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Experimental and theoretical study of the isomerisation of N-methylpyrrole

Alan Doughty, John C. Mackie, George B. Bacskay

Department of Physical and Theoretical Chemistry, University of Sydney, Sydney NSW 2006, Australia

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Abstract

The isomerisation of N-methylpyrrole to 2-methylpyrrole has been investigated experimentally by means of a single pulse shock tube over the temperature range 1000 to 1350 K and theoretically by ab initio calculations. Between 1000 and 1100 K the isomerization is found to occur via an intramolecular methyl shift. The experimental rate constant for this rearrangement was found to be $k_{\mathrm{iso}}=10^{12.8(\pm 0.4)}\exp[-56.2(\pm 2.0)\ \mathrm{kcal\ mol^{-1}}/RT]\ \mathrm{s^{-1}}$. Ab initio calculations gave Arrhenius parameters for the methyl shift in good agreement with the experimental values. Methyl shifting produces the intermediate 2-methyl-2H-pyrrole which undergoes a hydrogen shift of low activation energy to form the product of isomerisation, 2-methylpyrrole. Above about 1240 K there is a competing free-radical process which produces methane, pyrrole and traces of higher molecular weight products.

1. Introduction

This study of the isomerisation of N-methylpyrrole is part of a wider investigation of the thermal decomposition and isomerisation reactions of N-containing heteroaromatics. The motivation for these studies is to improve the understanding of the thermal reactions of nitrogen compounds similar to those known to be present in coal. Since coal nitrogen has been found by X-ray photoelectron spectroscopy to be largely in the form of pyrrollic and pyridinic structures [1], N-methylpyrrole is one of the molecules that has been chosen as the subject of a detailed kinetic investigation.

The thermal reactions of N-methylpyrrole have been previously studied by Jacobson et al. [2], who investigated the isomerisation of N-methylpyrrole to 2-methylpyrrole using a quartz plug flow reactor. The type of reactor employed could be prone to surface reactions, particularly under the low flow and high residence time conditions used by Jacobson et al., and these workers observed decomposition products at the higher temperatures of their study. In our work, the single pulse shock tube is used, so the reactant is heated homogeneously, avoiding complications caused by initiation reactions on hot surfaces. Lifshitz et al. [3] have recently published a shock tube study of the thermal decomposition of N-methylpyrrole but as they concentrated on the decomposition reactions of N-methylpyrrole, no measurements were made of the rate or products of isomerisation.

As a further probe of the kinetics and mechanism of isomerisation of N-methylpyrrole, theoretical calculations have also been undertaken in the form of ab initio calculations on the various molecular species and transition states that are relevant in the isomerisation reactions.

2. Experimental

The thermal isomerisation of N-methylpyrrole has been studied in a single pulse shock tube over the

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temperature range of 1000 to 1350 K. Typical reaction pressures were 13–14 atm, with an average residence time behind the reflected shock of 800 μs. Reactant concentrations were measured prior to each run using high-resolution gas chromatography (HRGC), with detection by nitrogen/phosphorus specific thermionic detector (NPD). Product analysis was carried out using HRGC/NPD. Details of the shock tube [4,5] and quantitative HRGC analysis have been given elsewhere [6]. Particular attention was paid to the collection system in the present study because of the lack of volatility of some of the products of decomposition. The products are collected through the endwall of the shock tube via a fast-acting (≈ 10 ms) relief valve and pass into a heated collection system maintained at about 100°C and are then rapidly injected into the GC by means of a gas sampling valve. Without a heated collection system and rapid product analysis, much of the less volatile products, 2-methylpyrrole (BP 146°C) and 3-methylpyrrole (BP 142°C) would be lost by condensation on walls and the measured product distribution would be strongly biased towards the more volatile products such as the open-chain nitriles, pyridine and unreacted N-methylpyrrole.

Identification of products was carried out by gas chromatography/mass spectrometry (GCMS) and confirmed by matching of retention times with samples of known composition. To identify the major isomerisation product of N-methylpyrrole, 2-methylpyrrole was synthesised using the method of Nenitzescu and Solomonica [7]. The identity of the synthesised 2-methylpyrrole was confirmed using ^{1}H and ^{13}C nuclear magnetic resonance spectrometry, and GCMS. To investigate the possibility that involatile products are formed from the thermal reaction of N-methylpyrrole, the shock tube exit tube was extracted with dichloromethane. Compounds contained in the extract were investigated using GCMS.

N-methylpyrrole (Aldrich, 99%) was thoroughly degassed and purified by bulb to bulb distillation under vacuum prior to use. Mixtures of the vapour were prepared dilute in argon to a concentration of 0.2–0.3 mol%. The only impurity detected in the reactant mixture was pyrrole, which was always present at levels less than 0.4% of the concentration of N-methylpyrrole (by HRGC). To assist in the interpretation of the experimental data, a second series of experiments was conducted containing 0.2–0.3 mol% N-methylpyrrole diluted in a bath gas consisting of 15% hydrogen in argon.

3. Computational

Ab initio quantum chemical techniques were used to calculate the geometries and energies of reactants, products and transition states involved in the formation of 2-methylpyrrole from N-methylpyrrole.

The geometries were optimised at the Hartree–Fock SCF level of theory using a double zeta (DZ) Gaussian basis set [8], followed by the calculation of the force field, yielding normal vibrational modes and frequencies that enables the calculation of the total zero-point vibrational energy. In addition, the normal mode analysis allows for the rigorous characterisation of the stationary point as a local minimum (equilibrium structure) or saddle point with a Hessian index of 1 (transition state).

The total energies were recalculated at the SCF/DZ geometries using a DZP basis, where the DZ basis was extended by 3d ($\zeta_{N,C}=0.8$) and 2p ($\zeta_H=1.0$) polarization functions. Electron correlation was also accounted for at the level of second order Møller–Plesset (MP2) perturbation theory.

Using the optimised geometries (in the form of rotational constants) and vibrational frequencies (scaled by 0.9, as recommended by Pople et al. [9]), the molecular partition functions of reactant and activated complex were calculated allowing the determination of the transition-state Arrhenius frequency factor for the initial rearrangement reaction of N-methylpyrrole.

The ab initio calculations were performed using the CADPAC5 programs [#1] on an IBM RS6000/320 workstation.

[#1] CADPAC5: The Cambridge analytic derivatives package. Issue 5, Cambridge 1992. A suite of quantum chemistry programs developed by R.D. Amos with contributions from I.L. Alberts, J.S. Andrews, S.M. Colwell, N.C. Handy, D. Jayatilaka, P.J. Knowles, R. Kobayashi, N. Koga, K.E. Laidig, P.E. Maslen, C.W. Murray, J.E. Rice, J. Sanz, E.D. Simandiras, A.J. Stone and M.-D. Su.

4. Results

The kinetic study of the isomerisation of N-methylpyrrole has been carried out over the temperature range 1000–1240 K. For this temperature range, the only major products detected are the isomerisation products 2- and 3-methylpyrrole, of which 2-methylpyrrole was always present in significantly higher concentrations. Only traces of 3-methylpyrrole were detected below 1100 K, so that over the temperature region 1000–1100 K, 2-methylpyrrole was the sole product of isomerisation. Above 1240 K isomerisation is accompanied by the decomposition of N-methylpyrrole to form the products methane and pyrrole, as well as a number of minor products such as pentenenitriles, butenenitriles, acetonitrile, HCN, pyridine and acrylonitrile. With this technique, quantitative collection of the methylpyrrole isomers could be effected. However, at the highest temperatures of this study some heavy nitrogen compounds were formed and these could not be quantitatively collected.

Mass balance calculations were conducted for each experimental run. In Fig. 1, the N-recovered in the post shock mixture (i.e. the sum of N in the products, including unreacted N-methylpyrrole) is plotted as a percentage of the unreacted N-methylpyrrole. Even considering the scatter in these measurements, the calculations show that above 1240 K a significant proportion of the reactant is being lost to a product not observable in the gas phase.

Also included in Fig. 1 is a plot of the recovery of carbon relative to nitrogen. The relative recovery is calculated assuming that 100% of the nitrogen is recovered, with 100% recovery of carbon relative to nitrogen corresponding to a C:N ratio of 5 in the products, the same C:N ratio as in N-methylpyrrole. Fig. 1 shows that although a significant proportion of the nitrogen has been lost from the system at temperatures above 1240 K, the relative recovery of carbon against nitrogen is maintained. This indicates that nitrogen is lost in the form of a species which has a similar empirical formula to the reactant molecule.

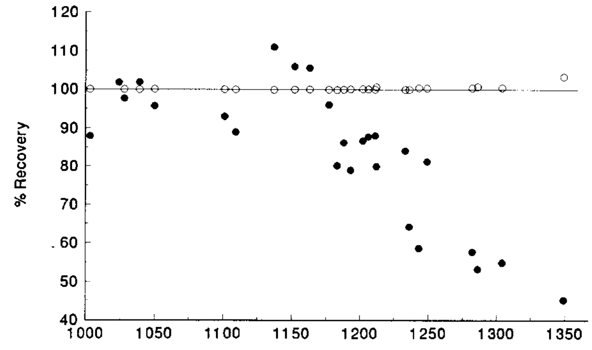

Fig. 1. Temperature dependence of mass balance data. (●) % N recovered; (○) % recovery of C relative to N.

Experimental runs conducted in H_2:Ar bath gas showed no change in the yields of the major products 2- and 3-methylpyrrole. In Fig. 2 the yields of these products in the presence and absence of 15% H_2 are illustrated. The yields of minor products, however, were significantly affected by the presence of 15% H_2. The yields of all minor products increased in the presence of hydrogen, particularly methane and pyrrole which both increased in yield by close to a factor of 10. In the presence of hydrogen, the nitrogen recovery at temperatures above 1240 K was significantly greater than in the absence of hydrogen.

GCMS conducted on the dichloromethane extract of the shock tube exit tube showed very few products to be deposited. In addition to traces of the methylpyrroles, a single peak corresponding to m/z 160 was detected. The shape of the peak suggested that there may have been more than a single compound of m/z 160 eluting at very similar retention times. Three peaks of m/z 132 were also detected, although the

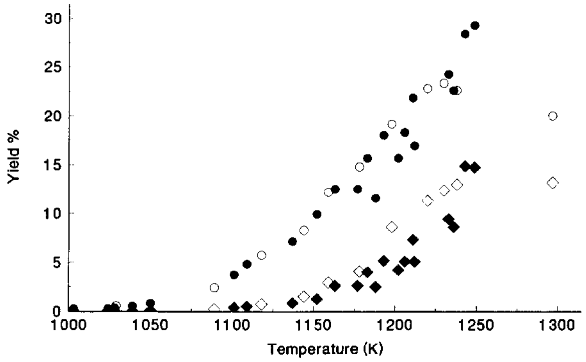

Fig. 2. Yield % of isomerisation products (based on the initial concentration of N-methylpyrrole). Circles: 2-methylpyrrole, diamonds: 3-methylpyrrole. Filled symbols: runs in Ar only, closed symbols: runs in 15% H_2 in Ar.

areas of these peaks were considerably smaller than the area of the m/z 160 peak.

In the experiments conducted in argon bath gas, the only major products were 2- and 3-methylpyrrole. The rate of isomerisation of N-methylpyrrole should therefore be equal to the rate of disappearance of the reactant. An Arrhenius plot for the first-order rate constant of the rate of disappearance of N-methylpyrrole (k_{dis}) is given in Fig. 3. Excluding data points above 1240 K, k_{dis} is given by

$$k_{\text{dis}} = 10^{12.8(\pm 0.4)}$$
$$\times \exp[-56.2(\pm 2.0)\ \text{kcal mol}^{-1}/RT]\ \text{s}^{-1}\,.$$

In the presence of hydrogen, the significant side reaction yielding pyrrole and methane prevents the rate of disappearance of reactant from equalling the rate of isomerisation of the reactant. The first-order rate constant for the isomerisation of N-methylpyrrole must therefore be calculated from the rate of formation of 2- and 3-methylpyrrole (k_{form}). Since an approximate expression for the first-order rate constant must be used, only data for low extents of decomposition of N-methylpyrrole are used in the calculation of Arrhenius parameters. An Arrhenius plot for k_{form} is included in Fig. 3, yielding the expression

$$k_{\text{form}} = 10^{12.7(\pm 0.5)}$$
$$\times \exp[-55.4(\pm 2.4)\ \text{kcal mol}^{-1}/RT]\ \text{s}^{-1}\,.$$

In both the experiments conducted with and without hydrogen, 2-methylpyrrole was detected before 3-methylpyrrole. In the study of Jacobson et al. [2], the only isomerisation product observed from the thermal isomerisation of 2-methylpyrrole was 3-methylpyrrole, and also from the thermal isomerisation of 3-methylpyrrole only 2-methylpyrrole was observed. Jacobson et al. concluded that N-methylpyrrole isomerised to 2-methylpyrrole which then equilibrates with 3-methylpyrrole. In this study the detection of 2-methylpyrrole as the only product of isomerisation at temperatures below 1100 K supports this conclusion. The Arrhenius parameters obtained for the isomerisation of N-methylpyrrole in this study would therefore correspond to the reaction

$$\text{N-methylpyrrole} \rightarrow \text{2-methylpyrrole}\,.$$

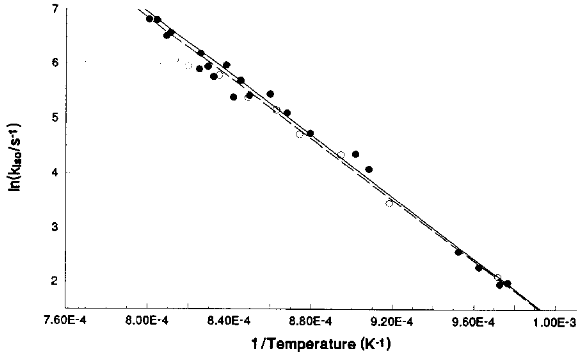

Fig. 3. Arrhenius plot of the rate constant for isomerisation (k_{iso}). Solid line: runs in Ar only, dashed line: runs in 15% H_2 in Ar.

The Arrhenius parameters for isomerisation determined in this study are in excellent agreement with the values obtained by Jacobson et al.

As can be seen from Fig. 1, the systematic loss of nitrogen above 1240 K has prevented the quantitative treatment of the decomposition of N-methylpyrrole. The increased yield of pyrrole in the presence of hydrogen suggests that there may be a competing free-radical process involving N–CH_3 bond fission in N-methylpyrrole to yield methyl and pyrrolyl radicals. It is expected that the pyrrolyl radical would be resonance stabilised. Rather than undergoing decomposition to yield volatile products, this radical could recombine to yield dipyrrolyl. The observation of species of m/z 132 in the exit tube extract by GCMS supports this postulate. In the presence of hydrogen pyrrolyl radicals could directly react with H_2 to form pyrrole and H atoms, leading to the observed increase in the yield of pyrrole and increased nitrogen recovery. In the absence of hydrogen, methyl radicals could H-abstract from the methyl group of N-methylpyrrole and also 2- and 3-methylpyrrole to yield a C_5H_6N radical which may also undergo recombination rather than decomposition. Recombination of the C_5H_6N radical so formed would yield an involatile species of mass 160. The prominent m/z 160 peak observed in GCMS of the exit tube extract suggests that recombination of the C_5H_6N radical may contribute to the loss of nitrogen from the system.

In the work of Lifshitz et al. [3], data on the decomposition of N-methylpyrrole were treated as if the recovery of nitrogen in the products were complete. To justify this approach, Lifshitz et al. demonstrated that there was no loss of carbon in their products relative to nitrogen. In the present study, however, we have shown that despite the invariant carbon to nitrogen ratio, there is a significant loss of nitrogen from the system at elevated temperatures (Fig. 1). In their kinetic model for decomposition of N-methylpyrrole, Lifshitz et al. have not included recombination reactions of pyrrolyl or C_5H_6N. In the light of the experimental data presented here, omission of recombination reactions may be a serious shortcoming of their kinetic model. Lifshitz et al. present their product profiles in term of log(concentration) plots versus temperature. From their plots, it appears that the onset of significant decomposition of N-methylpyrrole takes place above about 1200 K. Decomposition in our study commenced around 1240 K. Since the average residence time in the work of Lifshitz et al. was approximately 2 ms as opposed to 0.8 ms in our study, the onset of decomposition in the two studies would appear to be in agreement.

There is an apparent discrepancy in the product profiles, however. From their log plots maximum product yields of both pyridine and 2/3-methylpyrrole are approximately equal at about 10 mol%. (Lifshitz et al. did not differentiate between these two isomers.) There is evident scatter, however, of as much as a factor of five in their product concentrations. On the other hand, we observe pyridine to be only a minor product whose yield is at most 3 mol%. There are two reasons for this apparent anomaly. Firstly, pyridine is a secondary product of decomposition, arising probably from hydrogen abstraction from the methyl side chain in 2- and 3-methylpyrrole, followed by ring expansion and H-fission to form pyridine [3]. Secondary products of decomposition will be greatly favoured in the longer residence times of the Lifshitz study. Secondly, there may bias in the measured product distribution if nitrogen mass balance had not been achieved. Lifshitz et al. do not mention taking any precautions to collect products rapidly and through heated lines. We have found this essential to quantitatively collect the 2- and 3-methylpyrroles. Without such precautions there would be a considerable bias towards collection in the products of pyridine (BP 115.5°C) and unreacted N-methylpyrrole (BP 114°C) and away from the much less volatile 2- and 3-methylpyrroles. This would lead to an artificially high [pyridine]/[2/3-methylpyrroles] ratio.

5. Mechanism of N-methylpyrrole isomerisation

The simplest mechanism of isomerisation of N-methylpyrrole to 2-methylpyrrole would involve the unimolecular transfer of the methyl group from the 1- to the 2-position to form 2-methyl-2H-pyrrole, followed by the transfer of an H atom from the 2- to the 1-position to yield 2-methylpyrrole. Although Benson [10] strongly argues against such processes where the transition state implies a penta-coordinated methyl carbon atom, the experimental evidence suggests that isomerisation reactions involving methyl transfers may be feasible. An alternative explanation for the isomerisation of N-methylpyrrole to 2-methylpyrrole would be a free-radical mechanism involving the fission of the $N-CH_3$ bond of N-methylpyrrole. If this occurred, the presence of 15% hydrogen in the bath gas would have a dramatic effect on the rate of isomerisation. The experiments conducted in 15% hydrogen showed the rate of isomerisation to be unaffected by the presence of hydrogen, thus supporting the unimolecular mechanism for the isomerisation of N-methylpyrrole.

Rearrangements involving methyl or saturated alkyl groups have also been observed in other systems [11]. The isomerisation of 1,1-dimethylcyclopentadiene has been shown to proceed via transfer of a methyl group [12]. Patterson et al. [13] have discussed experimental evidence for the migration of alkyl, aryl and benzyl groups from the 1-position in pyrrole to the 2- and 3-position. For asymmetric substituents, Patterson et al. noted that the configuration is retained, suggesting that the mechanism is intramolecular.

The experimental evidence therefore suggests that intramolecular methyl transfer is a plausible mechanism for isomerisation of N-methylpyrrole. This conclusion is further strengthened by the results of ab initio calculations.

6. Ab initio results

The structures of the molecule studied are shown in Fig. 4, listing also the optimised (SCF/DZ) bond lengths and angles that are most relevant to this study. The calculated energies at these geometries are summarised in Table 1. Comparison of the results ob-

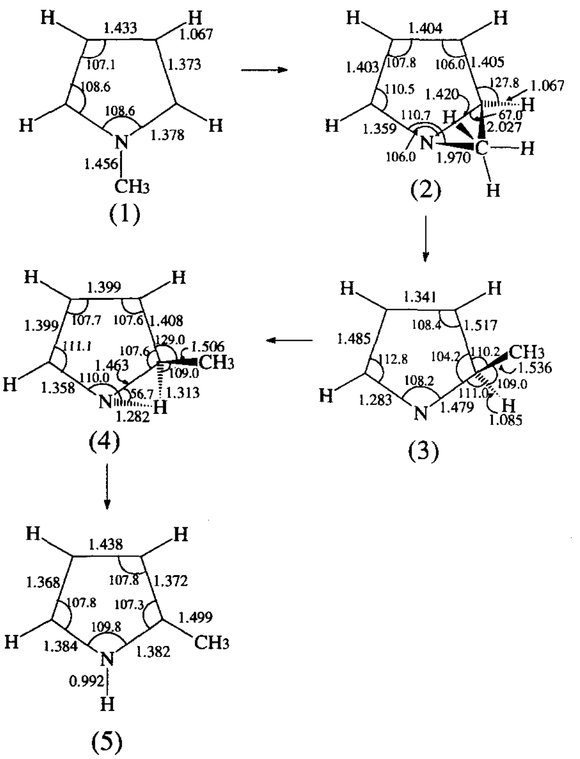

Fig. 4. Geometries of isomers and transition states of N-methylpyrrole (bond lengths in Å, angles in degrees). (The pyrrole ring is largely planar in all the systems and N-methylpyrrole has C_s symmetry.)

Table 1
Calculated energies (relative to N-methylpyrrole) [a] including zero-point correction (ΔZPE) for isomers and transition states of methylpyrrole (in kcal mol^{-1}) [b]

Molecule [c]	SCF/DZ	SCF/DZP	MP2/DZP	ΔZPE
1	0.0	0.0	0.0	0.0
2	74.9	69.4	59.7	−3.0
3	12.9	5.1	9.6	−0.4
4	57.1	46.2	36.6	−3.6
5	−9.0	−7.3	−6.0	0.1

[a] Total energies (in E_h) of N-methylpyrrole: E(SCF/DZ) = −247.76786, E(SCF/DZP) = −247.88813, E(MP2/DZP) = −248.80795, ZPE(kcal mol^{-1}) = 74.9.

[b] Calculated at SCF/DZ geometries.

[c] Formulae given in Fig. 4.

tained at different levels of theory indicates that the relative energies of the three isomers (molecules **1**, **3**, **5**) are fairly stable to variations in the basis set as well as electron correlation. However, the energies of the transition states and therefore, critical energies of reactions, are much more sensitive to both basis set and electron correlation effects. Unfortunately, due to the sizes of the molecules, it was not possible to extend the study of these effects by using a higher level treatment of correlation or larger basis sets. However, detailed studies [14] that had been done on the cyclopentadiene molecule, with special reference to the 1,5 hydrogen shift, suggest that the critical energies of reactions calculated at the MP2/DZP level are ≈ 5 kcal mol^{-1} too low in comparison with the analogous coupled cluster, viz. CCSD(T) [15] results, while extending the basis set to triple zeta with two polarization functions (TZ2P) and a set of 4f functions on the heavy atoms would reduce these energies ≈ 2 kcal mol^{-1} (at the MP2 level). The latter studies also showed that reoptimisation of the geometry at the MP2/DZP level would have a marginal effect on the relative energies, ≈0.1 kcal mol^{-1}. Thus, our conservative estimates of the critical energies of reactions for the methyl and hydrogen migration in the methylpyrrole system are 62.7 ± 3.0 and 39.6 ± 3.0 kcal mol^{-1}, respectively. The former is in acceptable agreement with the observed activation energy of 56.2 ± 2.0 kcal mol^{-1}.

More importantly, however, the ab initio estimates of the activation energies are consistent with experiment, inasmuch as the proposed isomerisation mechanism appears to be energetically quite feasible and the rate determining step is the formation of 2-methyl-2H-pyrrole. The calculated frequency factor of $10^{13.08}$ s^{-1} for that reaction (based on the ab initio prediction of rotational constants and vibrational frequencies) is in close agreement with the experimental value of $10^{12.8 \pm 0.4}$ s^{-1}, lending more credence to the proposed mechanism.

The calculations show that bonding in the transition state **2** can be described in terms of a two-electron three-centre bond involving an sp^3 hybrid orbital on the methyl group and, contrary to the arguments of Benson [10], an expanded valence shell need not be invoked. We note, nevertheless, that the migration of a hydrogen atom has a considerably lower barrier.

7. Conclusions

The isomerisation of N-methylpyrrole takes place by an intramolecular methyl transfer to form an intermediate 2-methyl-2H-pyrrole which further undergoes a hydrogen shift reaction of low activation energy to form the product of isomerisation, 2-methylpyrrole. Ab initio calculations and experimental measurements of the rate of isomerisation are in good agreement.

References

[1] S. Wallace, K.D. Bartle and D.L. Perry, Fuel 68 (1989) 1450.
[2] I.A. Jacobson Jr., H.H. Heady and G.U. Dinneen, J. Am. Chem. Soc. 62 (1958) 1563.
[3] A. Lifshitz, I. Shweky and C. Tamburu, J. Phys. Chem. 97 (1993) 4442.
[4] W.S. Cathro and J.C. Mackie, J. Chem. Soc. Faraday Trans. 68 (1972) 150.
[5] K.R. Doolan and J.C. Mackie, Combustion Flame 49 (1983) 221.
[6] A. Terentis, A. Doughty and J.C. Mackie, J. Phys. Chem. 96 (1992) 10334.
[7] C.D. Nenitzescu and E. Solomonica, Ber. 64B (1931) 1924.
[8] T.H. Dunning Jr. and P.J. Hay, in: Modern theoretical chemistry, Vol. 3, ed. H.F. Schaefer III (Plenum Press, New York, 1977).
[9] J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. DeFrees, J.S. Brinkley, M.J. Frisch, R.A. Whiteside, R.F. Hout and W.J. Hehre, Intern. J. Quantum Chem. Quantum Chem. Symp. 15 (1981) 269.
[10] S. Benson, Thermochemical kinetics (Wiley, New York, 1976).
[11] C.W. Spangler, Chem. Rev. 76 (1976) 187.
[12] J.W. de Haan and H. Kloosterziel, Rec. Trav. Chim. 84 (1965) 1594.
[13] J.M. Patterson and S. Soedigdo, J. Org. Chem. 33 (1968) 2057.
[14] G.B. Bacskay, S. Bray, A. Doughty and J.C. Mackie, to be published.
[15] K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, Chem. Phys. Letters 157 (1989) 479.