J. Am. Chem. Soc. 1984, 106, 5447-5451

Thermal Decomposition of TNT: Use of 1-Nitropropene To Model the Initial Stages of Decomposition

A. G. Turner[†] **and L. P. Davis**[*]

Contribution from the Frank J. Seiler Research Laboratory, USAF Academy, Colorado Springs, Colorado 80840. *Received December 19, 1983*

Abstract: We have used 1-nitropropene as a model compound to study TNT decomposition. When Dewar's MNDO and MINDO/3 methods were utilized, several potential first steps in the thermochemical decomposition of TNT have been tested theoretically against known experimental kinetic parameters. Calculated ΔH°'s for the processes indicate that 1-nitropropene is a valid model for use in studying TNT decomposition. Results show that several processes appear to be quite feasible as possible initial steps in the decomposition. Principal among these is the intermolecular hydrogen transfer from the methyl group of one molecule to a nitro group of a second molecule.

Semiempirical molecular orbital calculations based upon the MNDO[1] and MINDO/3 approximations[2] have been successfully used to estimate the enthalpy of activation and to provide information about the nature of the transition state involved in a chemical reaction for a wide variety of chemical systems.[3] This laboratory has been concerned with kinetic studies of the thermal decomposition of 2,4,6-trinitrotoluene (TNT) for the past several years.

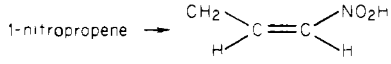
Isothermal differential scanning calorimeter studies (IDSC) showed a substantial (~1.7) kinetic isotope effect present upon methyl-group deuteration.[4] Electron paramagnetic resonance (EPR) studies showed conclusively that radicals are present in the initial and later stages of the thermochemical decomposition of TNT, and measurements of the intensity of the radical signals as functions of time and temperature produced an activation energy of 40.9 kcal mol^{-1} for the early radical-producing step in the decomposition.[5] Monitoring the signal of a later radical produced during the bulk-phase decomposition gave a bulk-phase-decomposition activation energy of 30.2 kcal mol^{-1}. The initial radical produced has an EPR spectrum consistent with a molecule having five equivalent hydrogen atoms and two equivalent nitrogen atoms.[6]

We recently decided to initiate the theoretical study of several alternative decomposition reaction channels for the TNT system. The large number of internal coordinates necessary to specify the geometry of the TNT molecule ($3N - 6 = 60$) and the trial and error nature of the process involved in identification of the reaction coordinate for a given reaction step[7] dictated that the calculations could be expected to be lengthy, time consuming, and relatively expensive. Accordingly, we decided to seek out a smaller, simpler system which might hopefully reflect the same behavior as TNT. We selected the 1-nitropropene molecule on the basis shown in Figure 1. This molecule, possessing the salient structural elements of the TNT molecule, might be expected to provide an accurate reflection of the TNT system provided the decomposition reactions considered are not dominated by electronic factors directly traceable to the conjugation effects present in the TNT ring.

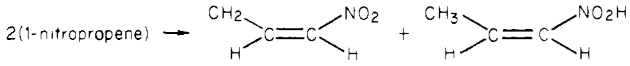
Reaction Mechanisms

On the basis of the experimental data available to us the following six decomposition channels were considered.

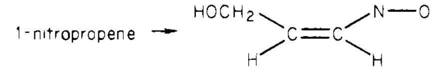
1. Intramolecular hydrogen transfer



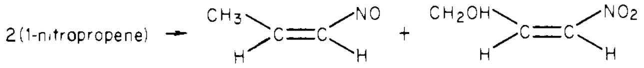
2. Intermolecular hydrogen transfer



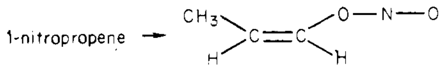
3. Intramolecular oxygen insertion JA9M33c



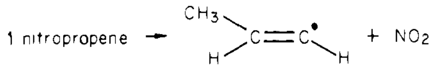
4. Intermolecular oxygen insertion



5. Nitro–nitrite rearrangement



6. Nitro-group removal



Calculations

MNDO and MINDO/3 calculations were carried out for 1-nitropropene, and each of the product molecules occurring in the preceding six mechanisms, as well as their TNT analogues. The energy of each molecule was calculated as a function of its geometry and the geometry of lowest energy determined, i.e., a full geometry optimization was carried out. The unrestricted Hartree–Fock (UHF) method was utilized for transition states suspected of high diradical character. The heats of formation and geometries of open-shell radical products were calculated via the half-electron (HE) method.

Some might question the use of these semiempirical methods with their use of single-determinant wave functions for calculations of nitro-containing compounds, since previous ab initio work has shown that a proper description of these compounds requires at least a two-determinant wave function.[8] Results for a wide variety of nitro-containing aliphatic and aromatic compounds indicate that the parameterization of MINDO/3 adequately takes electron

---

[†] University Resident Research Professor 1981–1983. Permanent Adress: Department of Chemistry, University of Detroit, Detroit, MI 48221.

(1) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(2) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(3) See: Kollman, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292. Oleksik, J.; Turner, A. G. *Inorg. Chim. Acta*, **1982**, *59*, 165.

(4) Shackelford, S. A.; Beckmann, J. W.; Wilkes, J. S. *J. Org. Chem.* **1977**, *42*, 4201.

(5) Guidry, R. M.; Davis, L. P. *Thermochim. Acta* **1979**, *32*, 1.

(6) Carper, W. R.; Davis, L. P.; et al., submitted for publication.

(7) In any but the simplest of systems, the reaction coordinate cannot be identified a priori as any one of or linear combination of the members of an arbitrary set of internal coordinates. Methods for doing this are under investigation in this laboratory and others. Turner, A. G.; Wulfman, C. E., to be published.

(8) Hariharan, P. C.; Koski, W. S.; Kaufman, J. J.; Miller, R. S.; Lowrey, A. H. *Int. J. Quant. Chem. Symp.* **1982**, *16*, 363.

0002-7863/84/1506-5447$01.50/0

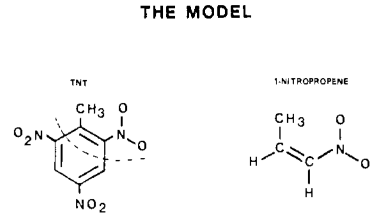


Figure 1. The choice of *cis*-1-nitropropene as a theoretical model for TNT.

Table I. Standard Enthalpies of Reaction (kcal mol^{-1})

	MNDO			MINDO/3		
reaction	1-nitropropene	TNT	Δ	1-nitropropene	TNT	Δ
intra-H transfer	8.6	16.6	8.0	7.6	19.8	12.2
inter-H transfer	16.2	16.8	0.6	38.2	38.7	0.5
intra-O insertion	−49.5	−49.9	−0.4	−18.7	−18.4	0.3
inter-O insertion	−51.3	−52.4	−1.1	−16.1	−21.9	−5.8
nitro–nitrite rearrangement	−38.9	−41.1	−2.2	−11.8	−7.5	4.3
nitro-group removal	29.8	26.9	−2.9	41.4	62.1	20.7

correlation into account for these compounds.[9] Indeed, the average absolute error for the heats of formation of these nitro compounds is essentially the same as all CHON compounds calculated with MINDO/3 (about 9 kcal mol^{-1}).[10] It is certainly true that MNDO results for nitro compounds give heats of formation that are far too endothermic,[9] but this is almost certainly because none of these compounds were included in the original parameterization of MNDO.[1]

There exists another version of MNDO (MNDOC) which takes explicit account of electron-correlation effects.[11] This explicit accounting for electron correlation does result in an improvement of calculated activation energies over MNDO, at least for some reactions.[11] We did MNDOC calculations for several of the possible steps at MNDO-optimized geometries and found that activation energies were lowered by about 5–10 kcal mol^{-1}. Since MNDO and MINDO/3 are far more widely used than MNDOC and the difference in results did not change the conclusions, we report the MNDO and MINDO/3 results in this paper.

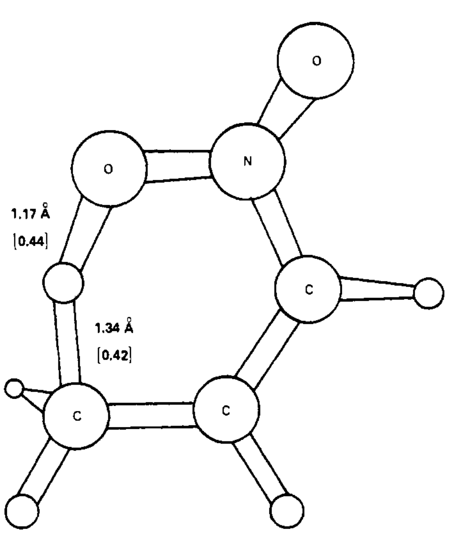


Figure 2. The MINDO/3-calculated transition state for the intramolecular hydrogen transfer. Numbers in brackets are bond orders. Unlabeled atoms are hydrogens.

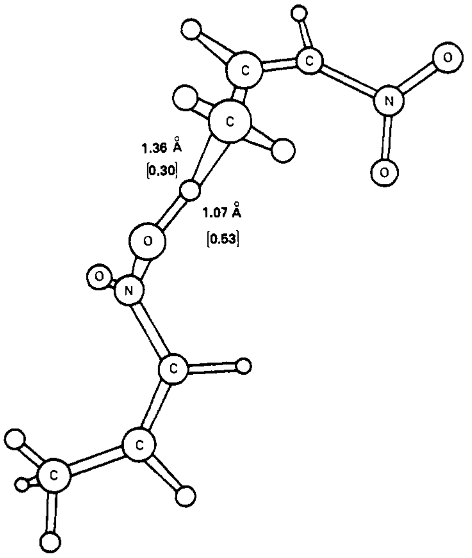


Figure 3. The MINDO/3-calculated transition state for the intermolecular hydrogen transfer. Numbers in brackets are bond orders. Unlabeled atoms are hydrogens.

Thermodynamic Considerations

If the use of the 1-nitropropene molecule as a model for the TNT molecule has any validity, it is necessary that the two potential energy surfaces have the same topology. For example, the standard enthalpy changes associated with the six reactions studied should be similar in the two systems. The enthalpy changes are tabulated in Table I for calculations employing both the MNDO and MINDO/3 methods, together with the difference in $\Delta H°$ for the nitropropene system and the TNT system for a particular reaction. The data substantiates the validity of the model. In almost every case (the exception being the NO_2 group removal, calculated by the MINDO/3 method) the differences in $\Delta H°$ for a given type of chemical pathway are relatively small, the difference being in the range of 0–12 kcal mol^{-1}. The MNDO model seems to provide the better degree of agreement for the two systems. The energetic order of the six steps is almost identical in TNT and 1-nitropropene; hence the model does exhibit about the same ordering of reactant and product states for both systems. This is an important point since it provides hope that the energetic order of the thermodynamic states of the model system parallel those of the TNT system.

In addition, the calculated geometries of 1-nitropropene are very close to the calculated geometries for the pertinent parts of the TNT molecule, which in turn agree well with experimental data.[12] The only difference of any consequence is the slightly longer C–C aromatic bond in TNT (~1.40 Å) compared to the formal C=C double bond in 1-nitropropene (~1.35 Å).

Calculation of Transition States

Since the 1-nitropropene model does exhibit almost the same ordering of reactant and product states as TNT, it is reasonable to expect that 1-nitropropene reflects the proper ordering of all the energy maxima on the potential surface, thus enabling the identification and ordering of the transition states for the six reaction channels considered. Under this assumption, tentative reaction coordinates were identified for each of the six mechanisms and the transition states located, using both the MNDO and MINDO/3 methods. The transition states were identified by the method of Hildebrandt by using the eigenvalues of the force constant matrix,[13] i.e., by the presence of one, and only one,

---

(9) Guidry, R. M.; Davis, L. P., Frank J. Seiler Research Laboratory Technical Report 83-0012, January 1984.

(10) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1302.

(11) Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1413, 1420, 1425.

(12) Carper, W. R.; Davis, L. P.; Extine, M. W. *J. Phys. Chem.* **1982**, *86*, 459.

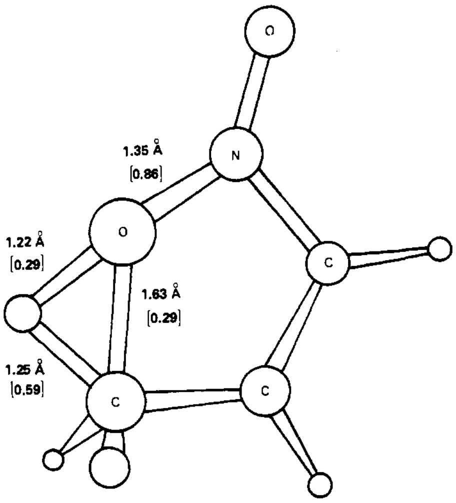


Figure 4. The MINDO/3-calculated transition state for the intramolecular oxygen insertion. Numbers in brackets are bond orders. Unlabeled atoms are hydrogens.

Table II. Activation Parameters for the 1-Nitropropene System

	MNDO		MINDO/3	
reaction	$\Delta H^{\ddagger}$, kcal mol^{-1}	freq, cm^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	freq, cm^{-1}
intra-H transfer	63.7 (59.5)	2734 (3715)	43.4 (43.4)	1896 (1896)
inter-H transfer	– (50.4)	– (3834)	– (39.6)	– (1701)
intra-O insertion	127.7	1733	49.9	936
inter-O insertion	108.7	1633	44.4	424
nitro–nitrite rearrangement	51.6	1051	35.0	705
nitro-group removal	29.8	–	41.4	–

[a] Parentheses indicate UHF calculation.

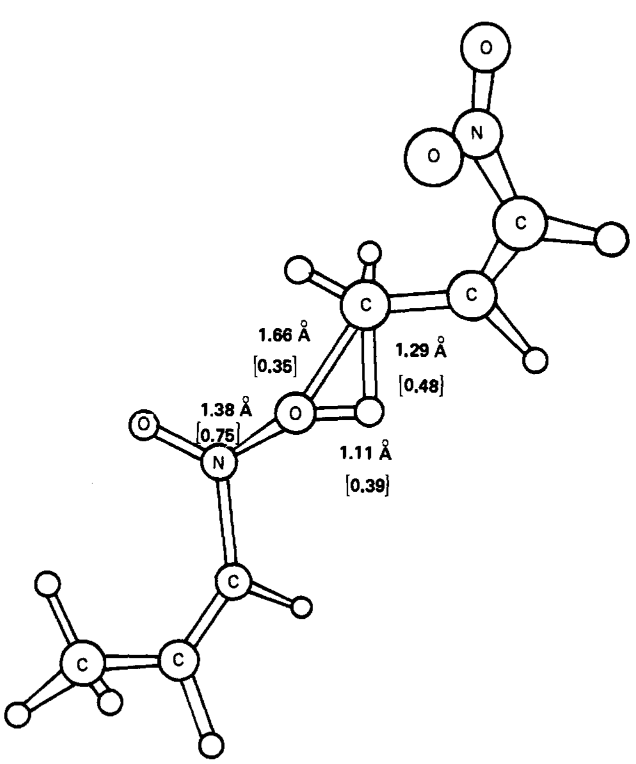


Figure 5. The MINDO/3-calculated transition state for the intermolecular oxygen insertion. Numbers in brackets are bond orders. Unlabeled atoms are hydrogens.

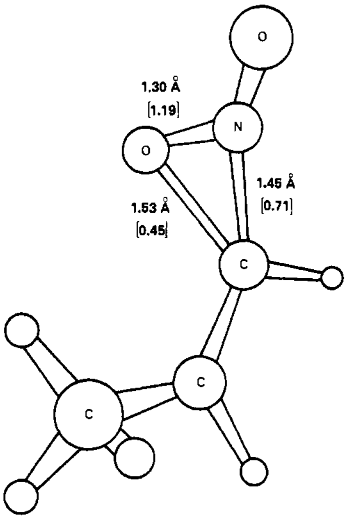


Figure 6. The MINDO/3-calculated transition state for the nitro–nitrite rearrangement. Numbers in brackets are bond orders. Unlabeled atoms are hydrogens.

negative eigenvalue. The transition states so identified are diagrammed in Figures 2–6, where we illustrate their geometries and specify the bond orders. In Table II we list the enthalpy of activation for each of the six mechanisms, together with the frequency associated with motion along the reaction coordinate (normal coordinate basis). The latter was calculated by carrying out a Wilson-FG type of vibrational analysis for each transition state.[14] Since we cannot anticipate a priori which internal coordinates will enter a given normal coordinate and which combinations of these coordinates will in turn correspond to the translational and rotational motions, the latter have been left in the analysis. The frequencies calculated for translational and rotational motions never turned out to be identically zero, but they were generally close to zero. In light of this, the frequencies calculated for motion along the reaction coordinate probably contain some error which we estimate could be as large as ±200 cm^{-1}.

Geometrically the transition states identified by the MNDO method and the MINDO/3 method were very similar. As previously discussed, since a careful study of the accuracies of MNDO and MINDO/3 for nitro-containing compounds has shown MINDO/3 to be superior,[9] we expect the MINDO/3 results to be more reliable. Accordingly, Figures 2–6 illustrate the MINDO/3-calculated transition states. We will now discuss each of these results in turn.

The transition state obtained for the intramolecular hydrogen atom transfer of a hydrogen atom from the CH_3 end of the three-carbon chain to the nitro group (Figure 2) is a cyclic structure wherein the hydrogen atom–carbon atom bond has been elongated from 1.10 to 1.34 Å (bond order of 0.42). The initial stages of O–H bond formation can be identified with the hydrogen–oxygen distance of 1.17 Å (bond order of 0.44). The transition state is nonplanar with the hydrogen being transferred about 0.5 Å out of the plane formed by the three carbon atoms. The force constant calculation gave excellent results: one large negative eigenvalue for the reaction coordinate and six close-to-zero results for the translations and rotations (all less than 6 cm^{-1}). The reaction coordinate corresponded primarily to motion of the hydrogen being transferred. The high frequency of the reaction coordinate also reflects that the motion is composed primarily of translational motion of the hydrogen atom.

The calculated activation enthalpy was somewhat higher for MNDO than MINDO/3 (63.7 kcal mol^{-1} compared to 43.4 kcal

---

(13) Hildebrandt, R. L. *Comput. Chem.* **1977**, *1*, 179.

(14) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill Book Co., Inc.: New York, 1955; Chapters 6–9.

mol^{-1}). This is consistent with MNDO normally giving slightly high activation enthalpies for hydrogen-transfer reactions. The MINDO/3 result is consistent with the experimental activation energy, and thus this process cannot be ruled out as a first step in the thermochemical decomposition on the basis of this calculated activation energy. We would expect the TNT activation enthalpy to be several kcal mol^{-1} higher, however, because of the loss of the aromatic character of the ring as TNT converts to the product state. This effect, of course, will not show up in our 1-nitropropene model compound. Because of the possible diradical character of the product, we also optimized the transition state using a UHF-type calculation. For MINDO/3, no spin imbalance was calculated and the results were the same as the RHF results. MNDO gave a slightly lower value for the activation enthalpy with UHF, but the difference was not significant.

The transition state for the intermolecular hydrogen transfer is shown in Figure 3. Since the product of this reaction is two radicals, the result shown and the numbers given in Table II are for UHF-type wave functions. Attempts to optimize an RHF transition state resulted, as could be expected, in the separated reactants. In contrast to the intramolecular hydrogen-transfer transition state, which was almost symmetrical in terms of the C–H and O–H bond orders, this intermolecular transition state shows that the C–H bond is more than half broken (C–H distance is 1.36 Å, with a bond order of 0.30) while the O–H bond is more appreciably formed (O–H distance is 1.07 Å, with a bond order of 0.53). The C–H–O bond angle is 166°, approaching linearity. The force constant calculation gave one large negative eigenvalue for the reaction coordinate, but the translations and vibrations did mix appreciably with the low-lying vibrations (frequencies for the translations and rotations exceeded 100 cm^{-1}). This mixing is not surprising considering the loosely bound nature of this bimolecular transition state, and it should not qualitatively affect the conclusions. Once again, the reaction coordinate and its associated frequency indicate the motion to consist primarily of hydrogen atom translations.

Again, the calculated activation enthalpy for MNDO is somewhat higher than that for MINDO/3 (50.4 vs. 39.6 kcal mol^{-1}), following the trend that MNDO overpredicts activation enthalpies for hydrogen transfer reactions. The MINDO/3 result for this reaction is also consistent with the experimental activation energy, although MINDO/3 UHF results typically may underestimate the activation enthalpy by several kcal mol^{-1}. Even so, the agreement with the experimental number is quite good.

Figure 4 shows the MINDO/3 transition state for the intramolecular oxygen insertion from the nitro group into a C–H bond of the methyl group. The N–O bond is stretched (distance of 1.35 Å, bond order of 0.86), the C–H bond is stretched (distance of 1.25 Å, bond order of 0.59), the C–O bond is partially formed (distance of 1.63 Å, bond order of 0.29), and the O–H bond is partially formed (distance of 1.22 Å, bond order of 0.29). The geometry of the transition state is slightly nonplanar, with the inserted oxygen atom and the hydrogen atom both about 0.1 Å out of the plane formed by the three carbon atoms. Indeed, the first attempt to optimize this transition state with MINDO/3 produced a planar geometry, but the presence of more than one negative force constant indicated that the structure was not a true transition state. The force constant calculation on the true transition state had only one negative force constant, with each of the translational and rotational modes having frequencies less than 10 cm^{-1}. The reaction coordinate corresponded to motion of all of the atoms involved in either bond making or bond breaking, with the oxygen and the hydrogen showing the largest effects. Interestingly, there was virtually no difference in the calculated heats of formation between the planar and nonplanar structure. The MNDO result was not quite as good. In spite of repeated attempts to displace the stationary point calculated by MNDO from planarity, we were not successful. The result is a planar stationary point which we believe to be very near the true transition state, but which nevertheless has two negative eigenvalues in the force constant matrix: one (corresponding to the true reaction coordinate) of 1733 cm^{-1} and the other (corresponding primarily to torsional motion of the hydrogen in and out of the plane of the molecule) of 303 cm^{-1}.

There is a large difference between the calculated enthalpies of activation for MNDO and MINDO/3 (127.7 vs. 49.9 kcal mol^{-1}), even though the overall geometries are similar. On the basis of previously discussed rationale, the MINDO/3 results are more believable. The MINDO/3 enthalpy of activation is slightly larger than the experimental activation energy, but the 10-kcal mol^{-1} difference does not completely rule this step out as a possible first step. We think, however, that it is less likely than the hydrogen transfer steps previously discussed.

The MINDO/3-calculated transition state for the intermolecular oxygen insertion into a methyl-group C–H bond is shown in Figure 5. Compared with the intramolecular-insertion transition state, the reaction has proceeded more toward product; the N–O bond is stretched (distance of 1.38 Å, bond order of 0.75), the C–H bond is stretched (distance of 1.29 Å, bond order of 0.48), the C–O bond is partially formed (distance of 1.66 Å, bond order of 0.35), and the O–H bond is partially formed (distance of 1.11 Å, bond order of 0.39). The N–O–C bond angle is 158°, approaching linearity. The force constant calculation gives a single negative force constant, with rather poor separation of the translational and rotational modes (maximum frequency of 69 cm^{-1}). Again, this mixing with low-lying vibrations is not uncommon for bimolecular transition states. The reaction coordinate consists of motion primarily by the atoms involved in bond breaking and bond making, but there are minor contributions from many of the other modes. The frequency is much lower than that for the intramolecular case (424 vs. 936 cm^{-1}), indicating the much looser nature of the bimolecular transition state.

Like the intramolecular oxygen insertion, there is a large discrepancy between MNDO and MINDO/3 in the calculated enthalpies of activation for this intermolecular oxygen insertion (108.7 vs. 44.4 kcal mol^{-1}). Again, assuming the MINDO/3 value to be more accurate, this calculated activation enthalpy is consistent with the experimental activation energy. This process is quite likely to be taking place in the initial stages of TNT decomposition.

Figure 6 shows the MINDO/3-calculated transition state for the nitro–nitrite rearrangement. In this reaction, one of the oxygens inserts into the C–N bond, resulting in the structure C–O–N–O. The transition state shows stretching of the C–N bond (distance of 1.45 Å, bond order of 0.71), stretching of the N–O partial double bond in the nitro group toward the single bond in the product (distance of 1.30 Å, bond order of 1.19), and partial formation of the C–O bond (distance of 1.53 Å, bond order of 0.45). The force constant calculation gives a single negative eigenvalue of frequency 705 cm^{-1}, with good separation of the translational and rotational modes (maximum frequency of 9 cm^{-1}). The reaction coordinate consists of movement primarily by the three atoms involved, C, N, and O.

The results for the activation enthalpies are 35.0 and 51.6 kcal mol^{-1} for MINDO/3 and MNDO, respectively. Both values are not far removed from the experimental activation energy, making this process a feasible first step on an activation enthalpy basis.

The last process considered was a simple C–N bond fission, resulting in the C_3H_5 radical and NO_2. A reaction-path calculation failed to produce a transition state, meaning that the reverse reaction should proceed without activation, a common occurrence for a radical-recombination reaction. Thus, the activation enthalpy and the reaction enthalpy are one and the same. The results are 29.8 kcal mol^{-1} for MNDO and 41.4 kcal mol^{-1} for MINDO/3. Both values make the C–N bond fission look feasible when compared with the experimental activation energy, but we feel that both numbers are in error. MNDO results for heats of formation of nitroaromatics generally are far too endothermic,[9] destabilizing the reactant and making the activation enthalpy too small. On the other hand, MINDO/3 gravely overstabilizes NO_2 by about 25 kcal mol^{-1}, again making the activation enthalpy too small. If one corrects the MINDO/3 result for this known error for NO_2, an activation enthalpy of about 65 kcal mol^{-1} is obtained. This number agrees with the 70-kcal mol^{-1} value one obtains for the

C–N bond strength in nitrobenzene if the experimental heats of formation for nitrobenzene and NO_2 and the MNDO-calculated value for phenyl radical are used. This 70-kcal mol^{-1} value is also in the area of a C–N bond strength according to conventional organic chemistry wisdom. Thus, we feel that a simple C–N bond fission is unlikely as a first step in the thermochemical decomposition of TNT.

Conclusions

cis-1-Nitropropene is a good theoretical model for studying TNT thermochemical decomposition. It reproduces all of the major structural features of a nitro group being ortho to the methyl group in TNT. Of all of the possible reaction steps we considered, only the intramolecular hydrogen transfer changes the aromaticity of the TNT system, making our 1-nitropropene model not quite as good for that case. Even so, we are able to deduce qualitative trends of this effect.

MINDO/3 results do appear to be more reliable than the MNDO results. We cannot explain the abnormally high values of the activation enthalpies that MNDO gives for the oxygen-transfer steps. It is quite feasible that, in spite of repeated attempts, we have still not obtained the transition states for these processes with MNDO. In the other cases, the MINDO/3 and MNDO results are similar.

Our original goal was to draw conclusions about possible first steps of TNT thermochemical decomposition by comparing our theoretical results with the EPR and IDSC results. On an activation energy basis, several processes appear to be likely: both hydrogen transfers, both oxygen transfers, and the nitro–nitrite rearrangement. The fairly large isotope effect, however, is difficult to explain with anything but the two hydrogen-transfer steps, although we are currently calculating deuterium isotope effects for all of these steps. The EPR signals indicate that radicals must be involved, and the spectrum shows two nitrogens and five hydrogens. The intermolecular hydrogen transfer has the attraction that it produces radicals directly, but not with the required two nitrogens. HONO loss from the hydrogen-transfer product does result in a radical with the required two nitrogens and five hydrogens, and further work is in progress to determine the feasibility of these follow-on steps.[15] On the other hand, intramolecular hydrogen transfer followed by OH loss would result in a radical, but with two nitrogens and only four hydrogens.

The intermolecular hydrogen-transfer process is consistent with all of the known experimental facts for TNT thermochemical decomposition. Thus, we feel that it is a major process early in the decomposition. The low activation enthalpies calculated for several other steps, however, make it probable that these other processes go on just as well. Indeed, all of the previous studies on TNT thermochemical decomposition indicate that the system is quite complicated, particularly in light of the multitude of intermediate products. Our calculations certainly indicate the complexity of the system.

Acknowledgment. We thank Ms. Judy Cross and Mrs. Missy Landess for the expert typing of this manuscript. We also acknowledge many helpful discussions with Profesor Michael J. S. Dewar, Professor William R. Carper, Dr. R. Martin Guidry, Professor Michael L. McKee, and others. One of us (A.G.T.) acknowledges the U.S. Air Force Office of Scientific Research for the award of an University Resident Research Professorship.

Registry No. TNT, 118-96-7; 1-nitropropene, 3156-70-5.

---

[15] Turner, A. G.; Davis, L. P. *J. Energ. Materials*, to be published.

Conformational Transmission in Trigonal-Bipyramidal P^V Compounds. Enhanced Gauche(–) Population around the $C_{4'}$–$C_{5'}$ Linkage in 5′-P^V Phosphorylated Tetrahydrofurfuryl Model Systems

Leo H. Koole,* Eric J. Lanters, and Henk M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands. *Received January 30, 1984*

Abstract: A 300-MHz ^1H NMR study on a number of 5′-phosphorylated (P^{IV}) tetrahydrofurfuryl model compounds (**1a**,**b**, **3a**,**b**, **4a**,**b**) and their P^V trigonal-bipyramidal (TBP) analogues (**1c**,**d**, **3c**,**d**, **4c**,**d**) has been performed. The results show a significantly greater population of the gauche(–) conformation for axially situated tetrahydrofurfuryl around the $C_{4'}$–$C_{5'}$ bond in the 5′-P^V TBP tetrahydrofurfuryls with respect to their related 5′-P^{IV} compounds which show dominant gauche(+) and gauche(trans) conformations. The conformation analysis of the P^V compounds was hampered by pseudorotation. With model compound **6**, in which both equatorial and axial sites that undergo pseudorotation bear a tetrahydrofurfuryl group, a precise analysis was possible resulting in an excess of gauche(–) for tetrahydrofurfuryl in an axial position (318 K, 61%; 217 K, 80%). The corresponding equatorial location shows a relatively small amount of gauche(–) compared with gauche(+) and gauche(trans) (318 K, 24%; 217 K, 13%). The latter values are similar to the P^{IV} counterpart **5**. This conformational transmission in the $C_{4'}$–$C_{5'}$ bond of tetrahydrofurfuryls agrees with quantum chemical calculations. It is suggested that the enhanced charge repulsion between $O_{5'}$ and $O_{1'}$ in the P^V TBP drives the rotation around the $C_{4'}$–$C_{5'}$ bond. The impact for conformational isomerizations in phosphorylated biomolecules (e.g., DNA) is briefly mentioned.

Recent quantum chemical calculations[1,2] on 5′-phosphorylated tetrahydrofurfuryl give cause for the conclusion that increase in coordination of phosphorus from 5′-P^{IV} to 5′-P^V trigonal-bipyramidal (TBP) with the tetrahydrofurfuryl group in axial position (opposite to the introduced ligand, H_2O, e.g.) results in a specific rotation of this group around the $C_{4'}$–$C_{5'}$ bond. The rotamer population then changes from gauche(+), (g^+) and gauche(trans), (g^t) toward gauche(–), (g^-). It was suggested that the enhanced charge repulsion between the exocyclic oxygen ($O_{5'}$) situated in the axial position of the 5′-P^V TBP and the endocyclic oxygen ($O_{1'}$) triggers the rotation around the $C_{4'}$–$C_{5'}$ bond.[3] Experimental

---

[1] van Lier, J. J. C.; Koole, L. H.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 148.

[2] van Lier, J. J. C.; Smits, M. T.; Buck, H. M. *Eur. J. Biochem.* **1983**, *132*, 55.

[3] Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 181.