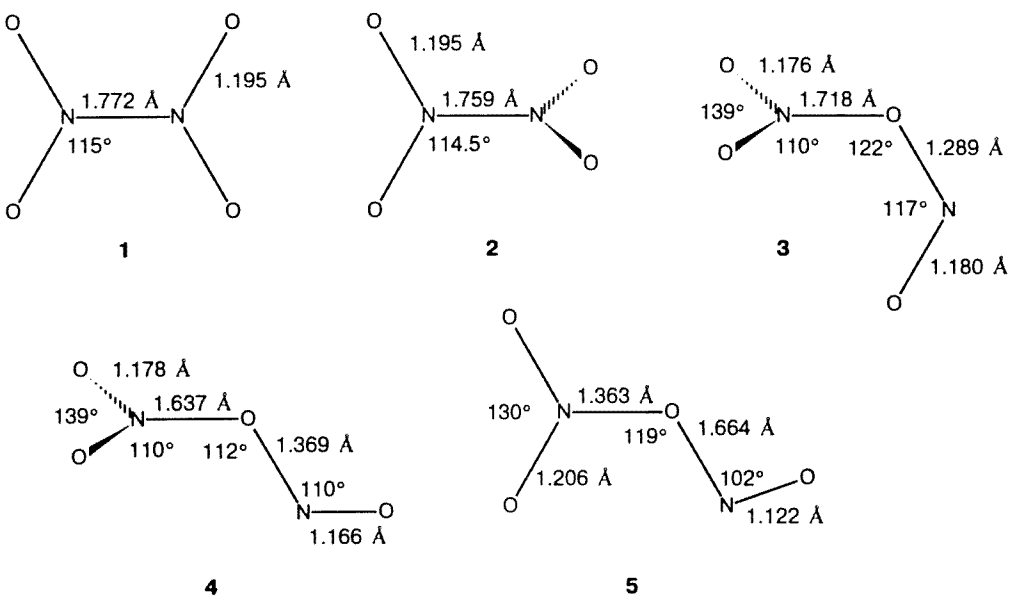


Fig. 1. Structures of isomers of dinitrogen tetraoxide calculated by the PM3 method.

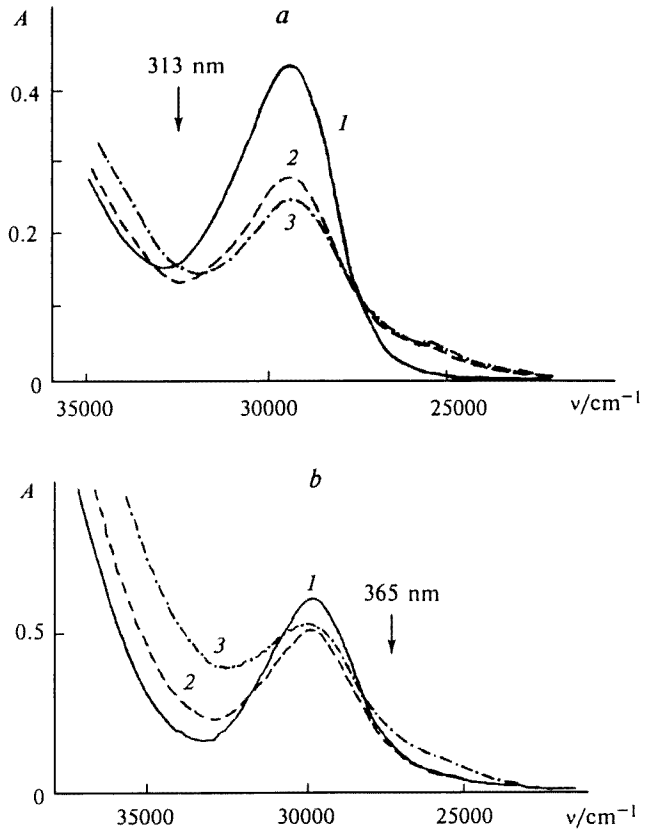


Fig. 2. Changes in absorption spectra upon photolysis of glassy solutions of dinitrogen tetraoxide in methylcyclohexane (77 K) at λ 313 (*a*) and 365 nm (*b*) at various times of photolysis: *a*. 0 (*1*), 30 (*2*), and 60 min (*3*); *b*. 0 (*1*), 15 (*2*), and 52 min (*3*).

than only one. Reverse photochemical reaction resulting in the formation of the initial isomer of N_2O_4 occurs when the sample is subjected to photolysis at λ 405 nm following irradiation at λ 365 nm. Prolonged photolysis at λ 365 and 313 nm can result in the stationary state, when the rates of direct and reverse reactions are equal. When the sample is heated to room temperature after irradiation and again frozen in liquid nitrogen, the absorption spectrum completely returns to the initial form observed before photolysis.

The formation of NO_2 radicals upon photodissociation of N_2O_4 was established by the ESR method. Double integration of the ESR spectra shows that the total amount of these radicals during the whole process is not greater than 0.1 % of the initial content of N_2O_4. Thus, irradiation results in photoisomerization involving at least two photochemical stages. Photodissociation is a less probable side process.

Analysis of the initial regions of the kinetic curves of the photochemical transformation of N_2O_4 and the formation of NO_2 molecules made it possible to determine the quantum yields of the photoisomerization and photodissociation of dinitrogen tetraoxide. It turned out that the probability of photoisomerization is close to unity (Φ_{365} = 1.0±0.15, Φ_{313} = 0.9±0.15). Reverse photoisomerization occurs with quantum yield Φ = 0.15±0.05. The quantum yield of photodissociation is ~$4 \cdot 10^{-5}$ upon photolysis at λ 313 nm and is more than an order of magnitude lower upon photolysis at λ 365 nm. The significantly lower yield of the photodissociation is likely associated with the fact that this reaction, unlike isomerization, requires molecular fragments to escape from the matrix cage.

Stability of products of photochemical transformations of N_2O_4. The stability of products of photochemical transformations of dinitrogen tetraoxide was determined in the following experiments. The sample was irradiated at 77 K, then heated to the chosen temperature, and again cooled to 77 K. A considerable growth in the optical density (Fig. 3) was observed in the absorption spectra after annealing at 100 K (this temperature is close to the temperature of vitrification of the matrix). It can be assumed by analogy with the experiments in frozen films of dinitrogen tetraoxide that this growth is associated with the appearance of a broad charge-transfer band in the $NO^+NO_3^-$ isomer. Perhaps, this isomer is stabilized by the formation of ion associates or the microphase, because diffusional migrations of molecules are facilitated at the temperature of vitrification of the matrix. Comparison of the absorption spectra obtained during irradiation and after annealing (see Figs. 2 and 3) shows that the content of nitrosonium nitrate in the irradiated samples is low. Thus, nonsymmetrical isomers O_2NONO are the main reaction products of photoisomerization. It is likely that the appearance of an absorption band of low intensity with maximum at ~25000 cm^{-1} upon irradiation is associated with the formation of these molecules.

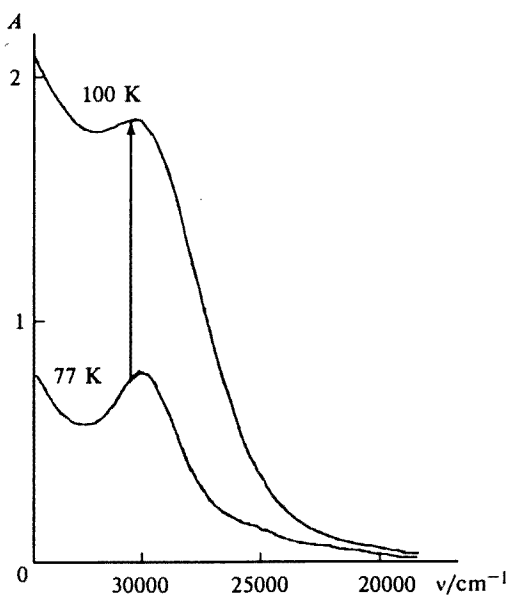
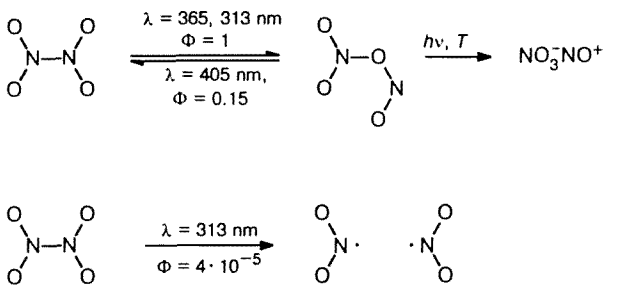


Fig. 3. Change in absorption spectrum of an irradiated glassy solution of dinitrogen tetraoxide in methylcyclohexane upon heating of the sample to 100 K.

The ESR spectra show a stepwise decay of NO_2 molecules (Fig. 4), which is typical of many solid systems containing radicals and radical pairs[13] and can be explained by the distribution of pairs according to the distance between the radicals in the pair. Pairs at a sufficiently short distance recombine at the specified temperature.

On the whole, the photochemical transformations of dinitrogen tetraoxide molecules in an inert matrix correspond to the Scheme 1.

Scheme 1



Rotational molecular mobility in the photoreaction of dinitrogen tetraoxide. Photochemical reaction using polarized irradiation makes it possible to involve only the molecules, whose dipole moments of transition are favorably oriented relative to the electric vector of the light wave. Therefore, the photoselection phenomenon appears in the course of the photochemical reaction in solids. Photoselection is the alignment of both the molecules of the initial compound and the molecules of the photochemical transformation product.[14,15] The photoselection phenomenon can be manifested experimentally as the photoinduced linear dichroism of the initially isotropic sample.

In the photochemical reaction with polarized irradiation, linear dichroism at the absorption band of the initial N_2O_4 molecules is observed. This attests to the absence of thermal rotational mobility of the molecules in the solid matrix. Linear dichroism of the opposite sign, whose value is close (in order of magnitude) to the theoretical value for the photochemical reaction product, is observed in the absorption band of the photoisomerization products.[15] Thus, the reacting molecules do not undergo substantial rotations in the photoisomerization reaction, because the rotational molecular mobility results in the relaxation of the orientational order and, hence, in the disappearance of linear dichroism.

The possible orientational order of the photodissociation product (NO_2 molecules) was analyzed by the ESR method. Since NO_2 molecules possess an anisotropic ESR signal, their alignment should be observed as the angular dependence of the ESR spectrum, *i.e.*, as the difference in amplitudes of the components of the spectrum at different angles between the direction of the magnetic field and electric vector of photolyzing light. However, it turned out in the experiment that the ESR spectrum of the NO_2 molecules obtained during photolysis of dinitrogen tetraoxide is almost independent of the orientation of the sample irradiated in the cavity of the spectrometer. This allows one to conclude that the spatial orientation of the reaction products is random.

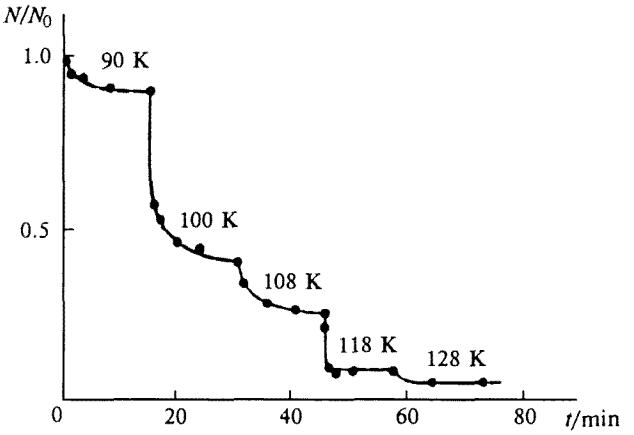


Fig. 4. Recombination curve of NO_2 pairs upon stepwise heating of the irradiated sample.

Thus, the experiments on photoselection confirm the intracage character of the photoisomerization of dinitrogen tetraoxide. It is likely that the photoisomerization occurs *via* the intramolecular mechanism without a considerable rearrangement of the matrix cage. Unlike the isomerization, the photodissociation requires significant migrations and escape of molecular fragments from the matrix cage.

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