J. Phys. Chem. A **2002,** *106,* 4645−4650

Quantum Chemical and Conventional Transition-State Theory Calculations of Rate Constants for the NO_3 + Alkane Reaction

Graciela Bravo-Pérez,* J. Raúl Alvarez-Idaboy,* Armando Cruz-Torres, and Ma. Esther Ruíz

Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México D.F., México

Received: October 18, 2001; In Final Form: February 22, 2002

The reaction paths of NO_3 with methane, ethane, propane, and isobutane have been modeled using accurate ab initio (MP2) and hybrid DFT (BHandHLYP) methods with large basis sets (6-311g(d,p)). The energies of the optimized geometries were recalculated with the CCSD(T) method. Rate constants were obtained with the conventional transition-state theory (CTST). For propane and isobutane, in addition to the respective secondary and tertiary H-abstraction channels, abstraction of primary hydrogen atoms was also considered. Taking into account the internal rotations in the partition functions is shown to be essential for the determination of the preexponential parameters. This correction has a strong influence on the transition state partition function of the primary channel of isobutane, producing a noticeable increase in the preexponential factor and an almost perfect agreement with the experimental values. The calculated rate constants for tertiary and primary H-abstractions are 2.28×10^4 and 3.41×10^4 L mol^{-1} s^{-1}, respectively, and the overall rate coefficient is 5.69×10^4 L mol^{-1} s^{-1}. In contrast, the rate constant for the primary H-abstraction in propane is about 1 order of magnitude lower than that of the secondary channel, a 4.71×10^3 value versus 4.47×10^4 L mol^{-1} s^{-1}. The calculated rate constants for methane (2.52 L mol^{-1} s^{-1}) and ethane (4.94×10^3 L mol^{-1} s^{-1}) reproduce remarkably well the experimental results. The tunnel effect is shown to be a very important factor for methane and ethane, and especially for the primary H-abstractions in propane and isobutane, the tunneling factor is about 5 times the one for the tertiary abstraction.

Introduction

Large quantities of volatile organic compounds (VOCs) are emitted into the troposphere from anthropogenic and biogenic sources. The worldwide estimated emissions of methane from biogenic sources are about 155−240 million tons yr^{-1}, while anthropogenic sources contribute approximately 350−375 million tons yr^{-1}.[1] In contaminated atmospheres, other alkanes, such as propane and butanes are also among the most abundant VOCs.[2] In fact, the chromatographic analysis of Mexico City Metropolitan Area (MCMA) air samples[3] shows that propane and butane account for the highest concentrations, probably due to the wide use of LPG in the area. Some researchers have linked the ozone pollution problem observed in Mexico City to these emissions.[4] A photochemical trajectory model evaluated with MCMA atmospheric VOC data also supports this suggestion.[5]

On the other hand, NO_x emissions are about 10 million tons yr^{-1} for biogenic sources and 40 million tons yr^{-1} from anthropogenic sources.[1,6] The abundance of NO_x in the troposphere leads to the formation of the nitrate radical NO_3, through the reactions

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (2)$$

The NO_3 concentration remains low during daylight because this species is rapidly photolyzed,[7] but at nighttime it increases to reach measurable levels. Measurements at ground level have yielded nighttime NO_3 average concentrations of 5×10^8 to 2×10^9 molecule cm^{-3}.[8,9] Therefore, in the last years, attention has been called to the NO_3 nighttime reactivity in urban zones with a large concentration of VOCs. The NO_3 radical contributes to the oxidation of alkanes and to the formation of HNO_3, which is also related to particulate formation and harmful health effects.[10]

Oxidation of alkanes by NO_3 (alkane + NO_3) proceeds initially by hydrogen abstraction with the formation of an alkyl radical (C_nH_{2n+1}) and nitric acid (HNO_3). Because the experimental and theoretical study of these reactions is complex, their oxidative role has only been partly investigated, in comparison to the analogous daytime reaction, OH + alkane, which is well-known to have important effects on atmospheric chemistry. For the OH + alkane reaction, numerous studies exist concerning the dependency of rate constants with temperature. For the NO_3 reaction instead, although some work has been done on the rate constant measurements,[11−13] only one experimental work for ethane, *n*-butane, and isobutane has been published in which the calculation of the rate constant dependency on the temperature[11] is reported. In the latter, the abstraction mechanism was assumed to involve only the most substituted C atom, in analogy to the OH reaction mechanism.[14] However, the experimental activation energies (E_a's) usually are the result of several competitive processes, and therefore, the tertiary, secondary, and even primary H-abstractions could be highly relevant.

Quantum-mechanical methodologies have proved to give a very good agreement with the experimental values, including predictive reaction mechanisms when experimental data are missing. In a recent publication of our group on the RCHO + NO_3 reaction,[15] which also occurs by way of a H-abstraction mechanism, the influence of the free internal rotations (FIRs)

---

* To whom correspondence should be addressed. E-mail: gbperez@imp.mx and jidaboy@imp.mx.

10.1021/jp013876g CCC: $22.00

in the partition functions of the transition states (TSs) was confirmed. The calculated values of the rate constants were found to agree very well with the experimental values. The work also explained the “abnormal” increase of the rate constants with the size of the aldehydes. The aim of the present work is to study the NO_3 alkane reaction and to predict the mechanistic behavior of the reaction. As a complement to the very few available experimental works, the Arrhenius parameters are also investigated, as well as the influence of the FIRs on the rate constants, and their dependence on the alkane size and symmetry.

The present work is based on the hypothesis that the H-abstraction reaction mechanism is a competitive process, therefore the relative selectivity for primary, secondary, and tertiary C atoms has been considered. Our results heavily support this hypothesis. We present a quantum-mechanical study of the reaction profiles of NO_3 with methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and isobutane (C_4H_{10}), including electronic correlation effects, and taking into account the FIRs, tunneling effect, and the basis-set superposition error (BSSE). The heats of reaction (ΔH_{reac}) and E_a’s are determined using the energies of reactants, TSs, and products. The methodology that we apply has been already used in previous works to reproduce experimental data with a very reasonable agreement.[15−17] The Arrhenius preexponential factors and rate constants are determined using statistical mechanics and the conventional TS theory (CTST).

Computational Methodology

Structure calculations of reactants, products, and TSs were performed with the GAUSSIAN98 program.[18] The geometries were fully optimized at the BHandHLYP and MP2 levels of approximation using the 6-311G(d,p) basis set. Unrestricted formalisms were used for radicals. The character of the TSs was confirmed by frequency calculations performed at the same level of approximation, presenting one imaginary frequency with transition vectors corresponding to the chosen reaction coordinate. To confirm local minima structures (reactants and products) frequency calculations were also carried out.

CCSD(T) energy calculations were carried out at the BHandHLYP and MP2 optimized geometries, and the CCSD(T)/BHandHLYP or CCSD(T)/MP2 energies were then used. The CCSD(T)/BHandHLYP energies were chosen for the rate-constant calculations because the results are in better agreement with experimental results when compared with the CCSD(T)/MP2 values. In our previous studies of aldehydes + NO_3[15] the best agreement was also obtained with the CCSD(T)/BHandHLYP energies. In the present work the CCSD(T)/MP2 E_a’s were considerably overestimated and yielded very low rate constants. Similarly, overestimated CCSD(T)/MP2 E_a’s were observed in the case of the amino acid + OH reaction study.[17] On the contrary, in a study of the alkene + OH reaction[16,19] the CCSD(T)/MP2 results showed excellent agreement with the experimental values.

The BSSE was introduced using the Counterpoise method[20,21] to correct the CCSD(T)/BHandHLYP energies of the TSs. The CCSD(T) E_a’s include the zero-point energy (ZPE) correction. These values were used in the expression

$$k = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_{NO_3} Q_{Alk}} e^{(E_{TS} - E_{Reac})/RT} = \kappa A e^{-E_a/RT} \qquad (3)$$

to determine the reaction rate constants. κ stands for the tunnel effect, which is included as a factor. It is calculated as the ratio of the quantum mechanical to the classical barrier crossing rate, assuming an unsymmetrical one-dimensional Eckart function barrier.[22] The numerical integration program of Brown[23] has been applied. The preexponential factor $A = (k_B T/h)(Q_{TS}/Q_{NO_3} Q_{Alk})$ includes the partition functions (Q) of the TSs and reactants obtained from the GAUSSIAN98 output.

TABLE 1: Total (au) and Relative (kcal/mol) CCSD(T) Energies Including the ZPE Correction for the BHandHLYP and MP2 Optimized Structures

	BHandHLYP[a]		MP2	
	total	rel[b]	total	rel
		Reactants		
$CH_4 + NO_3$	−320.008127	0.0	−320.008470	0.0
$C_2H_6 + NO_3$	−359.186933	0.0	−359.187910	0.0
$C_3H_8 + NO_3$	−398.370009	0.0	−398.371731	0.0
i-$C_4H_{10} + NO_3$	−437.556272	0.0	−437.558817	0.0
		Transition States		
CH_4-NO_3	−319.985762	14.03	−319.983555	15.63
$C_2H_6-NO_3$	−359.171224	9.86	−359.169972	11.26
$C_3H_8-NO_3$-sec	−398.359682	6.48	−398.358681	8.19
$C_3H_8-NO_3$-pri	−398.354528	9.71		
i-$C_4H_{10}-NO_3$-ter	−437.548906	4.62	−437.548462	6.50
i-$C_4H_{10}-NO_3$-pri	−437.541753	9.11		
		Products		
$CH_3 + HNO_3$	−320.004229	2.45	−320.012269	−2.38
$C_2H_5 + HNO_3$	−359.191239	−2.70	−359.196231	−5.22
$C_3H_7 + HNO_3$	−398.378033	−5.04	−398.383664	−7.49
i-C_4H_9-ter + HNO_3	−437.566764	−6.58	−437.573237	−9.05
i-C_4H_9-pri + HNO_3	−437.559263	−1.88		

[a] Including BSSE, for definition, see text. [b] Energy difference from products (ΔH_{reac} value) or TSs (E_a value) with respect to the energy of reactants, taken as a zero reference value.

The FIRs corrections to the rotational partition functions (Q_r’s) were additionally included for each Q, by replacing some of the harmonic vibrations by the corresponding FIRs, for example, the ones that correspond to rotations around the O−H interacting axis.

Results and Discussion

In Table 1 the total energies of reactants, TSs, and products, as well as the E_a’s and ΔH_{reac} are reported. One can see that the CCSD(T)/MP2 E_a’s, without including the BSSE are about 1.5−2 kcal/mol larger than the values obtained with the CCSD(T)/BHandHLYP method (including the BSSE the former will be even higher).

Experimental E_a and other Arrhenius parameters are reported in Table 2. For the ethane reaction, the CCSD(T)/BHandHLYP E_a is the one that best agrees with the experimental value of 8.80 kcal/mol. The 1.06 kcal/mol overestimation could be lowered by the inclusion of κ in the way that is discussed in the following section. For propane the E_a values for the abstraction of the most substituted C and for the primary H are given, although no experimental result is available. For isobutane, tertiary and primary H-abstraction mechanisms are also reported. The experimental E_a value lies between the two calculated values. It remains then to explain how the two competitive mechanisms combine to provide a theoretical E_a that agrees with the experimental number.

The TS structures and their relevant geometrical parameters are indicated in Figure 1. One can notice that the C−H and H−O distances have the expected values. Due to the similarity with the reactants one can also note that the TSs occur early, as expected for exothermic reactions. The TS geometry for methane is somewhat particular, halfway between reactants and products, although slightly closer to the reactants, and this

TABLE 2: Kinetic Parameters of the Arrhenius Eq 3, Tunneling Factor (κ), Partition Function Ratios ($Q_{TS}/Q_{NO3}Q_{Alk}$), and the Comparison of Experimental and the Calculated Values for the Pre-expontntial Factor (A), Activation Energy (E_a), and Rate Constants (k)

			A		E_a (kcal/mol)		k (L $mol^{-1} \cdot s^{-1}$)	
entity$^{(n)}$	k	$Q_{TS}/Q_{Alc}Q_{NO3}$	theo	exp	theo	exp	calc	exp
$CH_4^{(0)}$	41.11	1.91×10^{-4}	1.19×10^{9}		14.03		2.52	< 2.41 [1] < 482 [2] < 603 [3]
$C_2H_6^{(1)}$	5.77	2.32×10^{-3}	1.44×10^{10}	3.44×10^{9}[2]	9.86	8.80[2]	4.94×10^{3}	2.41×10^{3} [4] 1.21×10^{3} [5] 6.62×10^{3} [2]
C_3H_8-sec$^{(2)}$	1.66	2.44×10^{-4}	1.51×10^{9}		6.48		4.47×10^{4}	
C_3H_8-pri$^{(1)}$	5.38	1.86×10^{-3}	1.15×10^{10}		9.71		4.71×10^{3}	
C_3H_8-ove							4.94×10^{4}	1.32×10^{4} [6] 4.22×10^{4} [6]
i-C_4H_{10}-ter$^{(3)}$	1.11	8.08×10^{-6}	5.02×10^{7}		4.62		2.28×10^{4}	
i-C_4H_{10}-pri$^{(1)}$	5.31	4.93×10^{-3}	3.06×10^{10}		9.11		3.41×10^{4}	
C_4H_{10}-ove				1.39×10^{9}[1]		5.88[2]	5.69×10^{4}	6.78×10^{4} [5] $<3.61 \times 10^{5}$ [2] 5.90×10^{4} [3]

reaction is known to be endothermic.[24] The frequency calculations for the TSs confirmed that the main component of the transition vector for proton displacement pointed along the C to O axis.

Figure 2 shows the energy reaction profiles of the four alkanes. The two mechanisms considered for propane and isobutane are also shown. The profiles indicate a decrease in the E_a together with an increase in the exothermicity as the C associated with the abstraction becomes more substituted, which also agrees with the structures of the TSs. Consequently, the secondary and tertiary abstractions for propane and isobutane are energetically more favored.

Tunnel Effect (κ), Partition Functions (Q), and Rate Constant (k) Calculations

For a good description of the predicted H-abstraction processes, κ has to be taken into account. This effect is essential in cases where high barriers and large imaginary frequencies occur, and this is the case in the present reactions. Differently, in the case of the aldehyde + NO_3 reaction, although it also follows an H-abstraction mechanism, the transition vectors of the TSs have considerable contributions from motions other than that of the abstracted H.[15]

The κ has been calculated using an Eckart barrier[22] for the four alkanes considered and for all the possible reaction channels, i.e., primary, secondary, and tertiary H-abstractions. The results are shown in Table 2. The highest κ occurs for methane and decreases in a remarkably monotonic fashion for the other alkanes. The lowest value, 1.11, is for the tertiary H-abstraction in isobutane, while the corresponding value for the primary H-abstraction is 4.8 times larger. In propane, the κ value for the primary abstraction is 3.24 times larger than for the secondary channel. This is one of the factors that could cause primary abstractions to be efficient competitors with respect to secondary or tertiary H channels.

For the Q values of reactants and TSs, the spatial symmetry plays a very important role concerning the primary channels; isobutane has nine H's bonded to primary carbon atoms, while propane has six. These ratios are included in the calculation of the rate constants**.** Also, for isobutane, large differences are observed between the Q ratio of primary and tertiary H-abstractions. Note that in the isolated alkane a free methyl group has a $Q = 3.67$ and this value increases to 50 when an NO_3 is attached to form the TS structure of the primary channel. This increase is due to the large molecular weight of NO_3 relative to CH_3 and to the orientation of the tops relative to the O−H axis (see Figure 1). In fact, the lack of spatial symmetry in the TS structure of the primary channel produces an increment in the reduced inertial moment included in the calculation of the FIRs. The Q_r in this TS structure is then 67 times larger than the one in the tertiary channel. In propane, the spatial symmetries of the TSs do not have this very large impact on the relative weights of the Q's, but anyway the Q ratio of primary to secondary channel is about 13 times larger. Therefore, in propane and isobutane, primary H-abstraction reactions are the most entropically favored**.** The TS for isobutane in the tertiary channel has six FIRs, and due to the rotational symmetry two of them are divided by three. This implies a reduction factor of 9 with respect to the Q of the primary channel.

The effects mentioned above account for isobutane with a preexponential factor of the primary H-abstraction 2880 times larger than for the tertiary channel. But for the consideration of the rate constants, there are other parameters to take into account. Note the difference in the E_a's of these channels. It involves an increase of about 3 and 5 kcal/mol, respectively, from secondary and tertiary abstractions to the primary channel (see Table 2).

The exponential factor of isobutane, eq 3, is consequently 1950 times smaller for the primary than for the tertiary channel but the former 2880 factor overcomes the latter. Then, the primary abstraction is favored by a 1.5 yield factor at 298 K. At higher T a more noticeable difference should be expected. This result is one of the most important of the present work, since it predicts, despite the chemical intuition of the energy profiles of Figure 2, that the primary abstraction is favored.

Since for propane the spatial symmetry of the TS does not have a noticeable influence on the Q_r's, as has been already mentioned, only the value of κ and the presence of six equivalent H's for the primary abstraction may affect the competition with the two equivalent H's of the secondary channel. The rate constant for the primary channel is thus 1 order of magnitude smaller than in the secondary abstraction, i.e., about 10% of its value (see last two columns of Table 2). Therefore this channel could be discarded when calculating approximate Arrhenius parameters.

In Table 2 the experimental rate constants are also reported. Except for the reaction of methane, an excellent agreement between the calculated and experimental values is obtained. Notice the large differences among the experimental data for the last reaction.

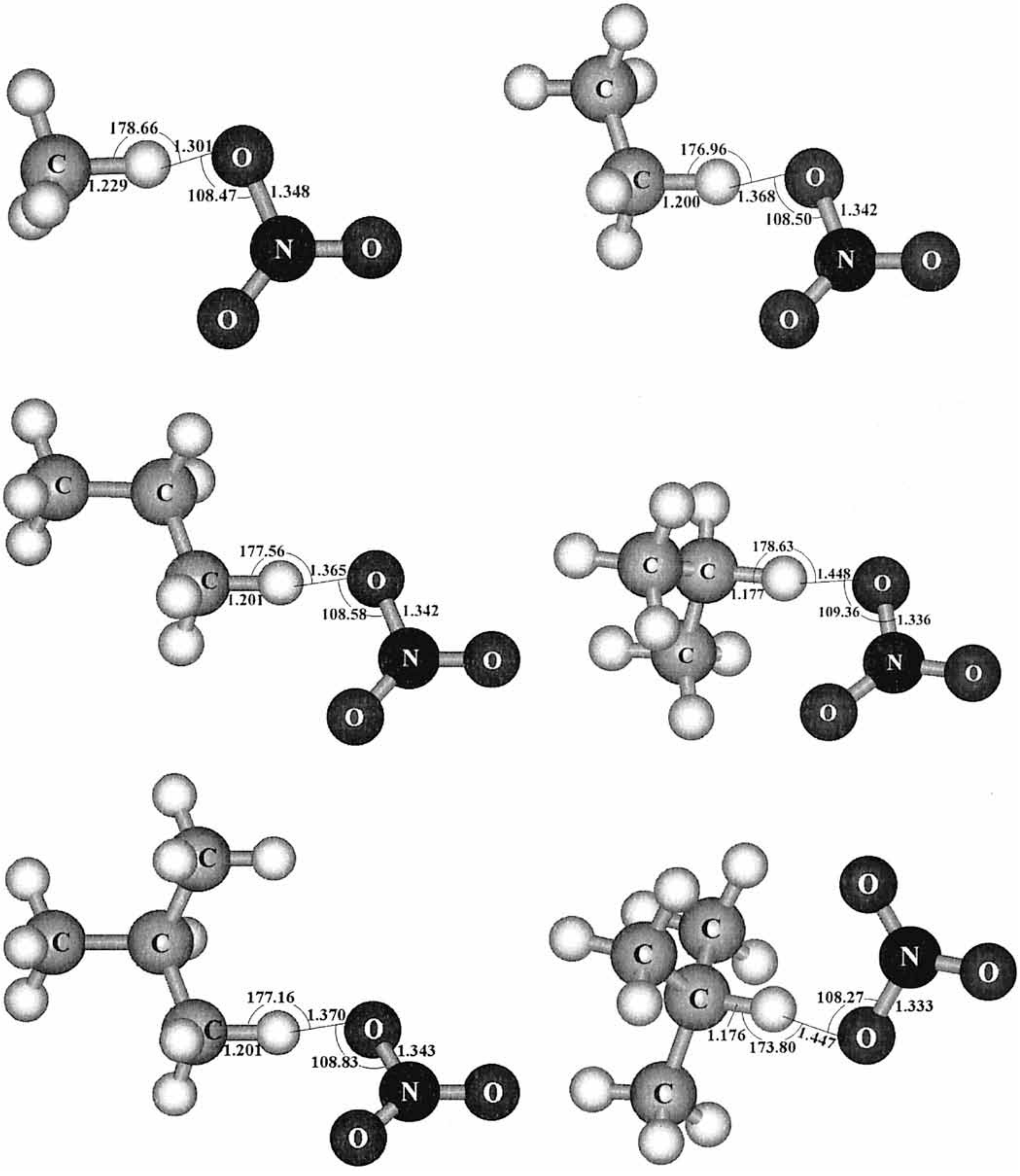

Figure 1. TS structures and their relevant geometrical parameters of the methane, ethane, propane, and isobutane with NO_3 interacting molecular systems.

For isobutane none of the calculated constants resembles the reported experimental values. The calculated values for both the primary and the tertiary rate constants are lower than the experimental data in refs 11, 25, and 26. They are also lower than the calculated values for propane. However, adding the two calculated rate constants, an overall value of 5.69×10^4 L mol^{-1} s^{-1} is obtained, which is in excellent agreement with the value reported in ref 25. This supports the hypothesis that the isobutane reaction is complex and that the primary H-abstraction channel plays a very important role. Normalizing the primary H-abstraction rate constant the resulting number, of 3.78×10^3 L mol^{-1} s^{-1}, is lower than that of the tertiary abstraction, which also shows to be higher than for ethane, for which the normalized value is 8.23×10^2 L mol^{-1} s^{-1}, compared to experimental values going from 2×10^2 to 11×10^2 L mol^{-1} s^{-1}. It is interesting to note that even though the E_a's tend to be

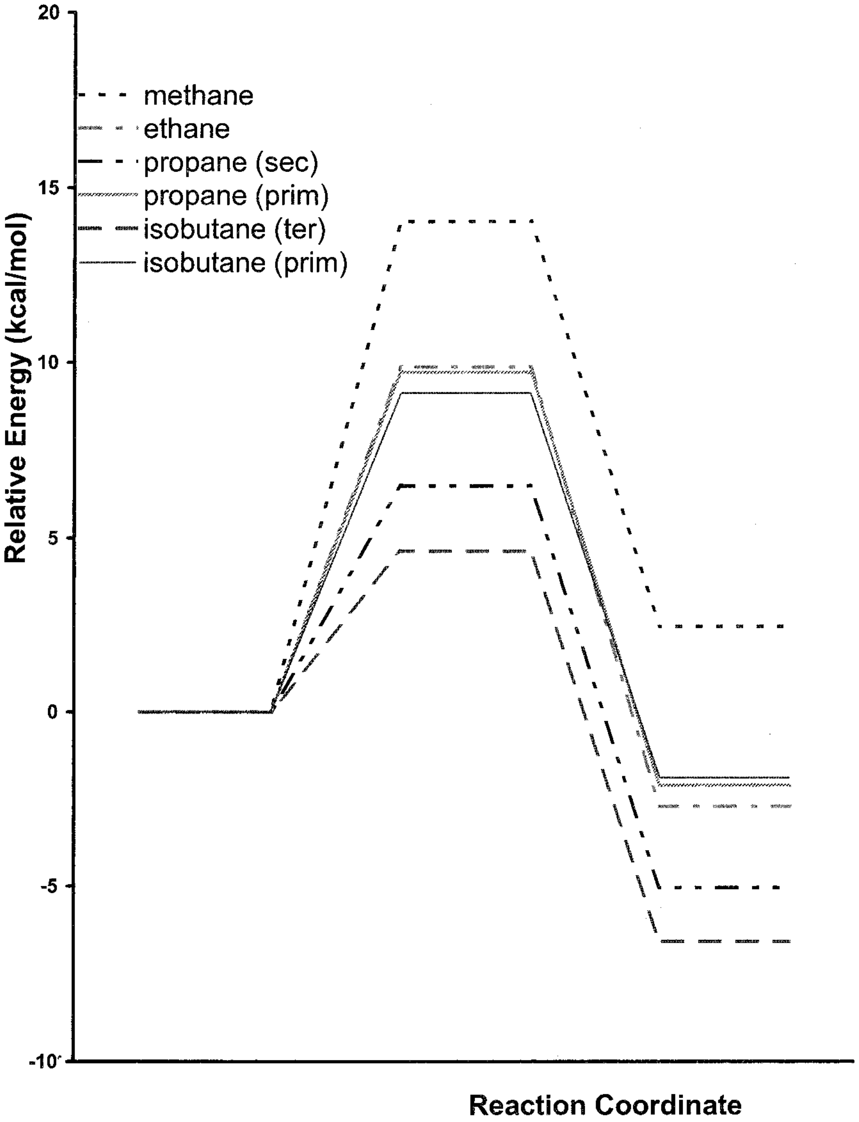

Figure 2. Energy profiles of the reaction paths for the methane, ethane, propane, and isobutane with NO_3 reactions.

similar for hydrogen atoms attached to carbons with the same degree of substitution, the preexponential parameters may not be equal, and consequently neither are the rate constants.

The calculated Arrhenius parameters are not directly comparable with the experimental ones, since the latter already include the κ. An estimate of the Arrhenius E_a value at $T = 298$ K, i.e., an effective E_a with the κ included, may be obtained from the product of the κ and the exponential factor in the Arrhenius equation, substituting the E_a value by the difference $E_a - RT \ln \kappa$, since κ can be represented as an exponential factor, $\kappa = \exp(x/RT)$. Applying this correction, the E_a's for methane, ethane, propane, and isobutane are 11.83, 8.82, and 6.18 kcal/mol (secondary abstraction), and 4.56 and 8.12 kcal/mol (tertiary and primary abstraction), respectively. The experimental value of ethane (8.80 kcal/mol at $T = 453$ K) is in excellent agreement with our E_a value. For isobutane we assumed that the experimental Arrhenius parameters should be a mixture of the two abstraction reactions. If the theoretical E_a is some intermediate between the E_a's for primary and tertiary abstractions, a value close to the experimental one is obtained. The agreement between the calculated and the experimental values for ethane and isobutane supports our claim that the E_a's for methane and propane represent adequate predictive values due to lack of experimental data to compare with. Furthermore, the value for propane is in excellent agreement with the experimental E_a reported for *n*-butane, of 6.45 kcal/mol,[26] under the assumption of a secondary H-abstraction mechanism. These two values may be expected to be similar due to the analogy of the character of the carbon atoms at which the H-abstraction occurs.

Normalized preexponential factors reported by Boyd et al.[11] for ethane, *n*-butane (secondary abstraction), and isobutane (tertiary) are 5.7×10^8, 3.8×10^8, and 1.4×10^9 L mol^{-1} s^{-1}, respectively. The calculated values of this work for ethane, propane in the secondary abstraction, and isobutane in the tertiary abstraction are correspondingly 2.4×10^9, 7.6×10^8, and 5.02×10^7 L mol^{-1} s^{-1}. It is interesting to note that as the C atom is more substituted, the preexponential factor diminishes. This trend has been observed both experimentally and theoretically when primary and secondary abstractions are compared. However, going from secondary to tertiary carbon atoms, theoretical calculations predict an even larger decrease in the preexponential factor, while the opposite is reported experimentally. The disagreement may be attributed to the importance of the primary abstraction of isobutane, which has been excluded in conclusions from experimental work. But it is difficult to explain why experimental values differ by almost 1 order of magnitude in going from secondary to tertiary abstractions[11] without considering various abstraction processes. This also disagrees with the trend in reported preexponential factors of reactions of ethane, propane, and isobutane with OH: 9.46×10^8, 3.37×10^9, and 3.77×10^9 L mol^{-1} s^{-1}.[14]

The fact that the experimental preexponential factor in the isobutane reaction can be well explained if a mixture of the preexponential factors of both abstraction channels is considered supports our proposal of an entropically favored primary channel.

Conclusions

The chemical mechanism occurring in the NO_3 + alkane reaction for methane, ethane, propane, and isobutane, has been investigated for primary, secondary, and tertiary H-abstraction channels. These various channel possibilities are shown to be important for the interpretation of the theoretical reaction profile as well as to get a better agreement with the experimental values.

The reactions are simple H-abstractions without intermediates. Abstractions take place predominantly from the most substituted C atom in propane, and from the less substituted C atom in isobutane. In the propane reaction the rate constant for the primary C-abstraction is 10% of the value of the secondary channel. For isobutane a competitive process between primary and tertiary abstractions has to be considered for a better agreement with experiment. The primary abstraction is shown to be particularly favored for $T \geq 298$ K.

Consideration of internal rotations influences noticeably the partition functions in the TS structures and entropically favors the primary H-abstraction reaction. This effect is mainly due to the large mass of NO_3. Consequently, this should not be expected to occur in other radical reactions with alkanes, such as those with OH or $O(^3P)$. Tunneling is also shown to be indispensable for the adequate description of the studied chemical mechanisms.

The rate constants and Arrhenius parameters reported in the present work are in excellent agreement with the experimental results. The values for those reactions for which experimental results are not available probably have predictive values.

In this paper, quantum-mechanical calculations using the CCSD(T)/BHandHLYP methodology with 6-311G(d,p) basis sets are shown to be appropriate for the study of the chemical mechanism of H-abstraction in the NO_3 + alkane reaction. The CCSD(T)/MP2 calculations overestimate the E_a values. Inclusion of the BSSE improves the theoretical correspondence with the experimental results.

Acknowledgment. We gratefully acknowledge the financial support from the Instituto Mexicano del Petróleo (IMP) through programs D00012 and G00058 as well as valuable discussions with Prof. Annik Vivier-Bunge. We also thank the IMP Computing Center for supercomputer time on the SGI Origin 2000.

References and Notes

(1) World Meteorological Organization, 1995.
(2) Atkinson, R. *J. Phys. Chem. Ref. Data* **1999**, *28*, 191.
(3) Arriaga, J. L.; Escalona, S.; Cervantes, A.; Orduñez, R.; López, T. Seguimiento de COV en el aire urbano de la ZMCM 1992−96. In *Contaminación Atmosféric* Vol II Colección CBI; García Colín, L., Rubén Varela Ham, J., Eds.; Universidad Autónoma Metropolitana, 1997; p 67.
(4) Blake, R. B.; Rowland, F. S. *Science* **1995**, *269*, 953.
(5) Hernández, F.; Ortíz, E. *Mol. Eng.* **1999**, *8*, 447.
(6) National Research Council, 1991.
(7) Magnotta, F.; Johnston, H. S. *Geophys. Res. Lett*. **1980**, *7*, 769.
(8) Aliwell, S. R.; Jones, R. L. *J. Geophys. Res*. **1998**, *103* (D5), 5719.
(9) Glasius, M.; Calogirou, A.; Jensen, N. R.; Hjorth, J.; Nielsen, C. J. *Int. J. Chem. Kinet*. **1997**, *29*, 527.
(10) http://www.cdc.gov/niosh/npg/npgd0447.html.
(11) Boyd, A. A.; Canosa-Mas, C. E.; King, A. D.; Wayne, R. P.; Wilson, M. R. *J. Chem. Soc., Faraday Trans*. **1991**, *87*, 2913.
(12) Cantrell, C. A.; Davidson, J. A.; Shetter, R. E.; Anderson, B. A.; Calvert, J. G. *J. Phys. Chem*. **1987**, *91*, 6017.
(13) Wallington, T. J.; Atkinson, R.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem*. **1986**, *90*, 4640.
(14) García-Cruz, I.; Ruíz-Santoyo, M. E.; Vivier-Bunge, A. *J. Comput. Chem.* **1999**, *20* (8), 845.
(15) Alvarez-Idaboy, J. R.; Galano, A.; Bravo-Pérez, G.; Ruíz, M. E. *J. Am. Chem. Soc*. **2001**, *123* (34), 8387.
(16) Alvarez-Idaboy, J. R.; Mora-Diez, N.; Vivier-Bunge, A. *J. Am. Chem. Soc*. **2000**, *122*, 3715.
(17) Galano, A.; Alvarez-Idaboy, J. R.; Montero-Cabrera, L.; Vivier-Bunge, A. *J. Comput. Chem.* **2001**, *22* (11), 1138.
(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.
(19) Alvarez-Idaboy, J. R.; Mora-Diez, N.; Russell, Boyd, J.; Vivier-Bunge, A. *J. Am. Chem. Soc.* **2001**, *123*, 2018.
(20) Jansen, H. B.; Ros, P. *Chem. Phys. Lett*. **1969**, *3*, 140.
(21) Boys, S. F.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553.
(22) Eckart, C. *Phys. Rev.* **1930**, *35*, 1303.
(23) Brown, R. L. *J. Res. Nat. Bur. Stand.* **1981**, *86*, 357.
(24) Wayne, R. P. *Atmos. Environ.* **1991**, *25A*, No. 1.
(25) Atkinson, R. J. *Phys. Chem. Ref. Data* **1991**, *20*, 459.
(26) Bagley, J. A.; Canosa-Mas, C.; Little, M. R.; Parr; A. D.; Smith S. J.; Waygood, S. J.; Wayne, R. P. *J. Chem. Soc., Faraday Trans*. **1990**, *86*, 2109.