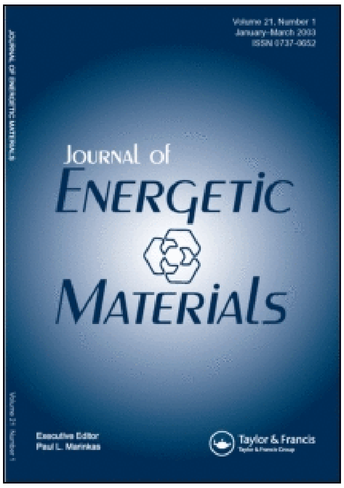

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Some Ab initio MO studies relevant to the thermal decomposition of TNT

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SOME AB INITIO MO STUDIES RELEVANT TO THE THERMAL DECOMPOSITION OF TNT

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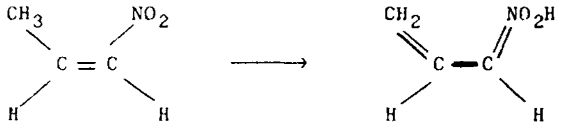
Ab initio molecular orbital calculations in a variety of basis sets and including electron correlation have been used to examine the energetics of the channel for TNT decomposition involving intramolecular hydrogen transfer. Calculations both for the model system, 1-nitropropene, and for TNT itself, are reported. These studies pay particular attention to the determination of the transition state for these reactions. It is shown that model systems have considerable value in such studies, as do semiempirical methods. The calculated barrier for intramolecular hydrogen transfer in TNT is found to be close to the measured activation energy for the induction reaction.

INTRODUCTION

There is now an increased awareness of the need to consider explosives at a molecular level and the value of molecular orbital (MO) methods to achieve this. Such theoretical studies allow the energy minima and transition states on the various possible potential energy surfaces for the possible modes of reaction to be located and their energetics determined. Due to the high pressures occurring in explosions both possible intra- and inter-molecular mechanisms need to be explored. Thus the size of the molecular systems which need to be studied may be considerable, so that it may not be possible to achieve this using "state-of-the-art" computational methods. For this reason two approaches have been considered in an attempt to reduce the computational effort required, whilst still retaining an acceptable level of accuracy. These are i) the use of simplified semi-empirical, rather than *ab initio* MO methods, and ii) the use of model systems to reduce the size of the systems under investigation. Of particular interest has been the possible decomposition channels of 2,4,6-trinitrotoluene (TNT). Here, *cis*-1-nitropropene has been used[1,2] as a theoretical model for TNT, with particular reference to the decomposition channel involving the intramolecular hydrogen transfer



(1)

1-nitropropene aci-nitropropene

The choice of this decomposition channel arises from experimental studies[3,4] of the thermochemical decomposition of TNT and from *ab initio* MO studies[2] of some decomposition reactions of 1-nitropropene. The experimental studies[3] showed products which were consistent with the rupture of a methyl C-H bond during the early stages of decomposition. In addition, isothermal differential scanning calorimetric experiments have shown[4] a significant primary hydrogen kinetic isotope effect (KIE) for the thermal decomposition of TNT indicating that methyl group C-H bond rupture may be rate-determining in the initial stages. On the theoretical side[2], the intramolecular hydrogen transfer shown in reaction (1), has been shown, on the basis of thermodynamics, to be preferred over other possibilities.

Calculated ΔH^{o}'s at the semi-empirical MNDO and MINDO/3 level[1] indicate that 1-nitropropene is a valid model for use in studying TNT decomposition, and ab initio calculations of the energy change accompanying reaction (1) lend support to the use of MNDO and MINDO/3 methods. However, it is only at these semi-empirical levels that the important problem of the transition state structure and energy have been addressed, and no ab initio calculations of the structures corresponding to intramolecular hydrogen transfer in TNT by the reaction analogous to (1) have been reported apart from the calculation of an optimized geometry of TNT itself[5].

In this paper we address the usefulness of semi-empirical methods and model systems further. We report ab initio calculations of the transition state associated with reaction (1) in a number of basis sets, and investigate the effects of both correlation energy and zero-point effects on the calculated barrier. We also describe ab initio calculations in a limited basis set, of the reactant, product and transition state associated with the corresponding intramolecular hydrogen transfer in TNT.

COMPUTATIONAL METHODS

All calculations described here are ab initio MO calculations using contracted gaussian basis sets. We use the standard basis sets of Pople and coworkers (STO-3G[6], 6-31G[7], 6-31G*[8]) and a triple zeta basis of Dunning[9], augmented[10] by a d polarization function on carbon, nitrogen and oxygen, and a p polarization function on hydrogen. We denote this basis TZP. Stationary points (minima and saddle points) on the potential energy surface of the reactions studied were located at the restricted Hartree Fock (RHF) level by the use of analytic gradients of the energy as implemented in the program GAMESS[11], and harmonic frequencies were calculated using analytic second derivatives of the energy using the program CADPAC[12]. Correlation effects were included by means of configuration interaction (CI) calculations, using the ATMOL system of programs[13]. The calculations were carried out on the CRAY XMP/48 of the SERC Rutherford Atlas Laboratory and the CYBER 205 of the University of Manchester Regional Computer Centre.

COMPUTATIONAL RESULTS

In table 1 we show the energies for the optimized structures of the reactant, product and transition state for reaction (1) obtained in a number of basis sets.

TABLE 1

Total Energies (a.u.) and Relative Energies[a] (kJ mol^{-1}) for Reactant, Product and Transition State of Reaction (1).

	STO-3G//STO-3G	6-31G//6-31G	6-31G*//6-31G*	TZP//6-31G*
Nitropropene	-316.3667	-320.3802	-320.5417	-320.6486
	(0)	(0)	(0)	(0)
Aci-nitropropene	-316.3494	-320.3704	-320.5124	-320.6274
	(45.4)	(25.7)	(76.9)	(55.7)
Transition State	-316.2896	-320.2972	-320.4492	-320.5612
	(202.5)	(218.0)	(243.0)	(229.5)

[a] The relative energies are given in parentheses.

The transition states are all characterized by having a single imaginary frequency corresponding to the reaction path. We note that in a comparison with the results of Turner[2] at the 6-31G*//6-31G* level, our calculated energy is significantly lower than his for nitropropene, leading to a calculated ΔH for reaction (1) of 77.1 kJ mol^{-1} (table 1) compared with the value of 44.7 kJ mol^{-1} given by Turner. Our largest basis RHF calculation, using the TZP basis at the optimized 6-31G* geometry gives energies significantly lower than those from the largest basis of Turner. However, the trend we observe in the variation of ΔH with basis set is similar to that reported by Turner, with the TZP value being smaller than the 6-31G* value. The calculated barrier height with respect to the nitropropene reactant shows less basis set dependence than the calculated ΔH values. Our calculated values of $\Delta H^{\ddagger}$, in the range of 203-243 kJ mol^{-1} depending upon basis set, can be compared with MNDO, MINDO/3 values[1] in the range 181-266 kJ mol^{-1}.

We turn now to the calculations including correlation effects (table 2).

TABLE 2

Total Energies (a.u.) and Relative Energies[a] (kJ mol^{-1}) for Reaction (1) at CI/TZP//6-31G* Level.

	Total Energy	Relative Energy	
Nitropropene	-321.1143	0	(0)
Aci-nitropropene	-321.0867	72.5	(72.4)
Transition State	-321.0382	199.8	(185.9)

[a] The values in parentheses include zero point effects.

The CI calculations reported here involved two reference configurations, the RHF configuration, and the dominant secondary configuration from a single and double excitation CI calculation from the RHF configuration. The CI expansion leading to the results of table 2 was generated by taking all single and double excitations of the valence electrons from these two reference configurations into the lowest 50 empty orbitals. We find that such an expansion increases the calculated value of ΔH by 17 kJ mol^{-1}, a trend found by Turner[2] who included correlation effects using Møller-Plesset perturbation theory. The calculated barrier is reduced upon the inclusion of correlation effects, due to the relatively poorer description of the transition state (which involves partial bonds) given by a RHF wavefunction, than of the reactant. The barrier is also reduced upon the inclusion of zero point effects, which we have calculated at the 6-31G* level (table 2).

Our finding that the barrier height is quite insensitive to basis set, and that the CI/TZP//6-31G* value (200 kJ mol^{-1}) is close to the STO-3G//STO-3G value (203 kJ mol^{-1}) gives us some confidence that a study of the reaction, analogous to that of (1), which involves TNT itself, is of value, using only a STO-3G basis. This is a formidable calculation even using vector machines (CRAY XMP/48), and to carry out the calculation in a larger basis than STO-3G is not really practical. The results of such a calculation are reported in table 3.

TABLE 3

Total Energies (a.u.) and Relative Energies[a] (kJ mol^{-1}) for the Reaction Analogous to (1), Involving TNT, at STO-3G//STO-3G Level.

	Total Energy	Relative Energy	
TNT	-868.5801	0	(0)
Aci-TNT	-868.5239	147.7	(147.1)
Transition State	-868.4907	234.8	(226.2)

[a] The values in parentheses include zero point effects.

The calculated value of ΔH is considerably larger than that found for the model reaction (1). However, our calculated barrier height, for which no MO calculations at all have yet been reported is not significantly larger than that found for the model system. It should be noted that this does not imply similar kinetic behaviour for the model, and real system, since the barrier shape is considerably different as shown by the transition state imaginary frequency being 1715i cm^{-1} for the model system and 1235i cm^{-1} for the reaction involving TNT. Such a difference is not unexpected in view of the different ΔH values for the two systems that we have discussed.

In view of the availability of KIE data for the induction period of TNT decomposition[4] we have estimated the KIE for the reaction analogous to (1) in the unimolecular high pressure approximation for the rate equation[14]. This calculation requires the structure and vibrational frequencies for the reactant, product and transition state, with and without d_3-substitution of the methyl group, which are obtained from the calculations previously described. An estimate of the correction due to quantum mechanical tunnelling was obtained by the approximation due to Bell[15], which assumes a parabolic form for the barrier. The KIE thus obtained at 542 K was 2.42, somewhat larger than the experimental value of ~1.7.

CONCLUSIONS

The extensive MO calculations reported herein have explored the value of both semiempirical MO calculations and of model systems to study the mechanisms of explosion at a molecular level. For the case involving TNT, investigated here, both approaches have considerable value. It is of interest to note that our calculated barrier for TNT decomposition (226 kJ mol^{-1}) is close to the measured activation energy (194 kJ mol^{-1}) for the induction reaction[4]. We shall report in a subsequent publication a detailed discussion of the calculated molecular structures, the vibrational frequencies of TNT and the calculation of kinetic parameters, particularly further calculations of the primary kinetic hydrogen isotope effect.

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