

Molecular Structure of N₂O₅ in the Gas Phase. Large Amplitude Motion in a System of Coupled Rotors

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Abstract: The structure of dinitrogen pentoxide has been investigated in the gas phase at a temperature of -11 °C. The molecules consist of two -NO₂ groups joined to a fifth oxygen atom by non-colinear bonds. The -NO₂ groups are undergoing large amplitude torsional motion about a point of minimum energy corresponding to C₂ symmetry for the molecule with the dihedral angles τ_1 and τ_2 between these groups and the N-O-N plane each about 30°. The torsional motion was modeled by a potential representing a competition between bonding forces tending to stabilize the planar conformation and repulsive forces between oxygen atoms on different -NO₂ groups tending to destabilize it. The results suggest the motions of the -NO₂ groups are loosely coupled in a way such that one torsion angle tends to increase from the minimum energy point as the other decreases. Conversion of molecules between the equivalent conformations τ_1/τ_2 equal to 30°/30° and -30°/-30° occurs most easily by a path that includes a saddle point at 90°/0° (or 0°/90°). With the assumption that the -ONO₂ groups have local C_{2v} symmetry, some of the more important distances (r_g), angles (\angle_a), and root-mean-square amplitudes of vibration (l) with estimated 2 σ uncertainties are $r(\text{N}=\text{O}) = 1.188$ (2) Å, $r(\text{N}-\text{O}) = 1.498$ (4) Å, $\angle\text{O}=\text{N}=\text{O} = 133.2$ (6)°, $\angle\text{N}-\text{O}-\text{N} = 111.8$ (16)°, $\angle\tau_1 = \angle\tau_2 \approx 30^\circ$ at potential minimum, $l(\text{N}=\text{O}) = 0.037$ (2) Å, and $l(\text{N}-\text{O}) = 0.064$ (5) Å.

The gas-phase molecular structures of the several oxides of nitrogen—N₂O, NO, NO₂, N₂O₃, N₂O₄, and N₂O₅—have been extensively investigated by electron diffraction and by spectroscopic methods. Of these structures, only that of N₂O₅ has evaded complete solution. It is known from the diffraction data²⁻⁴ that the molecule consists of two -NO₂ groups joined to a fifth oxygen atom by non-colinear bonds (Figure 1), and the vibrational spectrum⁵ as well as the results of molecular orbital calculations⁶ are consistent with this atomic arrangement. The diffraction data have also provided accurate values for the dimensions of the -NO₂ groups, which are found to be very similar to those in N₂O₄,^{7,8} N₂O₃,⁹ and NO₂ itself.^{8,10,11} and for the length of the bonds between the nitrogen atoms and the apical oxygen. The remaining features of the structure are less clear. Akishin et al.,² whose work was based on visual data, have reported that the molecule has a non-planar C_{2v} conformation with a bond angle at the apical oxygen of 95 ± 3°. Our sector-microphotometer data,^{3,4} however, were found to be incompatible with these aspects of the model and could be interpreted only in terms of a structure with a larger apical angle (112-116°) and with the -NO₂ groups undergoing large amplitude motion. By assuming the -NO₂ groups to rotate independently, each governed by a cosine-type torsional potential, and by applying Boltzmann weighting to a large number of pseudoconformers defined by pairs of values for the two torsion angles, we were ultimately able to obtain excellent agreement between calculated and observed distance distributions.⁴ Despite this success, we were not entirely satisfied. One troublesome aspect of our model concerned the assumed torsional interdependency of the -NO₂ groups: it was clear that interference between oxygen atoms on different groups had to be very important as the mo-

lecular conformation approached planarity, but elimination of pseudoconformers representing near-planar structures actually worsened the agreement. A second troublesome aspect concerned the analytical method that was based on linear combinations of weighted radial distribution curves rather than on intensity distributions. This approach was necessary because of limitations in our computational programs; it required making assumptions about the torsion-insensitive aspects of the structure that are obviated by a least-squares procedure based on the fitting of calculated to observed intensity distributions.

Recently, it was decided to take up the N₂O₅ problem again. We were confident that the unsatisfactory features of the dynamic model cited above could be overcome by our present, much more powerful computational methods, and that the reanalysis would provide a more appealing picture of the structure and the motions of the -NO₂ groups. The following is an account of this work, which was based on new microphotometric measurements of the plates from our second series of experiments.⁴ Because the data from the experiments³ obtained a decade earlier were in an inconvenient form, we chose not to use them.

Experimental Section

Samples of N₂O₅ were prepared by ozonolysis of NO₂ (Matheson) with use of the methods and apparatus previously described¹² modified slightly to dry the commercial grade O₂ with P₂O₅ before leading it into the ozonizer. The N₂O₅, trapped at dry ice temperature, was produced at a rate of about 1 g/3 h. It was transferred by evaporation under vacuum into a sample bulb, and after a visual check¹³ for purity, stored under vacuum in liquid N₂ until used.

The diffraction photographs were made in the Oregon State apparatus with an r³ sector. Conditions related to the experiment were the following: Nozzle-tip temperature, -11 °C; plates, 5 × 7 and 8 × 10 in. Kodak projector slide, medium contrast; development, 10 min in D-19 diluted 1:1; nominal distances between nozzle-tip and plates, 75 cm, 30 cm, and 12 cm; exposure times, 20-540 s; ambient apparatus pressure during exposures, 3-4 × 10⁻⁶ torr; electron wavelengths, 0.05736-0.05741 Å (calibrated from CO₂ with $r_a(\text{CO}) = 1.1646$ Å and $r_a(\text{O}\cdot\text{O}) = 2.3244$ Å); number of plates used from each camera distance, 4 (long), 3 (intermediate), and 2 (short); ranges of data, 2.00 ≤ s ≤ 8.50 Å⁻¹ and 2.00 ≤ s ≤ 12.75 Å⁻¹ (long), 8.00 ≤ s ≤ 32.00 Å⁻¹ (intermediate), and 25.00 ≤ s ≤ 48.50 Å⁻¹ (short). The procedures for deduction of the total scattered intensities ($s^4I_t(s)$), removal of the backgrounds, and generation of averages of the molecular intensities in the form $sI_m(s)$, as well as the formulas for these intensities, have been given elsewhere.^{14,15} The

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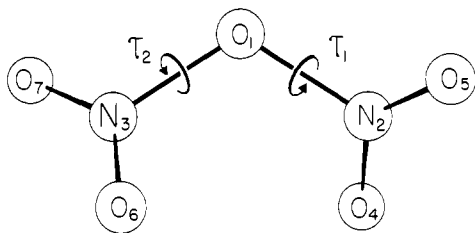


Figure 1. Atom numbering for N_2O_5 models.

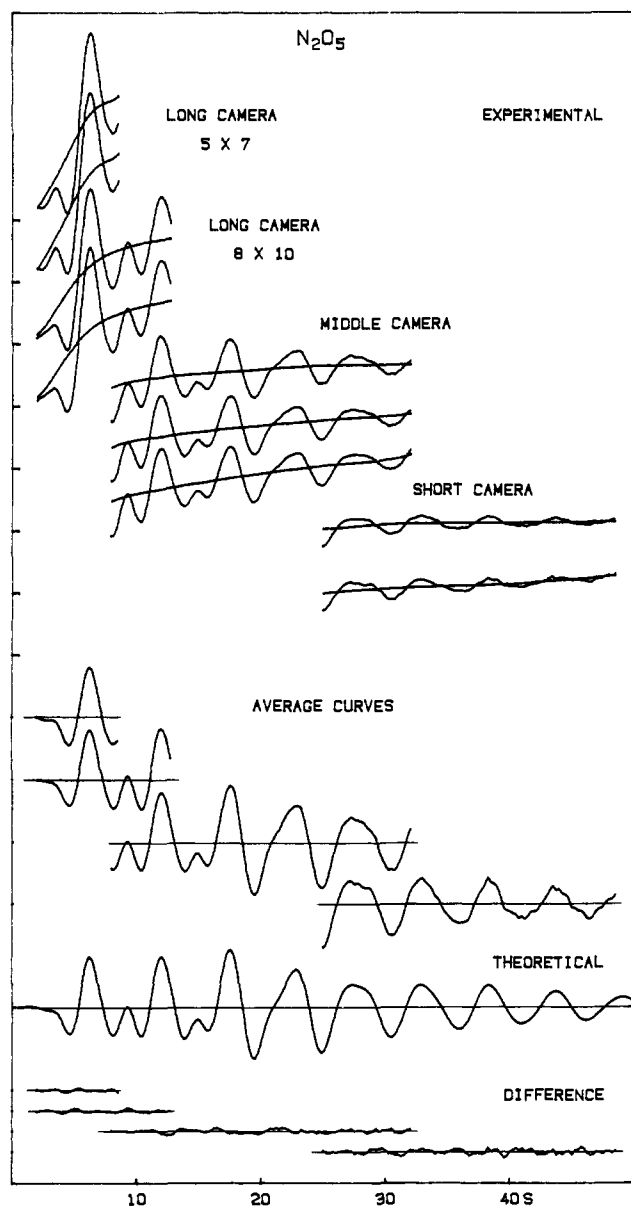


Figure 2. Intensity curves for N_2O_5 . Individual s^4I_1 curves from each plate, magnified 5 \times to reveal better the molecular scattering, are shown superimposed on their backgrounds. The average curves are the s^4I_1 ones minus background times s . The theoretical curve corresponds to the final model.

electron-scattering amplitudes for our experimental conditions were interpolated¹⁴ from literature values.¹⁶ Figure 2 shows curves of the total intensities and the averaged molecular intensities. Figure 3 shows the experimental radial distribution curve calculated from a composite of the average intensities multiplied by $[\exp(-0.0009s^2)]Z_N Z_O / (F_N F_O)$, using theoretical intensity data in the unobserved region $0 \leq s \leq 1.75 \text{ \AA}^{-1}$.

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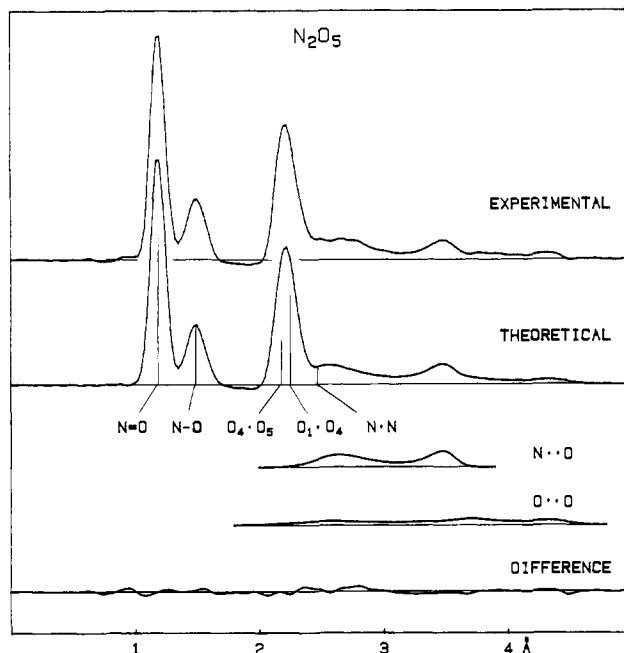


Figure 3. Radial distribution curves. The vertical lines indicate the locations and weights of the torsion-insensitive distances in the final model; the widely distributed torsion-sensitive $N \cdots O$ and $O \cdots O$ interactions are shown separately.

Structure Determination

Formulation of the Model. The nature of the structural problem in N_2O_5 is apparent in the features of the experimental radial distribution curve. The three well-resolved strong peaks may be identified with the distances in a planar $-ONO_2$ group that has the oxygens at the vertices of a nearly equilateral triangle and the nitrogen positioned in such a way as to give one longer ($\sim 1.5 \text{ \AA}$) and a pair of shorter ($\sim 1.2 \text{ \AA}$) nitrogen-oxygen bonds. The longer range details of the structure are not evident, but the diffuse character of the curve over the large range $2.5 < r < 4.5 \text{ \AA}$ clearly shows large amplitude motion of the $-NO_2$ groups. As mentioned in the introduction, our earlier work had led to models that incorporated large amplitude motion and gave excellent agreement with experiment, but were conceptually unsatisfactory, especially in the way the nonbond repulsions were handled. A more reasonable treatment of these repulsions required replacement of the billiard-ball, all-or-nothing interactions between the oxygen atoms on different $-NO_2$ groups with softer ones.

The calculation of the electron intensity scattered from a molecule containing rotating groups is done as follows. An appropriate expression for the torsion-angle dependence of the molecular potential is devised. A group of pseudoconformers is then carefully chosen to represent the continuum of conformations obtained by allowing the torsion angles to assume all possible values. Each pseudoconformer is assumed to experience molecular vibration entirely similar to that of a normal molecule, apart from torsional motion which the distribution of pseudoconformers is meant to represent. Theoretical intensities are calculated for the torsion-sensitive part of the structure of each pseudoconformer, weighted by the factor $P(\tau_1, \tau_2) = \exp(-V/RT)/Q$ and added to the intensity calculated for the rest of the molecule to obtain the desired result. The most important part of the procedure is the form of the potential, but once this is decided the method is straightforward and has led to satisfactory results in this laboratory for several cases of molecules with one internal rotation axis.

In the case of N_2O_5 , a molecule with two internal rotation axes connecting a pair of interfering rotors, the problem is much more complicated than it is for molecules having only a single rotation axis. For example, it is reasonable to assume that the part of the potential governing the orientation of an $-NO_2$ group as it is influenced by the other nitrogen atoms may be represented by a simple trigonometric function of the torsion angle. The intergroup $O \cdots O$ interactions, however, are surely nonlinear functions of the $O \cdots O$ distances, which are themselves rather complicated functions of the combinations of torsion angles. The torsion angles thus become rather unwieldy parameters for representing the potential of the $O \cdots O$ interactions and we resorted to a simpler alternative. One may view the torsional behavior of the $-NO_2$ groups in N_2O_5 as determined first by the bonding in the $N-O-NO_2$ moiety, which is reflected in the potential by trigonometric terms in the torsion

angles, and second by intergroup O...O repulsions, which can be represented by terms of a Lennard-Jones type. An appropriate form of the torsional potential is thus

$$V = \frac{1}{2}V_0(2 - \cos 2\tau_1 - \cos 2\tau_2) + U_0 \sum_{i,j} \sum_{l=1}^n (r_0/r_{ij})^n \quad (1)$$

With the angle values taken as zero for the planar conformation, the first term corresponds to lowest energy for planar arrangements of the N—O—NO₂ moieties; the choice is consistent with the known planar arrangements of nitric acid¹⁷ and the heavy atoms in methyl nitrate.¹⁸ In the second term the indices refer to oxygen atoms on different —NO₂ groups; the summations are thus over all intergroup O...O interactions. The parameters r_0 and U_0 are clearly analogous to the Lennard-Jones constants σ and 4ϵ . If it is assumed that the —NO₂ groups have local C_{2v} symmetry, the "structure" of a model incorporating the foregoing ideas may be viewed as described by the bond lengths $r(\text{N}=\text{O})$ and $r(\text{N}-\text{O})$, the bond angles $\angle\text{O}=\text{N}=\text{O}$ and $\angle\text{N}-\text{O}-\text{N}$, and values of the parameters V_0 , U_0 , r_0 , and n appearing in the potential function of eq 1 that determines $P(\tau_1, \tau_2)$, the probability density of —NO₂ torsion angles. For calculations based on this model to be made, it is necessary to find a set of torsion-angle combinations (i.e., a set of pseudoconformers) that represents satisfactorily the continuum of possible orientations of the —NO₂ groups. Tests showed that 21 pseudoconformers taken at intervals $\Delta\tau = 22.5^\circ$ over the space defined by the angle ranges $0^\circ \leq \tau_1 \leq 67.5^\circ$ and $0^\circ \leq \tau_2 \leq 90^\circ$ comprise such a set. With these pseudoconformers the model has a total of 87 interatomic distances of which 9 and 73, respectively, reflect the torsion-sensitive N...O and O...O interactions. In addition to the distance-, angle-, and potential-function parameters just described, there are a large number of vibrational amplitude parameters. Those associated with the bonds present no problem. The geminal amplitudes, however, are associated with similar distances, and the amplitudes associated with torsion-dependent distances are "frame" amplitudes peculiar to the structure of each pseudoconformer. These are best handled by keeping certain of the amplitude differences at theoretical values calculated from a suitable vibrational force field.

Calculation of Distance Corrections and Amplitudes. The formulas used to calculate the intensity distribution of electrons scattered from free molecules contain distances of the r_a type. In general, the effects of molecular vibration operate to make the set of r_a distances inconsistent with certain symmetry requirements. Although in the case of N₂O₅ this inconsistency was not expected to be serious, it was thought best to use r_a distances—a type that is consistent with symmetry requirements—and to generate the necessary r_g type from them. The connection between these distance types is given by the formula

$$r_a = r_g - l^2/r = r_\alpha + K + \delta r - l^2/r \quad (2)$$

where the perpendicular amplitude term K , the centrifugal distortions δr , and the mean square amplitudes l^2 may be calculated with the use of a suitable quadratic force field.

We began by deducing a set of symmetrized (point group C₂) force constants that reproduced the observed⁵ wavenumbers to within 10 cm⁻¹ by using a model having bond lengths and bond angles very close to those in our final one and torsion angles equal to 45°. The normal-coordinate program has been described.¹⁹ The two torsional coordinates were next removed and the three components of the distance corrections calculated for those pseudoconformers having torsion angles τ_1/τ_2 (in degrees) equal to 0/0, 0/45, 0/90, 45/45, 45/-45, 45/90, and 90/90. The values of δr , K , and l^2 from these calculations were then interpolated to obtain values for the 14 remaining pseudoconformers. The results of this rather elaborate procedure, which assumes separability of torsional motion from vibration of the molecular frame, were sets of distance corrections appropriate to each of the torsionally rigid pseudoconformers that, taken as a group, represents the effect of large amplitude motion. The quadratic force constants and symmetry coordinates from which the corrections were calculated are given in the supplementary material.

Structure Refinement. Refinement of the N₂O₅ structure was carried out by least squares,²⁰ fitting a theoretical intensity curve to the four average experimental curves shown in Figure 2. As described above, the parameters of the structure were the bond lengths $r_\alpha(\text{N}=\text{O})$ and $r_\alpha(\text{N}-\text{O})$, the bond angles $\angle\text{O}=\text{N}=\text{O}$ and $\angle\text{N}-\text{O}-\text{N}$, and the four parameters of the torsional potential function (eq 1). Local symmetry C_{2v} was

Table I. Structural Results for N₂O₅^{a,b}

Parameters Used to Define the Structure ^c					
$r_\alpha(\text{N}=\text{O}) = 1.183$ (2)	$V_0 = 1.90$ (24)				
$r_\alpha(\text{N}-\text{O}) = 1.492$ (4)	$U_0 = [0.1]$				
$\angle\text{O}=\text{N}=\text{O} = 133.2$ (6)	$r_0 = [2.8]$				
$\angle\text{N}-\text{O}-\text{N} = 111.8$ (16)	$n_0 = [12]$				
% impurity ^d = 11.6 (48)					
Distances and Amplitudes ^e					
	r_α	r_g	r_a	l	l_{calcd}^f
Torsion Independent					
N=O	1.183 (2)	1.188	1.186	0.037 (2)	0.039
N-O	1.492 (4)	1.498	1.495	0.064 (5)	0.055
O ₄ ·O ₅	2.172 (6)	2.176	2.175	0.045	0.051
O ₁ ·O ₄	2.242 (4)	2.249	2.247	0.062	0.068
N·N	2.470 (24)	2.479	2.473	0.123	0.129
Torsion Dependent, Corresponding to $\tau_1 = \tau_2 = 30^\circ$					
N ₃ ·O ₄	2.61 (3)	2.63	2.62	0.15	0.19
N ₃ ·O ₅	3.47 (2)	3.48	3.48	0.06	0.10
O ₄ ·O ₆	2.45 (5)	2.47	2.44	0.26	0.26
O ₄ ·O ₇	3.60 (3)	3.62	3.61	0.18	0.18
O ₅ ·O ₇	4.44 (11)	4.44	4.44	0.08	0.08

^a Distances and amplitudes in angstroms; angles in degrees; potential constants in kcal/mol. Parenthesized values are 2 σ uncertainties. Values in square brackets were assumed; those in curly brackets were refined as a group with constant differences. ^b The value 0.075 was obtained for $R = \sum w_i \Delta_i^2 / \sum w_i [s_i I_i(\text{obsd})]^2$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$. ^c For definition of V_0 , U_0 , R_0 , and n see eq 1. ^d Impurity taken as 2NO₂ + 1/2O₂. ^e For connections between types of r see eq 2. ^f Uncertainties for r_g and r_a assumed to be the same as for r_α . ^f This work.

assumed for the ONO₂ groups after tests indicated that the bisector of the O=N=O angle lay within $3 \pm 2^\circ$ of the N—O bond line. Anharmonicity corrections were included for bonds only; the usual diatomic approximation led to κ values of $0.64 \times 10^{-6} \text{ \AA}^3$ and $8.1 \times 10^{-6} \text{ \AA}^3$ for N=O and N—O, respectively. Root-mean-square amplitudes associated with bonds were taken as vibrational parameters. The amplitudes for the geminal distances were handled as a single parameter by keeping their differences at the calculated values. The frame amplitudes for the torsion-sensitive distances were handled as two parameters, one for the N...O group and one for the O...O; the differences between group members were kept at the calculated values. As expected, strong correlations between the parameters of the potential function revealed themselves during the course of the refinement. After exploration of the behavior of these parameters we set U_0 equal to 0.10 kcal/mol, r_0 to 2.80 Å, and $n = 12$. The values of the latter two are not inconsistent with typical corresponding Lennard-Jones constants; the value of U_0 represents the result of test refinements. In order to take account of possible impurities arising from sample decomposition during the experiments, we also included a composition parameter which adjusted the amount of 2NO₂ + 1/2O₂ (the assumed mole ratio is from the stoichiometry of the first-order decomposition) relative to that of N₂O₅. The structural parameters for the impurities were taken from the literature.^{8,21}

The results of the refinements are summarized in Table I and a correlation matrix for the more important parameters is given in Table II. The values of the defining parameters and the torsion-insensitive distances and amplitudes in Table I have their usual meanings. Those for the torsion-sensitive ones, however, do not: because of the large amplitude torsions, the N...O and O...O distances between atoms on different —NO₂ groups are changing in a way that cannot be represented by single distance values with associated harmonic vibrational amplitudes. The distances listed for these interactions correspond to a pseudoconformer with C₂ symmetry and torsion angles equal to 30°, a structure that is representative of molecules close to the potential minimum. The corresponding amplitudes are those for the molecular frame exclusive of the torsional motion.

Discussion

The molecules of gaseous N₂O₃, N₂O₄, and N₂O₅ are characterized in each case by the presence of an —NO₂ group linked through the nitrogen atom to the remainder of the molecule. The N—N bond lengths of 1.864 Å in N₂O₃⁹ and 1.782 Å in N₂O₄^{7,8}

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Table II. Correlation Matrix ($\times 100$) for N_2O_5

	σ^a	r_1	r_2	L_1	L_2	V_0	l_1	l_2	l_3	l_4	l_5	%
$r(N=O)$	0.0003	100	-18	2	24	-15	19	35	31	-7	-8	-61
$r(N-O)$	0.0012		100	46	4	-7	-1	-11	17	-3	-5	8
$\angle O=N=O$	0.23			100	5	-4	9	2	80	<1	-1	-13
$\angle N-O-N$	0.55				100	-13	13	13	15	11	-20	-26
V_0	0.12					100	-12	-10	-11	43	44	19
$l(N=O)$	0.0003						100	29	29	-7	-8	-29
$l(N-O)$	0.0014							100	20	-5	-7	-42
$l(O-O)^b$	0.0018								100	-2	-5	-42
$l(N \cdots O)^b$	0.0091									100	13	8
$l(O \cdots O)^b$	0.0366										100	12
%	1.7											100

^a Standard deviations from least squares. Distances and amplitudes in angstroms, angles in degrees, potential constant in kcal/mol. ^b These parameters represent amplitude groups.

are extraordinarily long compared to the sum of the Schomaker-Stevenson single-bond radii (1.48 Å),²² but in N_2O_5 the linking N-O bonds are only slightly longer than the single-bond radius sum corrected for electronegativity difference (1.44 Å). Because the character of the linking bond is evidently quite different in the three molecules (the empirical bond orders are respectively about 0.3, 0.4, and 0.8 in N_2O_3 , N_2O_4 , and N_2O_5), one might expect substantial differences in the structures of the $-NO_2$ groups themselves. While differences do exist, they are surprisingly small as the following data for these three molecules and for NO_2 ^{11,8} itself show. N=O bond lengths: $r_s = 1.209$ (7) Å in N_2O_3 , $r_a = 1.190$ (2) Å in N_2O_4 , $r_a = 1.186$ (1) Å in N_2O_5 , $r_s = 1.193$ (1) Å, and $r_a = 1.202$ (3) Å in NO_2 . O=N=O bond angles: 129.8 (11)° in N_2O_3 , 135.4 (6)° in N_2O_4 , 133.1 (7)° in N_2O_5 , and 134.1 (1)° and 134.0 (13)° in NO_2 . Bearing in mind that the r_s -type distance is most often shorter than the r_a , the distance data reveal a tendency for the N=O bond length to decrease as the bond order of the linking bond increases, suggesting that electrons for the linking bond are withdrawn from an orbital that is antibonding in the N=O region. There is no discernable trend in the bond-angle values.

The angle at the apical oxygen atom in N_2O_5 is similar to the corresponding angles in methyl nitrate, CH_3ONO_2 (112.7 (3)°),¹⁸ and in dimethyl ether (111.7 (4)°),²³ both of which have essentially single bonds to the oxygen atom. The apical angle in N_2O_5 is thus unexceptional. We have noted that Akishin et al.'s value for this angle at $95 \pm 3^\circ$ is much smaller than ours. It should also be noted that their values for the other torsion-insensitive parameters ($r(N=O) = 1.21 \pm 0.01$ Å, $r(N-O) = 1.46 \pm 0.02$ Å, $\angle O=N=O = 134 \pm 5^\circ$) are in excellent agreement with ours. It is clear from Figure 3 that the large amplitude motion obscures the N-N interaction and that an accurate location of this distance using only the visual estimates of the scattered intensity these authors had would be impossible.

Perhaps the most interesting structural feature of the N_2O_5 molecule is the correlated, large-amplitude torsional motion experienced by the $-NO_2$ groups. The consequences of the interplay between forces tending to stabilize the planar conformation of the molecule and the intergroup O...O repulsions tending to destabilize it are best represented graphically. Figure 4 shows the dependence of the torsional potential of eq 1 on the combinations of the two torsion angles τ_1 and τ_2 . The most likely conformation of the molecule is seen to have the two angles at values of about $+30^\circ$ (or -30°) from the planar form where the potential is a minimum; here the symmetry of the conformation is C_2 and is roughly represented by Figure 1. We have found no single-conformer models that give as good agreement with experiment as the dynamic one reflected by Figure 4, but the fits obtained with several of these are certainly not bad. Examples are models of symmetry C_2 ($\tau_1 = \tau_2$) or C_s ($\tau_1 = -\tau_2$) having $|\tau| = 35^\circ$ with large amplitude $-NO_2$ torsional motion. This result is not surprising because these models have nearly the same N...O distance distribution as the

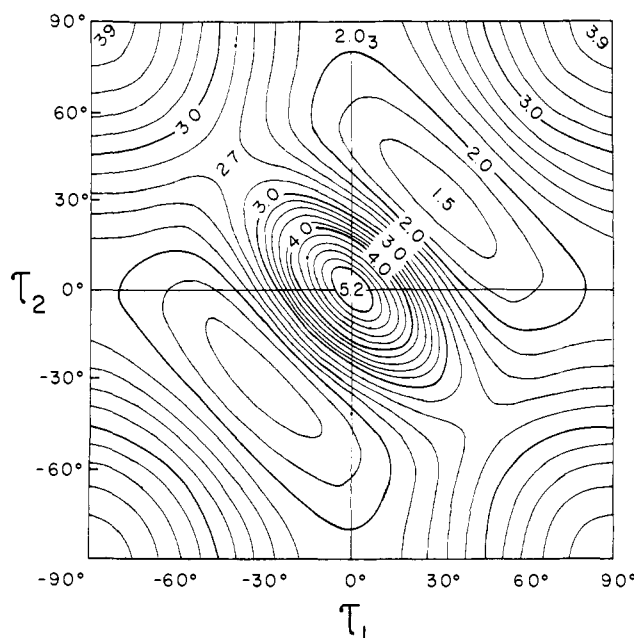


Figure 4. Contour map of the torsional potential, obtained from eq 2 with use of parameters of the final model.

dynamic one and, as is seen from Figure 2, it is the N...O terms that are responsible for the dominant part of the torsion-sensitive scattering.

Although the dynamic model is to be favored on experimental grounds, its principal appeal lies in the plausible picture it presents of the correlated torsions of the $-NO_2$ groups. As may be inferred from Figure 4, the planar ($0^\circ/0^\circ$) and nonplanar ($90^\circ/90^\circ$) conformations of C_{2v} symmetry are very improbable compared to the minimum-energy C_2 ones at about $30^\circ/30^\circ$ and $-30^\circ/-30^\circ$. Rough calculations based on Boltzmann weighting of points in the space depicted by Figure 4 indicate that about 50–60% of the molecules are found in the region bounded by the contour $V = 2.0$ kcal/mol, whereas only 2–3% are in the regions with $V > 3.0$ kcal/mol. The figure also suggests that the most likely pathway for interconversion of the two equivalent forms at $30^\circ/30^\circ$ and $-30^\circ/-30^\circ$ includes the point $0^\circ/90^\circ$ (or $90^\circ/0^\circ$), with a slightly less likely path over the point at $45^\circ/-45^\circ$ (or $-45^\circ/45^\circ$). The fact that interconversion is easily achieved is obvious from the 40–50% of molecules that at $-10^\circ C$ have energy sufficient to allow passage over the lower saddle point ($V > 2.0$ kcal/mol) and the roughly 10% that are able to pass over the higher one. The indication is that interconversion of stable conformers occurs primarily by way of a coordinate comprising an antisymmetric combination of the two torsion angles. Calculation suggests a root-mean-square amplitude of about 25–30° for this mode from which the corresponding wavenumber for the mode is estimated at 45–55 cm^{-1} . The symmetric combination of the torsional coordinates has an estimated amplitude of 10–15° and a wavenumber of 55–75 cm^{-1} . (Neither of the torsional modes appears

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to have been observed.) It is hard to know how reliable the quantitative aspects of our model for the torsional motion in N_2O_5 are because the consequences of the high correlations which were found to exist between some parameters of the potential were not explored. (The pairs U_0 , n and U_0 , V_0 have correlation coefficients greater than 0.6.) We do feel that the model correctly describes the torsional behavior of N_2O_5 molecules in a semiquantitative sense, but detailed conclusions based on our values for the parameters of eq 1 must be drawn with caution.

Finally, it is worth noting that the gas-phase structure of N_2O_5 is altogether different from its structure in the crystal²⁴ where linear nitronium and planar nitrate ions are arranged in layers with the axes of the former perpendicular to the planes of the

latter. In view of the ionic structure of the crystal and the covalent structure of the gas molecule, the high volatility of the solid is indeed remarkable.

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Supplementary Material Available: Tables of symmetry coordinates and force constants for N_2O_5 , total scattered intensities and calculated backgrounds for each plate, and averaged molecular intensities (14 pages). Ordering information is given on any current masthead page.

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High-Pressure Collisional Activation Mass Spectrometry

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Abstract: Ions produced under chemical ionization (CI) conditions can be collisionally activated and dissociated within the high-pressure ion source by the application of relatively large electric fields within the source. A new multiregion ion source that separates regions of CI reaction and high-pressure collisional activation (HPCA) is employed to study these processes. These HPCA spectra may differ significantly from single-collision CID spectra of protonated species. Reactions between fragment ions and the reagent/collision gas are observed that can be used to differentiate the structures of fragment ions. Both parent and fragment ions can be analyzed by high-resolution mass spectrometry under HPCA conditions. Dissociation mechanisms are investigated and analytical applications discussed.

Introduction

Chemical ionization (CI) mass spectra frequently contain ions characteristic of the molecular weights of the samples and fragment ions that provide some structural information. The extent of fragmentation in CI mass spectra is generally less than the extent of fragmentation in electron ionization (EI) mass spectra. Class-characteristic ions of the same mass (31 for alcohols, 127 for iodides, 77 for alkylbenzenes, etc.) are generally absent in CI mass spectra. The extent of fragmentation can be readily changed by using different reactant ions. The weaker the reactant ion is as a Brønsted or Lewis acid, the smaller the extent of decomposition of the $(M + H)^+$ or $(M - H)^+$ ions from the sample.^{1,2} The smaller the recombination energy of the charge-exchange reactant ion, the smaller the extent of fragmentation of the M^+ ions from the samples.³

Much research in CI mass spectrometry during the past several years has been directed toward the development of low-energy reactant ions that give only one ionic species per compound. The NH_3 and $i-C_4H_{10}$ spectra of many compounds, for example, are essentially one species spectra, $(M + NH_4)^+$ or $(M + H)^+$. No structural information is provided by these spectra. Individual components have been identified in complex mixtures without prior separation by the use of CIMS to produce $(M + H)^+$ ions for each component. These $(M + H)^+$ ions can be separated and collisionally dissociated to give characteristic fragmentation patterns by MS/MS. This combination has proved very useful for the identification of structures of molecules.^{4,5}

In addition to these low-pressure collisional activation or collisionally induced decompositions, similar decompositions have also been reported at high pressures within the source of a mass spectrometer. Very marked increases in fragmentation with increasing repeller voltages were reported several years ago for $i-C_4H_{10}$ spectra of a few compounds.⁶ Recently, collisionally activated decompositions within a drift tube source of a mass spectrometer were reported.⁷ By changing the field strength within the source, the extent of fragmentation could be varied over a wide range; from virtually no fragmentation to virtually complete fragmentation.

In the earlier work, sample ion production and collisional activation occurred within the same space. Although it was clear that the increased fragmentation resulted primarily from collisional activation of the $(M + H)^+$ ions from the samples, there were possible major effects from the changes in the reactant ion distribution as the field strength in the source was changed. Because the dissociation reactions occur at high pressures, reactions of sample fragment ions with the reagent gas are also possible. We report here a flexible multiregion ion source that effectively separates the region of sample ion production from the region of high-pressure collisional activation (HPCA). Principles and some applications of high-pressure collisional activation will be discussed.

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