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This technical report has been reviewed and is approved for publication.

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Quantum mechanical problems of Air Force interest have been studied using available semiempirical molecular orbital programs. Results for NF potential curves were not satisfactory. Studies of molecules involved in TNT thermochemical decomposition, organic electrochemistry, and rocket plumes have yielded promising results.

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MOLECULAR ORBITAL CALCULATIONS
ON MOLECULES OF AIR FORCE INTEREST

By

Capt Larry P. Davis
Capt R. Martin Guidry

TECHNICAL REPORT FJSRL-TR-78-0002

May 1978

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Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
US Air Force Academy, Colorado 80840

PREFACE

This interim report documents work done under Work Unit 2303-F4-03, Molecular Orbital Calculations of Excited State Species, and part of 2303-F3-04, Detonation Modelling and Predictions, between 1 November 1976 and 30 November 1977. Work is continuing in the areas mentioned in the report and will be documented as further technical reports and journal articles. The authors wish to thank Lt Col Ben A. Loving, Capt S. A. Shackelford, Maj Joel W. Beckmann, Capt Charles L. Hussey, and Lt Larry Wright of AFWL for helpful discussions. In addition, thanks are due to D. G. Reynolds and B. J. Darcy for typing the manuscript.

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I. INTRODUCTION

Many chemical problems are amenable to theoretical treatment with molecular orbital techniques. These calculations have now evolved to a point where they can be reliably used to predict molecular geometries, ionization potentials, potential energy curves, heats of formation, and reaction activation energies. The goal of this work unit is to apply available molecular orbital programs to chemical problems of Air Force interest.

Several of these problems have been investigated. First, application of available semiempirical programs to calculation of potential curves of diatomic molecules of laser interest was attempted. The most advanced of the semiempirical programs, MNDO, developed by Dewar and coworkers at the University of Texas[1], was employed to calculate potential curves for the molecule NF. This report concludes the effort to use semiempirical programs to do calculations on diatomics of laser interest.

The Air Force Rocket Propulsion Laboratory needs accurate molecular geometries and heats of formation for boron- and aluminum-containing species[2]. These heats of formation are used as inputs to rocket engine performance codes. MINDO/3 has been used to calculate heats of formation and geometries of boron-containing species. Work is currently underway to use MNDO to calculate heats of formation and geometries of boron- and aluminum-containing species.

Experimental studies on the decomposition rates and mechanisms of explosives have been underway in the laboratory for quite some time[3,4].

MINDO/3 and now MNDO are being employed to calculate energies of suspected decomposition products from TNT. These energies can be used to estimate activation energies for possible decomposition mechanisms. Thus the calculations can be used as an indication of mechanism. The eventual goal for this work is the correlation of explosives properties with the calculated molecular orbital properties.

It would be of great utility to be able to predict oxidation and reduction potentials for species in electrochemical systems. Since oxidation potentials are related to ionization potentials which can be calculated via Koopmans' theorem[5] from molecular orbital energies, one would expect to be able to correlate MO energies with oxidation potentials. The same relationship holds between reduction potentials and electron affinities. Attempts to make these correlations have been reasonably successful with Hückel theory[6]. In this effort, MNDO was employed to predict oxidation and reduction potentials for several aromatic molecules. In addition, electron affinities for several aluminum-containing species predicted to be present in a NaCl-$AlCl_3$ molten salt solution have been calculated to determine which species are more acidic.

II. THEORETICAL METHODS

Several semiempirical methods have been used in this work. All are based on a Hartree-Fock self-consistent field technique including only the valence electrons. Both open-shell and closed-shell molecules have been calculated.

The most basic program used was Quantum Chemistry Program Exchange (QCPE) Program Number 261, Complete Neglect of Differential Overlap Method Including Third Row Elements. The program is an extension of one developed by Pople and Beveridge[7]. It calculates molecular energies, dipole moments, molecular orbitals, and molecular orbital energies. It uses a fixed molecular geometry as input and is not capable of optimizing geometries. It has been used primarily in this work in its INDO (Intermediate Neglect of Differential Overlap) option to calculate ESR splitting constants for radical systems.

The CNDO/S program developed by Jaffe and Del Bene[8] was developed for calculating electronic transition energies. It is based on the CNDO method but contains parameters specifically to give a good fit for electronic transition energies of aromatic molecules. It has been used in this work to calculate transition energies for TNT. It is only capable of calculating closed shell molecules.

The MINDO series of programs developed by Dewar and coworkers at the University of Texas[9,10,11] have developed into useful analytical tools for studying reaction paths, reaction energies, and molecular geometries. The MINDO/3 version[11] has been used in the early stages of this work. MINDO/3 has been shown to give reliable geometries and heats of formation for a wide variety of molecules containing carbon, oxygen, nitrogen, and hydrogen[12,13]. Parameters for fluorine, chlorine, silicon, phosphorus, and sulfur have also been included in order to do calculation on molecules containing these atoms[14,15]. Recently a more sophisticated semiempirical program called MNDO based on an NDDO (neglect of diatomic differential overlap) scheme has been developed by Dewar's group[1]. It has been used exclusively for the molecular energy calculations since it was received in the spring of 1977. It is now capable of doing calculations on molecules containing C,N,O,H,F,Cl,Si,P,S and Al. Results with MNDO have been shown to be better than those from MINDO/3.

III. RESULTS AND DISCUSSION

Potential Curves of Diatomic Molecules

Accurate potential energy curves for electronic states of diatomic molecules are necessary for a consideration of these molecules as lasing species. In addition, the potential curves are used as input to calculations of the reaction rates between molecules. *Ab Initio* programs have been used to calculate these curves when experimental data has not been sufficient to construct RKR potential curves. If available semiempirical programs could be used instead of the *ab initio* programs, calculation of these potential curves would be much easier and quicker.

As a preliminary screening tool, we used the semiempirical programs previously described to calculate the ground state curve for HF. The CNDO/S program gave no minimum in the curve; this failure is not surprising because of its parameterization for transition energies. The CNDO/2 program (both in its CNDO and INDO options) and the MINDO/3 program gave curves of the appropriate Morse shape, but the results were not good at internuclear distance greater than 2Å. All of these correctly predicted the equilibrium internuclear distance to be slightly less than one Å. Since the CNDO/2 program and MINDO/3 are not capable of doing calculations on excited states, MNDO was chosen to do calculations on all possible excited state configurations of the NF molecule.

The NF molecule has 8 valence orbitals (four from each atom) and 12 valence electrons. The valence shell configuration is

$$\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^1$$

For the π orbitals, the first subscript referes to the unperturbed energy and the second refers to the value of the magnetic quantum number. Thus, $\pi_{1,-1}$ and $\pi_{1,+1}$ are a degenerate set of π orbitals; likewise for $\pi_{2,-1}$ and $\pi_{2,+1}$. The MNDO program allowed 16 configuration interaction states. These are listed below:

(1) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^1\sigma_4^{\circ}$

(2) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^2\pi_{2,+1}\sigma_4^{\circ}$

(3) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^{\circ}\pi_{2,+1}^2\sigma_4^{\circ}$

(4) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^1\pi_{2,-1}^1\pi_{2,+1}^2\sigma_4$

(5) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^1\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^2\sigma_4^{\circ}$

(6) $\sigma_1^2\sigma_2^2\sigma_3^1\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^2\sigma_4^{\circ}$

(7) $\sigma_1^2\sigma_2^1\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^2\sigma_4^{\circ}$

(8) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}\pi_{2,+1}^1\sigma_4^{\circ}$

(9) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^{\circ}\sigma_4^1$

(10) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^1\pi_{2,-1}^2\pi_{2,+1}^1\sigma_4^{\circ}$

(11) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^1\pi_{1,+1}^2\pi_{2,-1}^2\pi_{2,+1}^1\sigma_4^{\circ}$

(12) $\sigma_1^2\sigma_2^2\sigma_3^1\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^2\pi_{2,+1}^1\sigma_4^{\circ}$

(13) $\sigma_1^2\sigma_2^1\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^2\pi_{2,+1}^1\sigma_4^{\circ}$

(14) $\sigma_1^1\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^2\pi_{2,+1}^1\sigma_4^{\circ}$

(15) $\sigma_1^1\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^1\pi_{2,+1}^2\sigma_4^{\circ}$

(16) $\sigma_1^2\sigma_2^2\sigma_3^2\pi_{1,-1}^2\pi_{1,+1}^2\pi_{2,-1}^{\circ}\pi_{2,+1}^{\circ}\sigma_4^2$

All sixteen of these configurations were done in the singlet state manifold. For the triplet state manifold, configurations must have unpaired electrons. Configurations (1), (4), (11), and (16) can be mixed to form Σ^+ states. Configurations (2), (3), (5), and (10) are of Δ symmetry, and the remainder are of π symmetry. Thus, from these 16 configurations we expect $4\Sigma^+$, 2Δ, and 4π states in the singlet manifold. In the triplet manifold, we expect $3\Sigma^+$, 1Δ, and 4π states from the 13 configurations. The problem with identification of these states from the MNDO output is that the Hamiltonian is not symmetry-adapted, and therefore states of different symmetry do mix. For some situations, the mixing is not substantial enough to preclude state identification; in other cases, it is.

The program did predict the triplet state to be the most stable, and the equilibrium internuclear distance was predicted to be 1.220 Å. The heat of formation was predicted to be 31.6 kcal/mole. No potential curves will be presented because of the problems in identifying and separating states of different symmetry.

Rocket Plume Species

MINDO/3 was used to make calculations on a number of boron-containing species in order to determine its accuracy for these molecules. Both ground-state geometries and heats of formation were predicted. The results are given in Table I.

Table I shows that the worst predictions are made for the diatomic species. Both the heat of formation and the internuclear distance are considerably off for both BF and BO. Calculation of the heat of formation using experimental internuclear distances only improved the results slightly. The predictions, particularly the heats of formation, get considerably better for the larger molecules. In the case of BF_3, the MINDO/3 results are excellent, because BF_3 was probably one of the molecules used to deduce the semiempirical parameters for boron.

The geometry of BF_2 is not well known. The bond distance is an assumed one, and the 112° bond angle is deduced from ESR studies. MINDO/3 predicts a linear molecule, and its prediction for the heat of formation is considerably off. When the experimentally-deduced geometry is used, the MINDO/3-predicted heat of formation improves tremendously; it becomes -119.2 kcal/mole, in much better agreement than the previous result. This better agreement is a good indication that BF_2 is indeed a bent and not a linear molecule.

The predictions for BO_2 and FBO are both excellent. The assumed geometry for FBO agrees well with that predicted by MINDO/3. Both heats of formation are almost within the experimental error.

BF_2O caused some problems for the MINDO/3 calculation. When the geometry was optimized, the optimization resulted in a molecule with two

TABLE I

MINDO/3 vs. Experimental Parameters for Boron-Containing Molecules

MOLECULE	PARAMETER	EXPERIMENTAL[1]	MINDO/3
BF	B-F Bond Distance	1.265Å	1.196Å
	ΔH_f, 25°C	-27.7±3.3 kcal/mole	-107.5 kcal/mole
BO	B-O Bond Distance	1.2049Å	1.145Å
	ΔH_f, 25°C	0±2 kcal/mole	-55.9 kcal/mole
BF_2	B-F Bond Distance	(1.30Å)[2]	1.264Å
	F-B-F Bond Angle	112°	180.0°
	ΔH_f, 25°C	-141.0±3.0 kcal/mole	-207.3 kcal/mole
BO_2	B-O Bond Distance	1.263Å	1.206Å
	O-B-O Bond Angle	180°	179.9°
	ΔH_f, 25°C	-68±2 kcal/mole	-72.0 kcal/mole
FBO	F-B Bond Distance	(1.30Å)	1.304Å
	B-O Bond Distance	(1.20Å)	1.1.184Å
	F-B-O Bond Angle	(180°)	180.0°
	ΔH_f, 25°C	-144±3 kcal/mole	-145.4 kcal/mole
BF_3	B-F Bond Distance	1.307±.002Å	1.302Å
	F-B-F Bond Angle	120°	120.0°
	ΔH_f, 25°C	-271.42±.4 kcal/mole	-270.2 kcal/mole
BF_2O	BF Bond Distance	1.30±.05Å	1.318Å
	BO Bond Distance	1.40±.05A	1.247A
	O-B-F Bond Angle	117±5°	121.5°
	F-B-F Bond Angle	126±5°	117.0°
	ΔH_f, 25°C	-200±15 kcal/mole	-189.4 kcal/mole

[1] All data taken from JANNAF Thermochemical Data Tables.

[2] Brackets around a parameter mean that it is an assumed parameter.

different O-B-F bond angles. The results given are for those of a symmetry-enforced calculation which forced both O-B-F bond angles to the same value. In either case, the predicted geometry was considerably removed from the experimental geometry. However, in both cases the predicted heats of formation was within the experimental error of the experimental value.

Calculations are now continuing with MNDO on this same set of molecules. In addition, aluminum-containing species will also be studied.

ELECTROCHEMICAL STUDIES

A series of aromatic molecules have been calculated with MNDO in order to correlate the observed electrochemical oxidation potentials with calculated highest occupied molecular orbital (HOMO) energies. These oxidation potentials were measured in acetonitrile/0.5 sodium perchlorate solution vs. the Ag/0.1M Ag^+ electrode[16]. The correlation is shown in Figure 1.

The most obvious feature of Figure 1 is the excellent correlation between the oxidation potential and the HOMO energy for this series of compounds. A least squares fit (shown on the figure) gives a slope of -1.08 and an intercept of -7.17. Biphenyl was not included in the least squares fit because of a geometry optimization problem. When biphenyl is completely optimized, the angle between the rings is predicted to be 72°. The experimental gas phase angle is about 50°. Both results are shown on the figure. The results with the 50° angle are better to such a degree that one is tempted to use this correlation as a predictive tool to deduce the correct ring angle.

These results are very encouraging, not only from the standpoint of the straight line, but also because of the slope being very close to a value of 1.00. This is a strong indication that for these systems the solvent interactions are doing very little to perturb the molecular orbital energies, or at least they are all being perturbed in a like manner. This correlation will be used to predict oxidation potentials for anthracene derivatives. Deviations from the correlation will be used to indicate possible extensive solvent-solute interactions.

MNDO calculations are continuing on aluminum chloride species of an $AlCl_3$/NaCl molten salt system. The principal aim is to calculate electron affinities of these species to determine which are more likely to remove electrons from aromatic molecules.

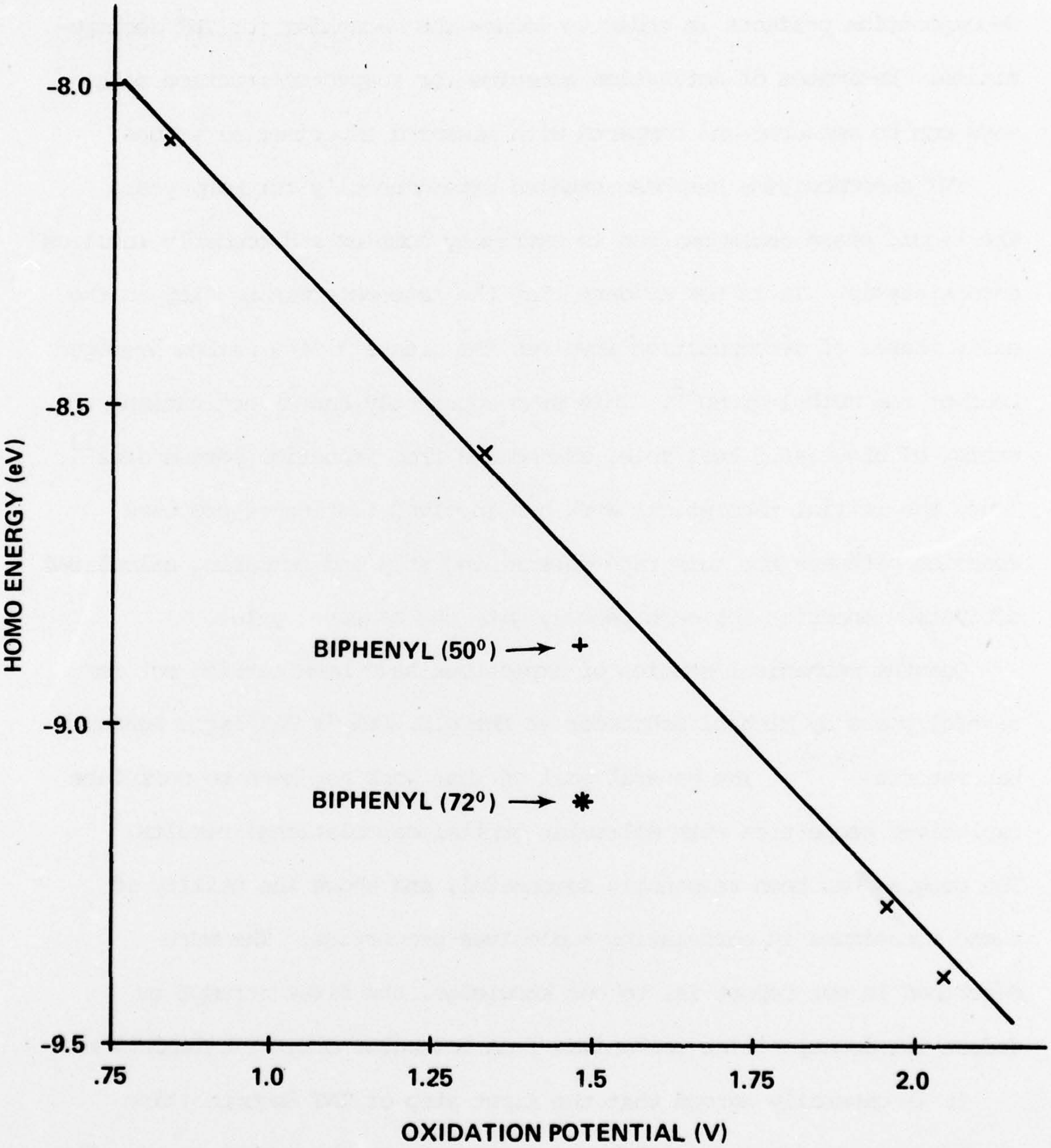


FIGURE 1. CORRELATION BETWEEN OXIDATION POTENTIALS AND HOMO ENERGIES.

TNT THERMAL DECOMPOSITION MECHANISM

Both MINDO/3 and MNDO have been used to calculate TNT and suspected decomposition products in order to deduce the mechanism for TNT decomposition. Estimates of activation energies for suspected reaction pathways can be measured and compared with measured experimental values.

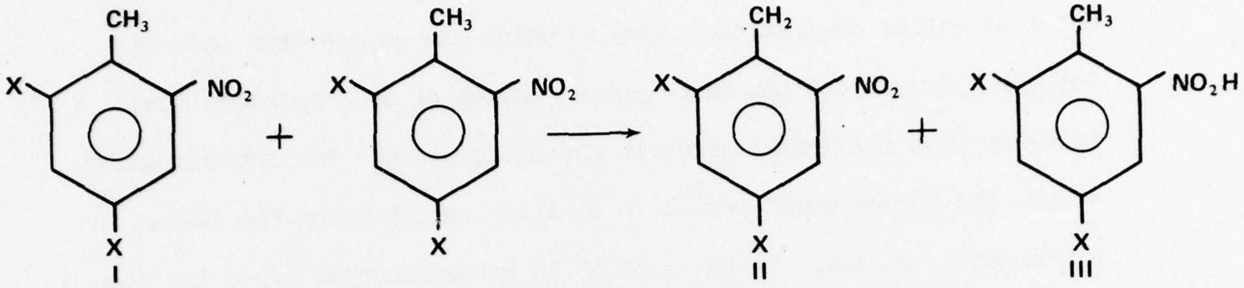
TNT decomposition has been studied experimentally for many years. The liquid phase decomposition is extremely complex and probably involves autocatalysis. It is now evident that the rate-determining step in the early phases of decomposition involves the breakage of a carbon-hydrogen bond of the methyl group[18]. This step apparently has an activation energy of about 46.5 kcal/mole, as deduced from induction period data[19]. Thus, the initial theoretical work has involved testing of proposed reaction pathways for this rate-determining step and comparing calculated activation energies for each pathway with the measured value.

Quantum mechanical studies of explosives have been carried out for several years by Michael Schroeder at the U.S. Army's Ballistic Research Laboratories[20-26]. The general goal of that work has been to correlate explosives properties with molecular orbital calculational results. The program has been reasonably successful, and shows the utility of these techniques in correlating explosives properties. The work described in our report is, to our knowledge, the first attempt to deduce TNT decomposition mechanisms from molecular orbital calculations.

It is generally agreed that the first step of TNT decomposition occurs as an oxidative attack by a nitro group on the methyl group. The possibility exists that this could occur in either an inter- or an intramolecular fashion. In addition, either of these processes could occur as either an insertion step in which the oxygen atom inserts between hydrogen and the methyl group carbon or as a hydrogen atom transfer from the methyl group to the nitro group. For intramolecular steps, the former would result in a nitroso alcohol and the latter in a diradical species. In the case of an intermolecular step, the insertion would result in a nitroso compound and an alcohol, and the transfer would produce two radical species. The para NO_2 group could also be involved in any of these steps. These possible first steps are shown in Figure 2.

As a first step in attempting to calculate molecular energies along the reaction paths mentioned above, nitrobenzene was studied[17]. Of primary interest was the correctness of the geometry prediction in terms of the angle between the phenyl group and the nitro group. The MINDO/3 program incorrectly predicted that the two are perpendicular; the experimental evidence indicates a planar molecule. MNDO does not predict a perpendicular conformation, but it still predicts a non-planar molecule. However, the energy differences between these conformations is only a few kcal/mole. Therefore, any errors made in the heats of formation for these nitro group-containing molecules will only be a few kcal/mole, and there probably will be at least partial cancellation between reactants and products of these errors.

MINDO/3 was used to calculate heats of formation of TNT and some of the possible intermediates shown in Figure 2. Species I, II, III, IV, and VI have been completed. In addition, the OH radical, hydroquinone (VIII), the hydroquinone radical (IX), and quinone (X) have been done in order



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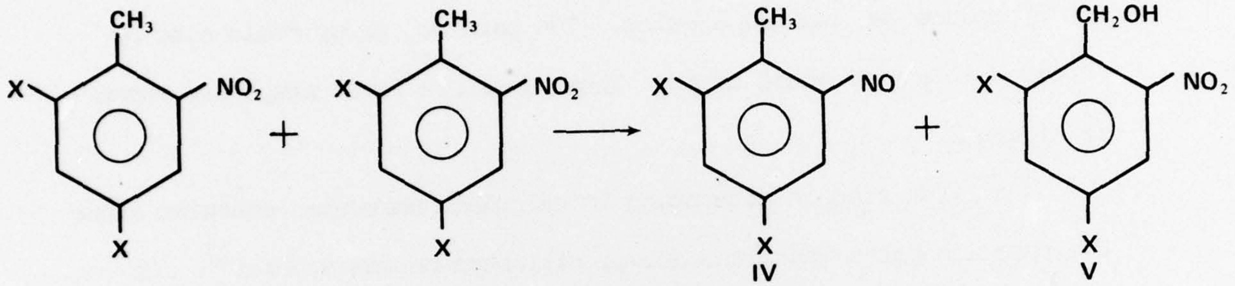

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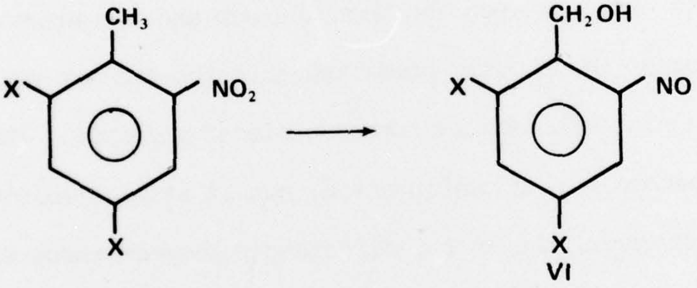

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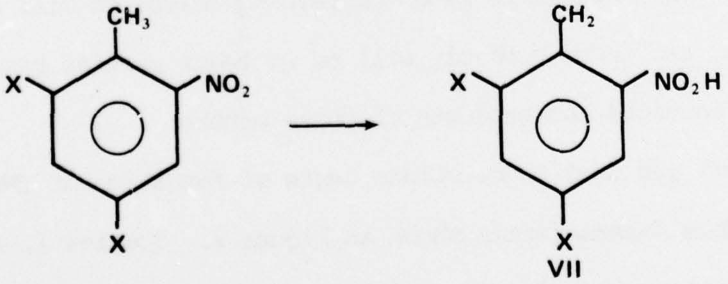

X ≡ NO$_2$

INTRAMOLECULAR OXIDATIVE TRANSFER

FIGURE 2. POSSIBLE FIRST OXIDATIVE STEPS FOR TNT THERMAL DECOMPOSITION.

to assess potential reactions between hydroquinone and TNT. The diradical species VII was also attempted, but the SCF calculation would not converge. Initially this was thought to mean that it would not be very stable, but it could very well mean that the initial approximation to the density matrix was not good enough to allow convergence. MNDO has been used to calculate these same species since it has been operable on our system. To date the hydroquinone species, OH, TNT, and II have been done. The results for all of these calculations are given in Table II. Efforts are continuing to calculate the remaining species with MNDO.

The results with the MINDO/3 method given in Table II were not done with complete geometric optimization. All aromatic rings were assumed planar, and the NO_2 groups ortho to a methyl or a methylene group were held fixed at a 45° angle to the ring. Para NO_2 groups were held fixed in a coplanar configuration with the ring. The MINDO/3 method uses the half-electron method to calculate radicals.

In the case of MNDO, complete geometry optimization was allowed. In the case of the radicals, geometry optimization was done with the unrestricted Hartree-Fock procedure (UHF). The final value for the heat of formation was then calculated with the half-electron method utilizing the UHF-optimized geometry. These procedures were followed because the UHF optimization was much more rapid than the half-electron optimization, but the MNDO parameters are set such that the heats of formation calculated with the half-electron method are more accurate than those calculated with the UHF method. Sample calculations on the hydroquinone

TABLE II

Heats of Formation for TNT Decomposition Products

	Heat of Formation at 25° (kcal/mole)	
MOLECULE	MINDO/3[1]	MNDO[2]
OH	16.9	0.5
TNT	-11.3	76.4
II	23.4	111.5
III	-1.4	-
IV	11.6	-
VII	-84.1	-74.0
IX	-49.9	-40.7
X	-40.8	-35.7

[1] All aromatic rings assumed to be planar, NO_2 groups ortho to methyl or a methylene group held fixed at a 45° angle to the ring; para NO_2 fixed coplanar with the ring.

[2] Complete geometric optimization allowed, heat of formation calculated with the half-electron method for radicals using the UHF-optimized geometry.

radical (IX) produced essentially the same heat of formation with the half-electron method utilizing its own optimized geometry. For both MNDO and MINDO/3 calculations on quinone, configuration interaction was included because of its possible diradical character.

Table II gives some interesting results. For the quinone species (VIII, IX, and X), MINDO/3 and MNDO results are reasonably close. However, the TNT species show quite a large discrepancy between the two methods. It is interesting to point out that the MINDO/3 results for TNT itself is much closer to the true experimental value of -17.8 kcal mole[27] than the more advanced MNDO method. The difference may lie in the difference in the method of optimization in each case, but since MNDO was completely optimized geometircally while MINDO/3 was not, one would expect MNDO to give a lower heat of formation than MINDO/3, but it does not. The difference in energy, however, between the TNT molecule and its derived radicals appears to be about the same for both methods. This, the estimated E_a's will be about the same. The two calculated values for the OH radical (16.9 kcal/mole for MINDO/3 and 0.5 kcal/mole for MNDO) bracket the experimental value of 9.49 ± .04 kcal/mole as taken from the JANNAF tables.

In order to compare with the measured activation energies, the transition state geometry would have to be found. For endothermic reactions, a calculation of ΔH for the reaction will give a lower bound to the activation energy. This ΔH for several potential system reactions can be calculated from Table II. Efforts are currently underway to obtain the transition state geometry and thus a better estimate of E_a.

One possible intermolecular first step for TNT decomposition from Figure 2 is:

2TNT → II + III

Using the tabulated heats of formation of *MINDO/3* from *Table II*, the *ΔH* for this reaction is 44.6 kcal/mole. The minimization for Species III has not yet been completed with MNDO, but the energy difference between TNT and Species II indicates that the MNDO-calculated E_a for this step will be close to that of MINDO/3. The MINDO/3 value is certainly close to the experimentally-measured value for the rate-determining step of TNT decomposition of 46.5 ± 1.5 kcal/mole[4].

Unfortunately, not all of the other species have been calculated, so that estimates of E_a for the other possible first steps given in Figure 2 could be made. These calculations are continuing. We can, however, estimate an E_a for the possible further degradation of species III:

III → IV + OH

ΔH for this process is calculated to be 29.9 kcal/mole with MINDO/3.

In addition, ΔH's for the intermolecular reactions of the quinone species with TNT can be calculated. The donation of a hydrogen to TNT can be written as:

VIII + TNT → IX + III

ΔH for this reaction is calculated to be 44.1 kcal/mole with MINDO/3. For the further donation from IX to another TNT:

IX + TNT → X + III

ΔH is calculated to be 19.0 kcal/mole. The first donation has an activation energy only slightly less than the TNT-TNT transfer, but only needs to be slightly less in order to speed the decomposition significantly. Also, the second donation from the hydroquinone radical species IX has a much lower activation energy. Experimentally, the induction period of the decomposition decreases markedly when hydroquinone is added to TNT.

Several points need to be made about these calucalations used for estimating E_a for these reactions. First, the calculated ΔH's obtained thus far are only lower bounds to the actual calculated activation energies. Second, these MO calculations are on isolated molecules, and thus are strictly applicable only for gas phase reactions. However, if intermolecular effects on the reactions are negligible in the liquid phase, then the calculated energies will be good approximations to the experimental activation energies. Third, use of activation energies alone to predict relative reaction rates for different reactions is not valid unless the frequency factors or preexponentials in the Arhennius expression are similar.

IV. CONCLUSIONS AND RECOMMENDATIONS

The attempt to use semiempirical molecular orbital techniques to calculate potential energy curves for the electronic states of NF has not been successful. The MNDO program produces electronic states which cannot be identified with the proper diatomic symmetry for certain values of the internuclear coordinate. Also, one would like to include many more configurations in the configuration interaction than the program allows. Our recommendation is that potential surfaces for small molecules be left to the more sophisticated *ab initio* schemes.

Heats of formation and geometry of boron-containing species of rocket plume interest with MINDO/3 are remarkably good in some cases and rather bad in others. The MNDO program results are needed in order to make an assessment of the usefulness of this technique for these applications.

Calculations of kinetic parameters for TNT decomposition have really only begun. The initial attempts have already produced an estimate for a first-step activation energy value for the rate-determining step. These calculations should prove extremely useful in deciding among potential mechanisms for TNT decomposition.

Initial attempts to correlate oxidation potentials for aromatic molecules with the calculated molecular orbital energies have been very successful. These correlations can hopefully be used to identify anomalous systems in which appreciable solute-solvent interactions are occurring.

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