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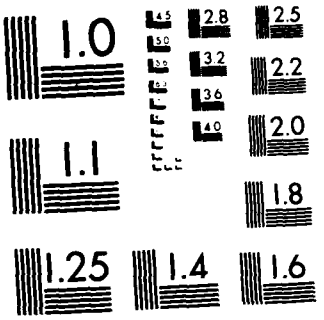

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FINAL REPORT

A MODEL FOR THE THERMAL DECOMPOSITION OF TNT; THEORETICAL REACTION PROFILES

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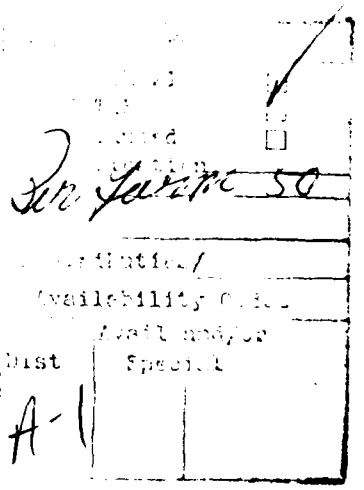


A MODEL FOR THE THERMAL DECOMPOSITION OF TNT; THEORETICAL REACTION PROFILES

by

Almon G. Turner

ABSTRACT

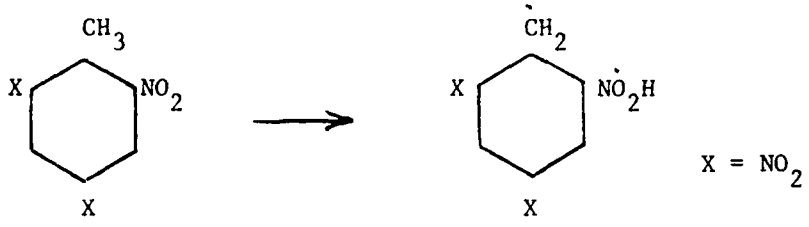
The molecule 1-nitropropylene has been investigated as a model system for the simulation of the thermal decomposition of TNT. Two distinct types of reaction mechanisms were considered: Intramolecular Mechanisms and Bimolecular Mechanisms. Intramolecular mechanisms investigated include an oxidative hydrogen atom transfer to form the diradical aci nitropropylene and an oxidative oxygen atom insertion reaction to form 1-nitro-3-hydroxy propylene. Semi empirical molecular orbital calculations (MNDO and MINDO/3) were carried out to obtain a reaction profile for these mechanisms, and indicated that the oxygen atom insertion reaction should lead to the reaction products, methyl nitrite and acetylene. This is not in accord with experiment. The profile for the oxidative hydrogen atom transfer was found to reproduce many of the features known for the thermal decomposition of TNT.

Bimolecular mechanisms considered included an oxidative hydrogen atom transfer from one nitropropylene molecule to another to form the 1-nitropropylene radical and the aci form of nitropropylene and an intermolecular oxidative insertion reaction to form 1-nitro-3-hydroxy propylene and 1-nitroso propylene. Preliminary reports are given for these bimolecular mechanisms.

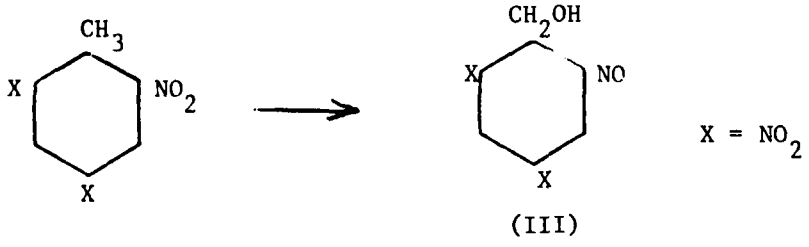
I. INTRODUCTION:

A large number of experimental studies have been carried out in an effort to obtain an understanding of the thermal decomposition of trinitrotoluene (TNT)[1]. These studies have resulted in the proposal of four different possible reaction mechanisms for the process[2]. The mechanisms proposed are:

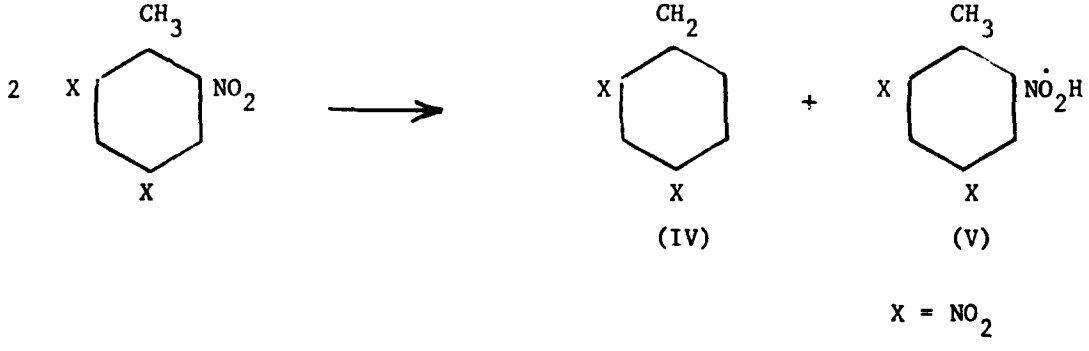
a. Intramolecular Oxidative Hydrogen Atom Transfer.



b. Intramolecular Oxidative Oxygen Atom Transfer.



c. Intermolecular Oxidative Hydrogen Atom Transfer.



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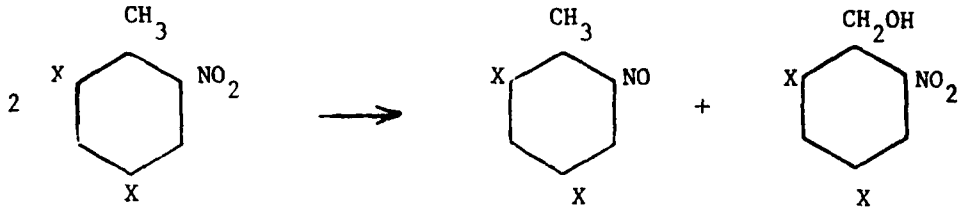


(VI) (VII)

X = NO_2

Recent advances in semiempirical molecular orbital methods (MNDO, MINDO/3) have demonstrated that the standard enthalpies of formation, ΔH_f°, can be calculated with some confidence for small molecules[3]. These same methods have been utilized to study reaction mechanisms for elementary processes of the type which occur in the above mechanisms[4]. The shear size of the TNT molecules prohibits an exhaustive investigation of the proposed mechanisms by the MNDO method. Accordingly it would be advantageous to find a smaller molecular system which might possess the salient features of TNT, and could thus be used to model the mechanisms proposed above. The author has suggested that the 1-nitropropylene molecule might be suitable for these purposes. The research reported below is concerned with the use of 1-nitropropylene to model the thermal decomposition of TNT.

II. OBJECTIVES

The main purpose of this research was to ascertain the extent to which mechanisms analogous to those listed above but studied in the system 1-nitropropylene can be used to model the decomposition of TNT. Specific objectives were:

(1) To study the thermodynamics of the proposed reactions and compare the results to the corresponding values for the TNT system.

(2) To obtain reaction profiles for each of the proposed mechanisms and to identify the transition state for each of the mechanisms. Successful identification of a transition state enables one to calculate

the energy of activation for the process, which in turn can be compared to results obtained from the experimental study of the decomposition.

III. THEORETICAL METHODS

The principal method employed to study the decomposition of 1-nitropropylene was the MNDO (Modified Neglect of Differential Overlap) molecular orbital method of Dewar et. al.[3,4]. The method was applied in its "closed shell" form to those mechanisms which did not involve radical species, while it was combined with the method of configuration interaction to treat radical species[5]. 3 x 3 configuration interaction was carried out using the ground state configuration and the two configurations obtainable from it using the two lowest unoccupied molecular orbitals obtained from the ground state calculation.

IV. THERMODYNAMIC STUDIES

The specified chemical reaction (mechanisms) studied were:

i. Intramolecular Hydrogen Atom Transfer

$CH_3CHCHNO_2 \longrightarrow \cdot CH_2CHCHNO_2H$

1-nitropropylene (I) ACI-nitropropylene (II)

ii. Intramolecular Oxygen Atom Transfer

$CH_3CHCHNO_2 \longrightarrow HOCH_2CHCHNO$

1-nitroso-3-hydroxy propylene (III)

iii. Intermolecular Hydrogen Atom Transfer

$2\ CH_3CHCHNO_2 \longrightarrow \cdot CH_2CHCHNO_2$ (IV) $+$ $CH_3CHCHNO_2H$ (V)

iv. Intermolecular Oxygen Atom Transfer

$2\ CH_3CHCHNO_2 \longrightarrow CH_3CHCHNO$

1-nitrosopropylene (VI)

$+ HOCH_2CHCHNO_2$

1-nitro-3-hydroxy propylene (VII)

The ground state energies and heats of formation were calculated for species I - VII and the corresponding heats of reaction calculated. The 1-nitropropylene molecule was calculated in a geometry where the nitro

group was rotated about the carbon atom so as to have it in the same conformation that it would have were it a part of a TNT molecule. The energy of the true ground state form (unrotated) was found to be 18.10 Kcal/mole. The energy of the rotated "TNT like" form was calculated to be 18.99 Kcal/mole. The results of these calculations are shown below.

Calculated Standard Heats of Formation

Mechanism	Reactant	Product(s)	ΔH_f°	TNT Case
i	18.99	33.50	+14.51	16.6
ii	18.99	-30.32	-49.31	-49.9
iii	37.98	IV 48.63; V 8.88	19.53	16.8
iv	37.98	VI 12.45; VII 022.98	-48.51	-52.4

The experimental activation energy for the initiation step in the decomposition of TNT is known to be 40-46 Kcal/mole. Since the ΔH_f° for the reaction is a lower bound for the corresponding activation energy all the above mechanisms are possible. The corresponding enthalpy changes have been calculated for three of the four mechanisms in the case of TNT. The values are given in the last column of the table. Note the relative order of agreement is good. On the basis of thermodynamics the 1-nitropropylene system seems to reflect the same energetic behavior as the TNT system.

V. INTRAMOLECULAR HYDROGEN ATOM TRANSFER MECHANISM

Optimization of the ground state energy of aci nitropropylene yielded a value of 33.50 Kcal/mole for the heat of formation of the product molecule. The hydrogen atom transfer was initially viewed by using the hydrogen atom oxygen atom distance as the reaction coordinate. The distance varies from 3.73 Å in 1-nitropropylene to 0.95 Å in product aci form. A reaction profile was calculated along this path at values for the reaction coordinate of 3.73, 3.27, 2.77, 2.27, 1.77, 1.50, 1.40, 1.35, 1.30, 1.25, 1.20, 1.175, 1.15, 1.125, 1.10, 1.00, 0.95 Å. A maximum was obtained in the vicinity d_{O-H} = 1.20 where ΔH_f° = 81.4 Kcal/mole, which corresponds to an activation energy of 62.4 Kcal/mole. The product state was identified at a heat of formation of about 27.4 Kcal/mole and did not correspond geometrically

to the aci form of 1-nitropropylene. Attempts were made to start from this new product state and back calculate to the initial state. These attempts were unsuccessful.

The next series of calculations performed consisted of starting the reaction profile in the product state and attempting to find a path which would lead to the starting material. This was done by defining the reaction coordinate to be the hydrogen atom - methyl carbon atom distance. This distance varies from 3.234 Å, to 1.497 Å in the reactant. Points were calculated at values of 3.20, 3.00, 2.50, 2.00, 1.75, 1.60, 1.50, 1.40, 1.35, and 1.30 Å. A profile was obtained with a maximum energy of 86.3 Kcal/mole corresponding to an activation energy of 52.8 Kcal/mole occurring at d_{C-H} = 1.37 Å. An attempt was made to reverse the calculation and it was found that the path was not reversible, the reverse path leading to a new maxima in energy in excess of 76 Kcal/mole. The two profiles intersected at about 1.59 Å with an energy of about 69 Kcal/mole. Application of the MINDO/3 method led to the same basic results. From these calculations it was concluded that neither the hydrogen - oxygen atom distance nor the hydrogen atom - methyl carbon atom distance was a suitable reaction coordinate. It is probably necessary to use both. In addition as the molecule proceeds from reactant to product a considerable readjustment occurs in the $H_3C_1-C_2=C_3-N_4$ framework. The C_1-C_2 and C_3-N_4 bonds are shortened considerably, while a lengthening occurs in the C_2-C_3 bond. Accordingly, a series of calculations were carried out for d_{O-H} distances of 0.96, 1.00, 1.10, 1.20, 1.70, 1.40, and 1.50 where the $C_1-C_2=C_3-N$ framework was fixed at values which corresponded to one third, one half, and two thirds of the way along the progression from starting material to product material. The results of these calculations are in Table 1. Listed are the ΔH_f°'s and the algebraic sign of dE/dX.

Table 1 **GRID MOVING FROM REACTANT TO PRODUCT**

	d_{O-H} 0.96	1.00	1.10	1.20	1.30	1.40	1.50
Starting Material	62.6-	63.8+	91.6-	81.8-	71.5-	61.8-	53.0-
1/3	42.9-	43.7+	52.0+	83.1-	73.4-	64.0-	55.4-
1/2	76.6-	37.4+	45.7+	85.8-	76.8-	67.8-	59.3-
2/3	32.6-	33.7+	45.6+	89.3-	81.2-	72.4-	64.0-
Product Material	27.6-	28.4+	36.9+	56.1+	96.8-	88.9-	81.1-

The line delineates the region of the hypersurface where maxima are located.

The largest maxima being in the region of $120 < d_{O-H} < 1.30$ with the geometry being virtually TNT or product like. Calculations were then performed to test the reversibility of the reaction coordinate d_{O-H}. Starting with the TNT like geometry (two thirds) at $d_{O-H} = 1.10$, d_{O-H} was allowed to increase to 1.20, 1.30 and 1.40. At each point a lower energy form was found. This indicated that the $C_1-C_2 = C_3-N$ framework must also be relaxed.

A grid search was conducted by performing calculations which start with a TNT like geometry and allowing d_{O-H} to vary from 1.00 to 1.60 and at the same time allowing d_{C-H} to vary from 1.20-1.80. The results are shown in Table 2.

Table 2 **GRID SEARCH HYDROGEN ATOM TRANSFER**

		d_{O-H}			
		1.00	1.20	1.40	1.60
	1.20	119.9-	84.0-	61.8-	48.0-
	1.40	86.5-	83.5-	72.0-	63.3-
d_{C-H}	1.60	66.2-	78.9+	91.2-	88.2-
	1.80	54.9+	72.1+	108.2+	110.5-
	2.00				

The solid line in the table defines points in the hypersurface along which maxima occur.

Calculations were next carried out by starting with the product like geometries for d_{O-H} equal to 1.00 and attempting to proceed to the TNT like geometries for each C-H distance. It appears that some points of lower energy can be located in this manner.

In summary, the location of transition state for this mechanism is particularly difficult and involves a great deal of trial and error calculation. It is felt that a transition state is being approached asymptotically but the calculation points to the severe need for an analytical approach to the problem.

VI. INTRAMOLECULAR OXYGEN ATOM TRANSFER MECHANISM

A calculation of the optimized ground state energy of the product molecule, 1-nitroso-3-hydroxy propylene yielded a standard enthalpy of formation of -30.32 Kcal/mole. The methyl carbon-oxygen atom distance was employed as a reaction coordinate and it was allowed to vary from 3.73 Å (starting material) to 1.40 Å (product material). A reaction profile was obtained which showed an activation energy of 96 Kcal/mole and a maximum present at d_{C-O} = 1.75 Å. An examination of the product state (ΔH_f° = 21.71 Kcal/mole) showed it to consit of molecular acetylene, C_2H_2; and methyl nitrite, CH_3ONO. A rerun of the calculation using configuration interaction led to new transition state of a higher heat of formation than that calculated previously. As such, it was not pursued further. An attempt was made to establish a reaction profile in the direction product to reactant. It also led to a higher activation energy.

VII. INTERMOLECULAR MECHANISMS

Work was just being initiated on these mechanisms as the period of my fellowship came to end. Planary calculations were begun on a mechanism in which the 1-nitropropylene molecules were stacked end to end with the hydrogen atom to be transferred of one molecule located symmetrically between the two oxygen atoms of the nitro group of the second molecule. The distance from the oxygen atom of the second molecule to the methyl carbon atom of the first molecule was used as a reaction coordinate. These efforts are continuing at the present time.

VIII. AN ANALYTICAL APPROACH

The principal difficulties encountered in these studies seems to be the recognition of what to use for a reaction coordinate in a given mechanism. The reaction coordinate is generally not a simple atom-atom distance, bond angle or dihedral angle but rather it is expressible as a linear combination of those atom-atom distances, bond angles and dihedral angles which change markedly as one proceeds from reactant to product. As such, it can be uniquely identified once it is recognized what internal coordinates (bond distance - bond angle basis) enter into it. One way to proceed would be to do a few planary calculations to identify which internal coordinates, $|q|$ enter the reaction coordinate, ϕ and then solve the required set of linear equations to identify the reaction coordinate. Explicitly, let

$$\phi = \sum_i a_i q_i \qquad i = 1, n \tag{1}$$

Consider the energy as a function of ϕ,

$$E = E(\phi) \tag{2}$$

Since we are always seeking a transition state, E is a maximum for such a state,we can write

$$E = X\phi^2 + Y\phi + Z \tag{3}$$

and we know that $X < 0$ and $Y > 0$. The reaction coordinate must belong to one of the irreducible representations of the point group which is appropriate to the transition state geometry.

From a set of n^2 values for the $|q|$ one can calculate n^2 values of the energy ε. Since the energy is a quadratic function of the $|q|$ we can write

$$\varepsilon_1 = b_{11}q_{11}^2 + b_{12}q_{12}^2 + \cdots b_{1n}q_{1n}^2 + b_{1o}q_{11} + b_{2o}q_{12} + b_{no}q_{1n} + b_1$$
$$\vdots \tag{4}$$
$$\varepsilon_{n2} = b_{11}q_{n1}^2 + b_{12}q_{n2}^2 + b_{1n}q_{n,n}^2 + b_{10}q_{n,1} + b_{no}q_{n,n} + b_1$$

The linear equations (4) can be solved to obtain the coefficients $|b|$. These coefficients in turn are related to coefficients $|a|$ of equation (1). Namely

for quadratic terms

$$b_{ij} = X\, a_i a_j \tag{5}$$

for linear terms

$$b_{lo} = Y_{al} \tag{6}$$

and

$$b_1 = Z \tag{7}$$

From eqn. (6) we in effect know the coefficients $|a|$ to within the normalization constant Y. If we redefine the norm of the space spanned by the reaction coordinate, we can calculate the $|a|$ and then obtain our reaction coordinate.

IX. RECOMMENDATIONS

On the basis of the above research the following recommendations can be made:

1. That the grid search method employed in part V be continued until a transition state is obtained which will reversibly interconnect reaction and product for the intramolecular hydrogen atom transfer mechanism.
2. That the intramolecular oxygen atom transfer be rejected as a possible reaction path in the initiation of the thermal decomposition of TNT.
3. That the analytical approach (part VIII) to finding a reaction coordinate be tested in the context of a known reaction mechanism and if successful then used to pursue the study of the bimolecular mechanisms of part VII.
4. That the questions concerned with the effects of overcompleteness and undercompleteness in the choice of the set of variables $|q|$ be investigated on the analytical approach (part VIII).

REFERENCES

1. For representative studies see:

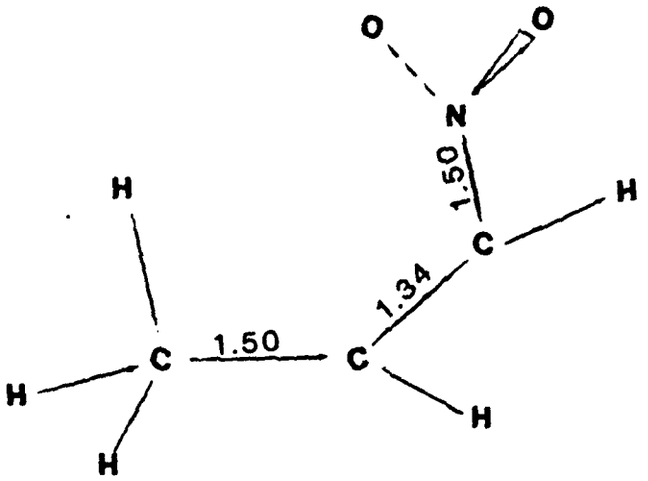
R. Robertson, J. Chem. Soc. 119, 1 (1921); Trans. Far Soc. 44, 977 (1948); M. A. Cook and A. B. Taylor, Ind. Eng. Chem. 48, 1090 (1956); J. C. Dacons, M. J. Kamlet, and D. V. Sickman, NAVORD Rept. 6831 (1970); J. C. Dacons, H. C. Horst, and M. J. Kamlet, J. Phys. Chem. 74, 3035 (1970); R. N. Rogers, Anal. Chem. 39, 730 (1967); J. M. Rosen and J. C. Dacons, Explosivstoffe, 11 250 (1968); J. W. Beckmann, J. S. Wilkes, and R. R. McGuire, Thermchim. Acta, 19, 111 (1977); S. A. Shackelford, J. S. Wilkes, and J. W. Beckmann, J. Org. Chem. 42, 4201 (1977).

2. R. M. Guidry and L. P. Davis, Proc. of the Ninth Annual Pittsburg Conference, American Instrument Society, Volume 9, Modeling and Simulation, Page 331, 1978.

3. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. 97, 1285 (1975).

4. M. J. S. Dewar and W. Thiel, J. Amer. Chem. Soc. 99, 4899 (1977).

5. The open shell structure of radical species necessitates the inclusion of neighboring configurations of the same spin multiplicity. We assume that we are operating at a "near" Hartree Fock level of approximation and include only configurations obtainable from the parent configuration by "two electron jumps".



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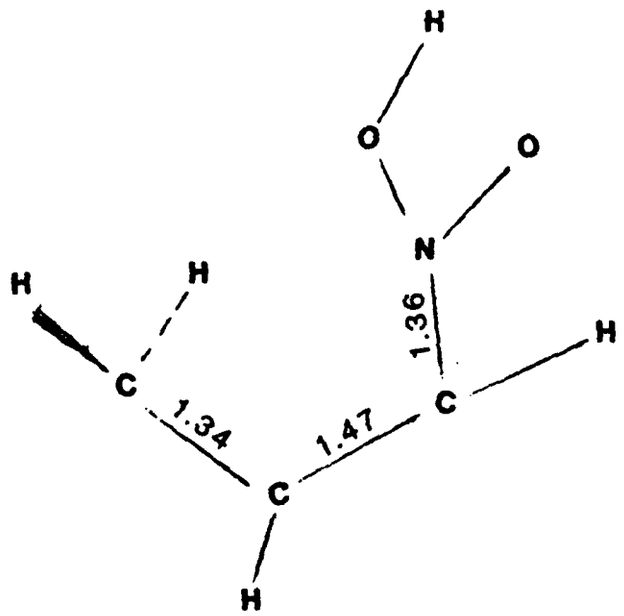

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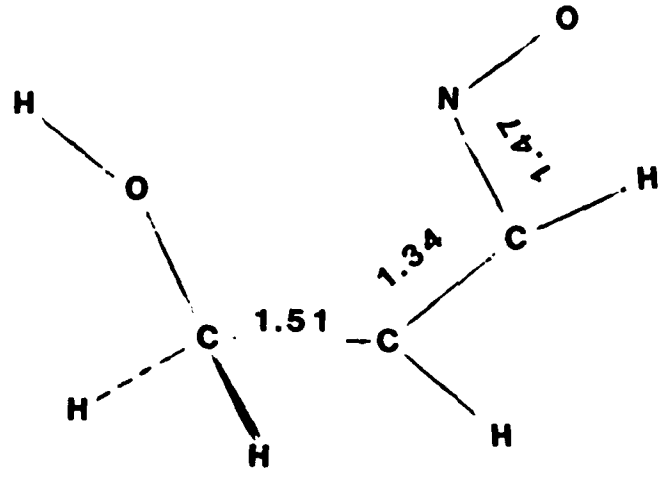

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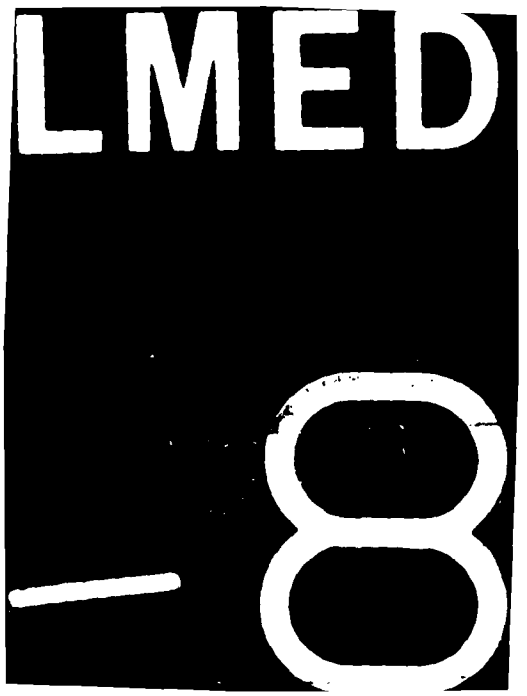
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