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Rate Constant Dependence on the Size of Aldehydes in the NO₃ + Aldehydes Reaction. An Explanation via Quantum Chemical Calculations and CTST

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Abstract: The reactions of NO₃ with formaldehyde, acetaldehyde, propanal, *n*-butanal, and isobutanal have been modeled using accurate ab initio and hybrid DFT methods with large basis sets. The results clearly indicate that the reaction is a simple aldehydic H atom abstraction; no adduct was found to support the idea of a complex mechanism. Alternative hydrogen abstractions were modeled for the α carbon hydrogen atoms and for the C β of *n*-butanal; the differences in activation energies ruled out the possibility that competitive abstraction could be responsible for the anomalous increase of the rate constants with the size of aldehydes. The anomalous behavior was found to be a consequence of the preexponential factor increase, due to the enlargement of the internal rotation partition functions with the size of the aldehydes. The reaction rate constants, calculated using the conventional transition-state theory as applied to a proposed simple mechanism, reproduce remarkably well the reported experimental results. Consideration of the internal rotation partition functions is shown to be essential for the determination of the preexponential parameters and thus for the correct calculation of the rate constants. The tunneling correction was found negligible due to the features of the transition vector.

Introduction

Aldehydes play an important role in both clean and polluted atmospheres because of their participation in the oxidation of volatile organic compounds (VOC) and in the OH radical and ozone formation. Large amounts of aldehydes are emitted into the troposphere from biogenic and anthropogenic sources.^{1–7} Many abundant VOC produce aldehydes as important products.^{8,9} Some examples are the reactions of the OH radical with alkenes and aromatic compounds and the addition of ozone to alkenes. In the troposphere a C_{*n*} aldehyde reacts to form mainly the C_{*n*–1} aldehyde.^{8,10} It is widely accepted that the most important sink of aldehydes is the hydrogen abstraction reaction

by an OH radical. The OH yield comes primarily from photolysis, therefore at nighttime its concentration is very low and the reaction with NO₃ becomes relevant, particularly for large aldehydes.¹¹ The rate coefficients of the aldehydes + OH reactions are usually comparable to the rate coefficients of the OH addition to alkenes. Nevertheless, comparing them with the aldehyde + NO₃ reaction, one finds, for example in the case of acetaldehyde, that the rate coefficient becomes 10 times the coefficient of an OH addition in the reaction with ethene.⁸

The aldehyde + OH reaction has been widely studied by experimental techniques,^{8–10,12–18} as well as by theoretical methods.^{14,19–21} The reaction of aldehydes with NO₃ has been

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(1) Nondek, L.; Rodler, D. R.; Birks, J. W. *Environ. Sci. Technol.* **1992**, 26, 1174.

(2) Hoekman, S. K. *Environ. Sci. Technol.* **1992**, 26, 1206.

(3) Ciccioli, P.; Brancaleoni, E.; Frattoni, M.; Cecinato, A.; Branchetti, A. *Atmos. Environ.* **1993**, 27A, 1891.

(4) Grimaldi, F.; Bacle, D.; Viala, A. *Indoor Environ.* **1995**, 4, 297.

(5) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J. Geophys. Res.* **1995**, 100, 8873.

(6) Kesselmeier, J.; Bode, K.; Hofmann, U.; Müller, H.; Schäfer, L.; Wolf, A.; Ciccioli, P.; Brancaleoni, E.; Cecinato, A.; Frattoni, M.; Foster, P.; Ferrari, C.; Jacob, V.; Fugit, J. L.; Dutaur, L.; Simon, V.; Torres, L. *Atmos. Environ.* **1997**, 31, 119.

(7) Fall, R. Biogenic Emissions of Volatile Organic Compounds from Higher Plants. In *Reactive Hydrocarbons in the Atmosphere*; Hewitt, C. N., Ed.; Academic Press: San Diego, CA, 1999; pp 41–96.

(8) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1999**, 28 (2), 191.

(9) Atkinson, R. *Atmos. Environ.* **2000**, 34, 2063.

(10) Atkinson, R. *J. Phys. Chem. Ref. Data, Monograph* **1994**, 2, 1.

(11) Ullerstam, M.; Langer, S.; Ljungström, E. *Int. J. Chem. Kinet.* **2000**, 32 (5), 294.

(12) Finlayson-Pitts, B. J.; Pitts, N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; Wiley-Interscience: New York, 1986.

(13) The NIST Chemical Kinetics Data Base, NIST Standard Reference Database; U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology: Gaithersburg, MD, 17-2Q98.

(14) Taylor, P. H.; Rahman, M. S.; Arif, M.; Dellinger, B.; Marshall, P. *Symp. Int. Comb. Proc.* **1996**, 26, 497.

(15) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1984**, 88, 5342.

(16) Butkovskaya, N. I.; Setser, D. W. *J. Phys. Chem. A* **1998**, 102, 9715.

(17) Michael, J. V.; Keil, D. J.; Klemm, R. B. *J. Chem. Phys.* **1985**, 83, 1630.

(18) Papagni, C.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **2000**, 32 (2), 79.

(19) Dupuis, M.; Lester, W. A., Jr. *J. Chem. Phys.* **1984**, 81, 847.

(20) Francisco, J. S. *J. Chem. Phys.*, **1992**, 96, 7597.

(21) Alvarez-Idaboy, J. R.; Mora-Diez, N.; Boyd, R. J.; Vivier-Bunge, A. *J. Am. Chem. Soc.* **2001**, 123, 2018.

(22) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical kinetics and photochemical data for use in stratospheric modeling*; Evaluation No. 12 JPL, Publication 97-4, 1997.

less studied than that with the OH radical.^{11,14,22–25} According to the NIST chemical kinetics database,¹³ up to the second quarter of 1998 only three papers reported Arrhenius parameters for the acetaldehyde + NO₃ reaction.^{22–24} No Arrhenius parameters for the other aldehydes were reported. In the last three years the interest in these reactions has increased.^{11,18} One of the reports includes the study of the rate coefficient dependence on temperature for *n*-butanal and isobutanal.¹¹

There is an experimental fact in this reaction that has not yet been explained and that has been the subject of theoretical speculations: the rate coefficients increase “abnormally” fast with the increase in the size of the aldehydes.²⁵ On the basis of the dissociation energies a smoother increase of the rate constant should be expected as the dissociation energies decrease. As a consequence of this “anomalous” behavior, no correlation is observed between the rate coefficients of the aldehyde hydrogen abstraction by OH and by NO₃, nor between the rate coefficients for NO₃ hydrogen abstraction from aldehydes and from alkanes.

Different explanations have been proposed to justify these observations. Some authors have suggested that a complex mechanism occurs, with the formation of an exothermic adduct, followed by the aldehydic C–H bond cleavage. Therefore, the rate coefficient would depend not only on the C–H bond dissociation energy but also on the surrounding molecular structure, on the ability to form a stable adduct, and on the possibility of redistributing the reaction energy.²⁵ This seems to properly explain the experimental behavior, but from the point of view of the electronic structure of the radicals, it is not strictly justified. The OH and NO₃ radicals abstract a hydrogen from aldehydes, but NO₃ is less reactive in all cases. In a *D*_{3h} conformation NO₃ is nonpolar, and its spin density is homogeneously distributed, while it is localized on the oxygen atom in OH. Based on this fact, any interaction with NO₃ is expected to be weaker than that with the OH radical. Therefore there is no reason to expect that an adduct that is not formed in the OH interaction with aldehydes will be formed with NO₃. The formation of an adduct by the addition reaction, suggested to explain the observed negative activation energies for the reaction of OH with aldehydes,^{14,17} was recently ruled out on the basis of accurate quantum chemical calculations.²¹

An alternative explanation to the “abnormal” increase of the rate coefficients with the size of aldehydes could be that other hydrogens away from the CHO group could be abstracted.¹⁸ This explanation seems to be more realistic than the previous one, because C α and C β atoms could be activated. However, this hypothesis cannot explain why the rate coefficients of isobutanal and *n*-butanal are almost the same, nor why that of *n*-pentanal is larger than that of isobutanal, although H abstraction from a tertiary carbon atom should be more favored than that from a secondary one. Another argument against this hypothesis is, again, the comparison with the analogous reaction with an OH radical. It is widely accepted and justified that the more reactive are the radicals the less selective they behave. Thus, the NO₃ radical should be more selective than OH, which itself is selective enough to abstract almost exclusively the H from the CHO group.

An entire hypothesis to explain this behavior has not been demonstrated to date. From our point of view, the proposed explanations are, to some extent, not fully consistent with the theoretical foundations. Although modern experimental techniques are extremely powerful, they have not been fully applied

in this kind of reaction. The Arrhenius parameters have not been systematically calculated, no experiments including isotopic effect have carried out, and the pressure dependence of the reaction rate has not been studied.

On the other hand, modern quantum chemical methods have been proved to be very useful in the study of chemical reactions and, specifically, in atmospheric radical–molecule reactions. Several gas-phase reaction rates have been accurately calculated.^{26–28} For example, the uncertainties about the mechanism of OH reactions with aldehydes and alkenes that occur with apparent negative activation energies have been successfully explained.^{21,29}

In this work we model the reaction mechanism of the hydrogen abstraction from C₁ to C₄ aldehydes by the NO₃ radical, by the calculation of reaction profiles of different possible reaction paths. The evaluation of the different channel activation energies helps to discriminate among them and investigate if other than CHO hydrogen can be abstracted. Besides, the comparison between calculated and experimental rate coefficients might demonstrate if the assumed mechanism is correct. The calculation of the intrinsic reaction coordinate (IRC) of one of the reaction profiles could prove whether any other adduct might connect reactants and products.

Additionally, Arrhenius parameters consistent with the rate coefficients and with available recommended parameters will be proposed. For those reactions for which Arrhenius parameters have not been accurately calculated yet, the results of the present work could be used as a good approach to real values.

Computational Methodology

Electronic structure calculations have been performed with the system of programs Gaussian98³⁰ with the 6-311G(d,p) basis set. The unrestricted formalism was used to calculate the energies of the radicals. The correlation energy corrections were introduced with the coupled cluster method at the CCSD(T) level.

The best experimentally known reaction of this type is the acetaldehyde + NO₃ reaction and it was used here to test several methods of calculation. Geometries were optimized at the MP2 and BHandHLYP levels using 6-311G(d,p) basis set. The stationary points were characterized by frequency calculation. The zero point energies (ZPE) and thermal corrections to the energy (TCE) at 298.15 K were computed. The resultant geometry in each case was used to obtain single-point energies at the CCSD(T)/6-311G(d,p) level, corrected using the corresponding TCE. The CCSD(T)/MP2 activation energy was overestimated. The best agreement between the calculated activation energy at 298.15 K and the experimental values was obtained with the CCSD(T)/6-311G(d,p)/BHandHLYP/6-311G(d,p) method. Therefore this level of calculation was chosen for the modeling of the reaction in other cases.

All the geometries for formaldehyde, acetaldehyde, propanal, *n*-butanal, and isobutanal were fully optimized at the BHandHLYP/6-

(26) González, Carlos; Molecular Simulation Seminar at the Instituto Mexicano del Petróleo, México D.F., September 2000.

(27) Truong, T. N.; Truhlar, D. G. *J. Phys. Chem.* **1990**, *93*, 1761. Truong, T. N.; Truhlar, D. G. *J. Phys. Chem.* **1992**, *97*, 8820.

(28) Melissas, V. S.; Truhlar, D. G. *J. Phys. Chem.* **1994**, *98*, 875.

(29) Alvarez-Idaboy, J. R.; Mora-Díez, N.; Vivier-Bunge, A. *J. Am. Chem. Soc.* **2000**, *122*, 3715.

(30) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98*, Revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Dlugokencky, E. J.; Howard, C. J. *J. Phys. Chem.* **1989**, *93*, 1091.

(24) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459.

(25) D'Anna, B.; Nielsen, C. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3479.

311G(d,p) level and the character of the transition states was confirmed by a frequency calculation, performed at the same level, and presenting only one imaginary frequency corresponding to the expected transition vector. An Intrinsic Reaction Coordinate (IRC) calculation was performed only for formaldehyde. Because of the similarity between the geometry of the latter and the other transition states, as well as the similarities in their transition vectors, it was assumed that all of them correctly connect reactants and products. The Basis Set Superposition Error (BSSE) was calculated using the Counterpoise method^{31,32} for all aldehydic hydrogen abstraction transition states.

For the modeling of the alternative hydrogen abstraction only relative energies are necessary, therefore the calculations were done at the BHandHLYP/6-311G(d,p) level, without BSSE. The activation energies are obviously underestimated, and some of them are negative, but the ones corresponding to aldehydic hydrogen abstraction correlate perfectly with the ones calculated at the CCSD(T) level, suggesting that the relative values are accurate.

The rate constants were calculated using Conventional Transition State Theory (CTST) and the partition functions obtained from the Gaussian output. The tunneling corrections were expressed as the ratio of the quantum-mechanical to classical barrier crossing rate, assuming an unsymmetrical, one-dimensional Eckart function barrier.³³ For this purpose we have used the numerical integration program of Brown.³⁴

The rate constants for the reactions were obtained by the following expression:

$$k = \kappa(k_B T/h)(Q_{TS}/Q_{NO_3} \cdot Q_{Ald})e^{(E_{TS}-E_{react})/RT} = \kappa A e^{-E_a/RT} \quad (1)$$

The activation energies are those obtained in the CCSD(T)/6-311G-(d,p)/BHandHLYP/6-311G(d,p) approximation, with the BHandHLYP/6-311G(d,p) ZPE correction included. The ratio $Q_{TS}/Q_{NO_3} \cdot Q_{Ald}$ of the Gaussian output has been corrected by replacing some of the harmonic contributions of large amplitude vibrations by those calculated as internal rotations.

Results and Discussion

Competitive Hydrogen Abstractions. One of the most relevant aspects in the study of reaction mechanisms is usually to determine the positional selectivity of the reactant. In refs 21 and 24 it has been concluded that for the aldehydes + OH the preferred process appears to be the abstraction of the aldehydic hydrogen. Nevertheless, in the ketones + OH reaction it has been reported that H atoms at β carbons are more activated than those at α carbons.^{36,39} The explanation proposed for this behavior was the formation of a hydrogen bonded pre-reactive complex.^{37,40,41} In a recent work, we have reported that these kind of interactions remarkably stabilize the transition states.⁴²

If the abstraction occurs by the attack of the NO_3 radical, there are no such interactions. Consequently, in this case, there is no reason to expect an activation of β carbons over the α carbons. In addition, it is well-known that the ease of abstraction is higher when the hydrogen is originally attached to a secondary carbon than when it is attached to a primary one. Therefore, if

Table 1. Comparison of Activation Energies (kcal/mol) of NO_3 Hydrogen Abstraction from the $-CHO$ Group and from $C\alpha$ at the BHandHLYP/6-311G(d,p) Level of Calculation

	activation energy ^a		
	$-CHO$	$C\alpha$	$C\beta$
acetaldehyde	-0.06	9.20	
propanal	-0.28	5.56	
<i>n</i> -propanal (α)	-1.68	4.86	4.44
isobutanol	-0.54	2.85	

^a Including ZPE but not BSSE corrections.

a secondary β carbon is not activated there is no reason to assume that a primary one should be. Taking into account all the facts discussed above some competitive sites were included in this work. The aldehydic and the α channels were modeled for all the studied aldehydes, the β channel was modeled for the only aldehyde with a secondary β carbon (the *n*-butanal). This selection was made within the assumption that it should be the most reactive of all the β carbons of the studied aldehydes.

The calculated activation energies, at 0 K and the BHandHLYP/6-311G(d,p) level of calculation, are reported in Table 1 for all the aldehydes studied in this work. Some of them are negative, since we have not included the BSSE, but relative values should be accurate enough. The transition state geometries of both channels are shown in Figures 1 and 2, respectively.

There is a clear difference between the transition state geometries corresponding to the CHO α and β abstractions. The transition state structure (TS) for H abstraction takes place earlier for the aldehydic H, with the $O \cdots H$ distance of 1.62 Å for formaldehyde, compared to 1.46 Å in the α TS for isobutanol, with the former the latest aldehydic TS and the latter the earliest nonaldehydic one. The earlier the transition state the looser it is and the larger its partition functions. Since the reactants are the same, this geometrical difference implies that we should expect a larger preexponential factor for aldehydic than for $C\alpha$ hydrogen abstraction.

From an energetic point of view it is even clearer that α hydrogen atoms cannot compete with the carbonyl ones. There is a difference of 3.38 kcal/mol between both activation energies for isobutanol. At ambient temperature, such a difference in activation energy implies a decrease in the rate coefficient of about 3 orders of magnitude. The energetic gap between the two channels is about 9 kcal/mol in the case of acetaldehyde. This difference are larger than any error that can be expected in the calculation. Therefore these results allow us to conclude that, in aldehydes at atmospheric temperature, the only hydrogen atom able to be abstracted by NO_3 is the aldehydic one, even in the limiting case of a hydrogen atom attached to a tertiary α carbon.

In the case of *n*-butanal, the hydrogen abstraction was modeled for α and β sites. Since both are secondary carbons, the difference in activation energies could be considered due to the influence of the carbonyl group. Both transition states have similar geometries and similar activation energies, but the activation energy for the $C\beta$ position is lower than the $C\alpha$ one by 0.4 kcal. In view of the fact that the activation energy for the abstraction of the aldehydic H is 6.1 kcal/mol lower than that for the $C\beta$ position, it is not expected that it will be activated for this reaction. However, this would be important for reactions of NO_3 with ketones where no aldehydic hydrogen is present. According to our results it should be expected that the $C\beta$ position will be slightly more activated than $C\alpha$ ones, as in the

(31) Jansen, H. B.; Ros, P. *Chem. Phys. Lett.* **1969**, 3, 140.

(32) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, 19, 553.

(33) Eckart, C. *Phys. Rev.* **1930**, 35, 1303.

(34) Brown, R. L. *J. Res. Natl. Bur. Stand.* **1981**, 86, 357.

(35) Michael, J. V.; Keil, D. G.; Klemm, R. B. *J. Chem. Phys.* **1985**, 83, 1630.

(36) Kwok E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, 29, 1685–1695.

(37) Wallington, T. J.; Kurylo, M. J. *J. Phys. Chem.* **1987**, 91, 5050.

(38) Dagaut, P.; Wallington, T. J.; Liu, R.; Kurylo, M. J. *J. Phys. Chem.* **1988**, 92, 4375.

(39) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1995**, 27, 261.

(40) Klamt, A. *Chemosphere* **1996**, 32, 717.

(41) Frank, I.; Parrinello, M.; Klamt, A. *J. Phys. Chem. A* **1998**, 102, 3614.

(42) Galano, A.; Alvarez-Idaboy, J. R.; Montero-Cabrera, L. A.; Vivier-Bunge, J. *Comput. Chem.* **2001**, 22 (11), 1138.

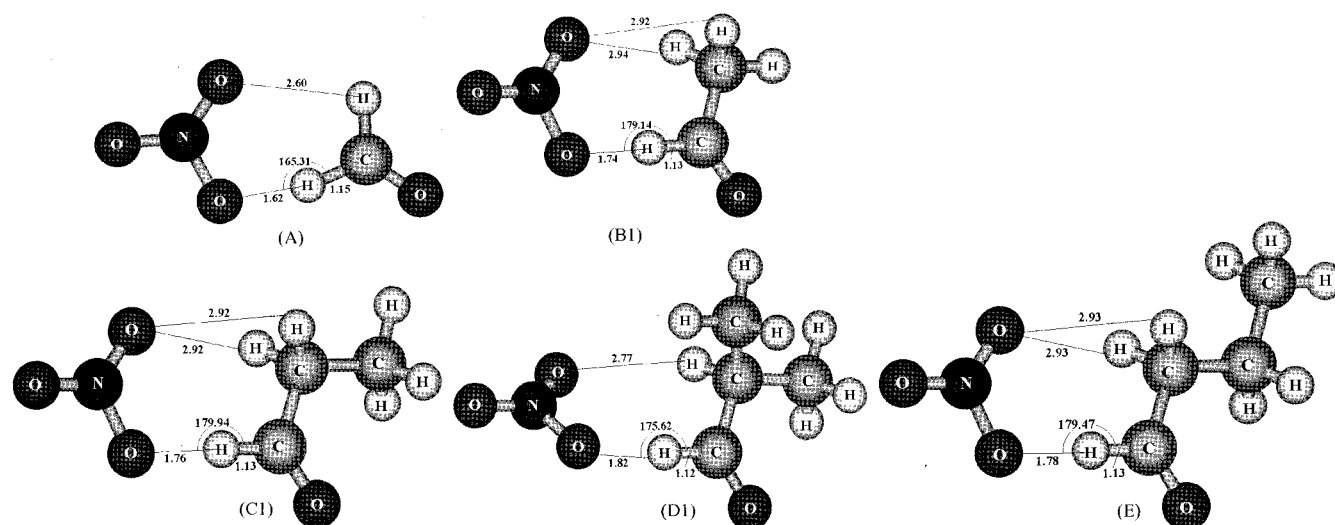


Figure 1. Transition state geometries of aldehydic hydrogen abstraction (A) formaldehyde, (B1) acetaldehyde, (C1) propanal, (D1) isobutanal, and (E) *n*-butanal.

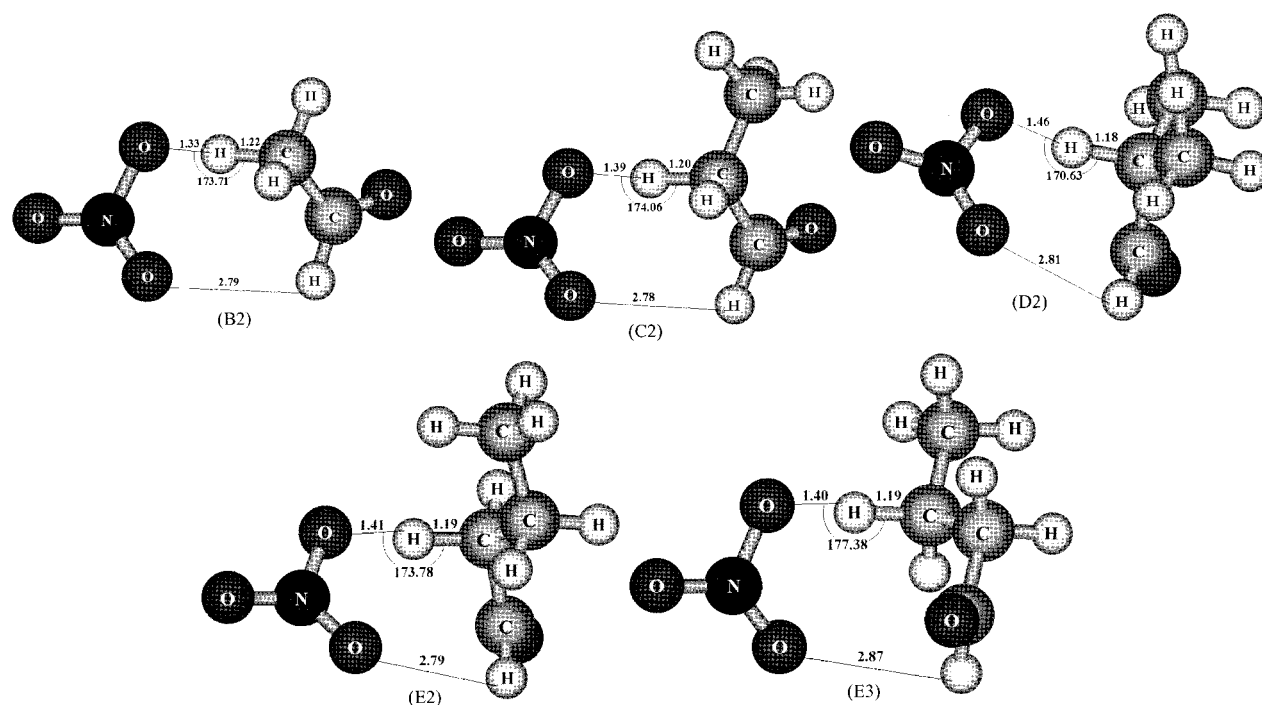


Figure 2. Transition state geometries of $C\alpha$ hydrogen abstraction (B2) acetaldehyde, (C2) propanal, (D2) isobutanal, and (E2) *n*-butanol and of $C\beta$ (E3) *n*-butanol.

ketones + OH reaction. The difference in activation energies between aldehydic and primary $C\beta$ channels is expected to be larger than 6.1 kcal/mol; therefore there is no reason to expect that this channel could be relevant in the reaction.

Alternative Adduct. There is no way to prove that a hypothetical adduct does not exist in a reaction. What can be done is to verify that, in a specific reaction path, it is not present. Then, if the proposed mechanism describes adequately the experimental findings including the rate constant of the reaction, we can conclude that such a hypothetical adduct does not exist.

An IRC calculation was performed and the results are shown in Figure 3. The calculation started from a transition state, with only one imaginary frequency, and followed the reaction coordinate in the direction of both the reactants and the products. Thirty steps were taken in each direction to follow very closely

the path from the reactant complex to the product complex. The energy of the system was found to decrease monotonically and continuously in each direction. The molecular geometries of the two final structures are also shown in Figure 3, and they perfectly resemble the reactant and product complexes. Therefore according to the mechanism proposed in this work, no additional stable adduct was found in the reaction path.

It is necessary to prove now that our one-step mechanism is consistent with experimental data, including the “abnormal” increase in rate coefficients with the increase in the size of the aldehydes.

Reaction Profiles. The reaction profiles corresponding to the aldehydic hydrogen abstraction from the five aldehydes studied are shown in Figure 4. Only three stationary points have been included: the isolated reactants, the transition state, and the

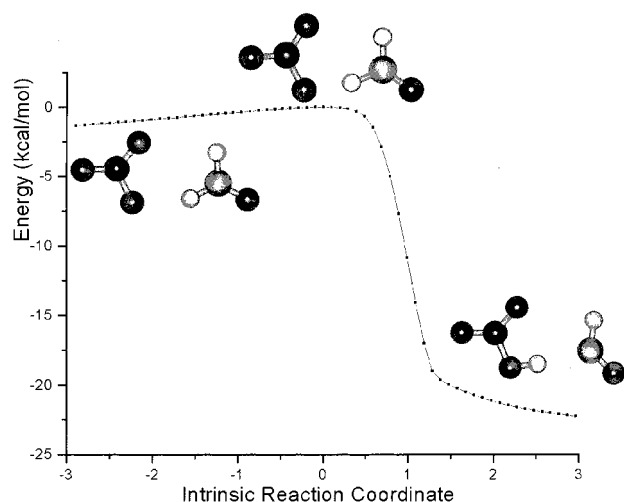


Figure 3. Intrinsic reaction coordinate for the formaldehyde- NO_3 reaction.

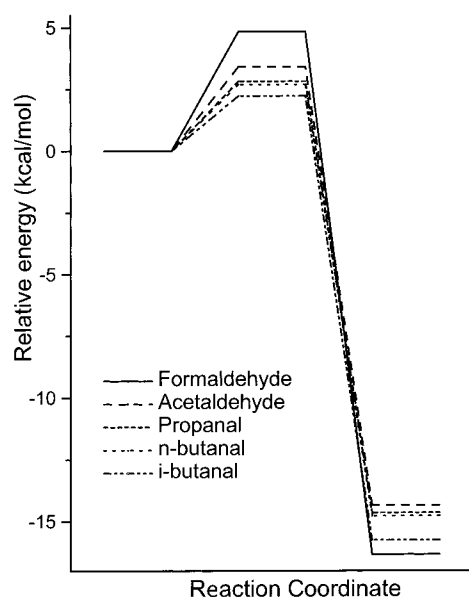


Figure 4. Reaction profiles of aldehydic hydrogen abstraction.

Table 2. Activation Energies and Heats of Reaction (kcal/mol) of NO_3 Hydrogen Abstraction from the $-\text{CHO}$ Group at the CCSD(T)/6-311G(d,p)//BHandHLYP/6-311G(d,p) Level of Calculation, Including BSSE and ZPE for Activation Energies and Thermal Corrections to Enthalpy for Heats of Reactions

	activation energy		heat of reaction	
	calcd 0 K	calcd 298 K	exptl	calcd
formaldehyde	4.84	5.01	4.78 ^a	-16.34
acetaldehyde	3.41	3.94	3.70 ^b	-14.35
propanal	2.82	3.38	NA	-14.65
n-butanol	2.69	3.35	2.87 ^c	-14.78
isobutanol	2.23	2.65	3.35 ^c	-15.76

^a From ref 8. ^b From ref 23. ^c From ref 11.

isolated products. The corresponding numerical values of the activation energies and the heats of reaction are reported in Table 2.

In previous works,^{21,43,44} the importance of pre-reactive complexes in some radical-molecule reaction has been pointed

out. In particular, in the aldehyde + OH reaction, a pre-reactive complex was identified whose energy is about 3 kcal/mol more stable than that of reactants. The stabilization is caused by two interactions: the OH oxygen is attracted by the aldehydic H and the OH hydrogen is attracted by the carbonyl oxygen, the second being more important than the first.²¹ In the case of aldehyde + NO_3 the only significant interaction occurs between one of the oxygen atoms of NO_3 and the aldehydic hydrogen, and it is expected to be appreciably weaker than any of the OH aldehyde interactions. For these reasons the pre-reactive complexes were not calculated in this work.

The presence of a pre-reactive complex becomes relevant in the calculation of the rate constant only in two cases: either by the existence of negative apparent activation energy or by the presence of a significant tunneling effect. It will be shown below that this is not the case for the present reaction

The energetic profiles of the reaction have a typical behavior: as the number of methyl groups attached to the α carbon atom increases from 0, in formaldehyde, to 2 in isobutanol, the activation energy decreases; however, the activation energies of *n*-butanol and propanal are very close to each other. This behavior is the expected one, since no dipole-dipole interaction between the large aldehydes and NO_3 occurs that could selectively stabilize their transition states with respect to the smaller ones. Nevertheless, the potential energy surface was explored for such a transition state, with no success. This can be explained because the difference between small and large aldehydes is the aliphatic hydrocarbon residue, which is nonpolar and does not interact with NO_3 . All the transition states (see Figure 1) have similar structures, with the $\text{C}\cdots\text{H}\cdots\text{O}$ angle very close to 180° , with the exception of the corresponding to the formaldehyde- NO_3 reaction. In this particular case the $\text{C}\cdots\text{H}\cdots\text{O}$ angle is equal to 163° due to a hydrogen bond-like interaction between the second aldehydic hydrogen and one of the oxygen atoms in the NO_3 radical.

The energetic profiles are consistent with the geometries of the transition states (Figure 1). The $\text{C}\cdots\text{H}$ distance decreases and the $\text{H}\cdots\text{O}$ distance increases from formaldehyde to isobutanol, i.e., the transition states occur earlier as the activation energies decrease. The $\text{C}\cdots\text{H}$ and $\text{H}\cdots\text{O}$ distances are very similar in *n*-butanol and propanal in correspondence with their also very similar activation energies.

The most interesting feature of the transition states is the transition vector (see arrows in Figure 5a), whose components show the atoms displacement in the vibrational mode corresponding to the imaginary frequency, i.e., the motion of the atoms in the vicinity of the transition state. In a typical hydrogen abstraction transition state (Figure 5b) the hydrogen moves between two heavy atoms and all the other atoms remain almost fixed. In the case of the aldehydes + NO_3 transition states, the whole aldehyde approaches the NO_3 group up to within bonding equilibrium distance, as in an addition reaction, and then the carbonyl radical moves away, as in an elimination reaction. Therefore the transition vectors resemble the behavior that would be expected in a one-step addition-elimination process. That is very unusual and it must be proved. That the transition structure properly connects reactants and products was verified by performing an IRC calculation. This kind of transition vector has as a relevant consequence: it should not be expected an appreciable tunneling effect should not be expected.

The tunneling correction is relevant for reactions in which the mass of the atoms that move along the reaction coordinate

(43) Sekusak, S.; Sabljic, A. *Chem. Phys. Lett.* **1997**, 272, 353.

(44) Uc, V. H.; Garcia-Cruz, I.; Hernandez-Laguna, A.; Vivier-Bunge, A. *J. Phys. Chem. A* **2000**, 102, 1583.

(45) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ.* **1991**, 25A (1), 203.

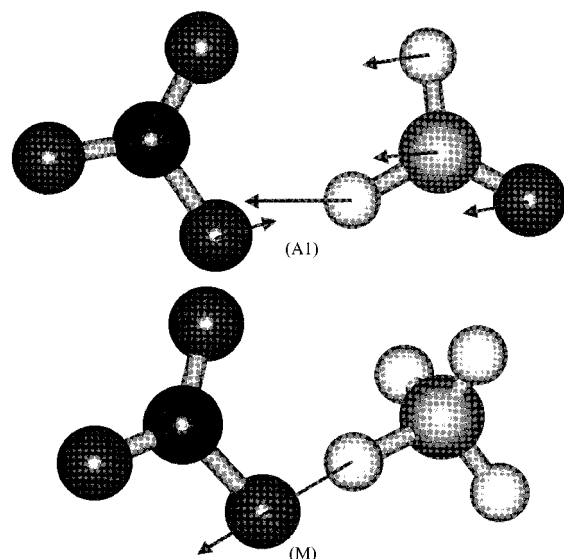


Figure 5. Transition vector components of the formaldehyde- NO_3 (A1) and methane- NO_3 (M) transition states.

is very small. This is the case for typical hydrogen abstraction reactions, because the only atom that moves along the reaction coordinate, in the vicinity of the transition state, is the hydrogen atom. In the present case most of the atoms in the molecule move and the imaginary frequency is very small with respect to the typical ones, since it depends on the masses of the atoms involved in the vibrational mode. In turn, the tunneling correction that depends strongly on the value of the imaginary frequency is close to unity. The transition vector obtained in this work could be an artifact of the calculation. In such a case, the artificial absence of the tunneling effect would yield underestimated rate constants. For similar barriers in a typical H abstraction reaction from aldehydes by an OH radical, the tunneling correction was found to be about 3.0.²¹ Therefore, if this is an artifact of the calculation we should expect the rate coefficient for formaldehyde + NO_3 to be underestimated by a factor of 3.

Rate Coefficients Calculations. To calculate the rate coefficients we used the results of the thermochemical calculation included in the Gaussian 98 vibrational output, with some corrections. This program, in its standard version, calculates internal rotation with the harmonic oscillator approximation; the hindered rotation approximation is not fully implemented yet. This implies that, for systems with internal rotations, the partition functions are underestimated. In the transition states of the aldehydes + NO_3 reaction there are three internal rotations that can be considered free, the largest barrier being 0.6 kcal/mol. In the reactants, acetaldehyde and larger aldehydes, there may be several hindered rotations corresponding to alkyl groups. In this work all internal rotations are considered to be free. This obviously introduces an error in the calculation of individual partition functions, but a cancellation occurs because most of the rotations are similar in the transition states and in free aldehydes.

The tunneling correction was also calculated, although it was expected to be very small. All the necessary parameters to calculate the rate constants are reported in Table 3: The ratio of the transition state and the reactant partition functions (from Gaussian output and corrected by free rotations), the tunneling corrections, the preexponential factors, and the calculated rate constants. The activation energies at 0 K were reported in Table 2.

There is an excellent agreement between the calculated rate coefficients and the recent or recommended experimental values. The largest disagreement with experimental value is found for acetaldehyde, the calculated value is $k = 1.19 \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and the recommended value is $1.64 \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$.⁸ However, in this case the reported experimental error is $\Delta\log k = \pm 0.2$ at 298 K, implying that the experimental rate constant interval goes from 1.03×10^6 to $2.60 \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and consequently our value lies within the experimental range. The discrepancy between the calculated and experimental result for acetaldehyde is about 26%. For formaldehyde, propanal, isobutanal, and *n*-butanal, it is 17%, 8%, 7%, and 9%, respectively, and all of them lie within the experimental errors. In the cases of propanal, *n*-butanal, and isobutanal our results are in good agreement with those of D'Anna and Nielsen,²⁵ but for *n*-butanal the comparison with the results of Papagni, Arey, and Atkinson¹⁸ shows an even better agreement. The worst agreement with experimental results was found with Ullaertan *et al.*¹¹ They reported two values for the rate coefficients of isobutanal and *n*-butanal, obtained from absolute and relative sets of measurements. Surprisingly, the relative rate coefficient for isobutanal and the absolute one for *n*-butanal are in perfect agreement with our results. The others are appreciably different from ours, especially the absolute rate coefficient for isobutanal. There is not a clear explanation for this behavior.

A linear correlation between calculated and experimental rate constants reported by D'Anna and Nielsen²⁵ and those recommended by Atkinson, for formaldehyde and acetaldehyde,⁸ is observed (Figure 6). The correlation coefficient is 0.997. This excellent correspondence with experimental values advances our model as a good representation of the experimental behavior. In Figure 6 are included other experimental values for comparative purpose as well as to figure out about the dispersion among the different experimental values.

The agreement between calculated and experimental rate constant evidences that (1) the tunneling correction is almost negligible in this reaction, and this is not an artifact of the calculations, (2) the direct, one-step mechanism explains entirely the experimental behavior, without the need to postulate the formation of an additional adduct, and (3) the consideration of abstraction of other hydrogen atoms is not necessary for the explanation of observed rate constants.

The rate coefficient depends on the activation energy as well as on the preexponential factor. On the basis of the good agreement between the calculated and the experimental values of the rate constants, let us try to identify the cause of the "abnormal" behavior of these kinds of reactions. The preexponential factor depends on the partition functions ratio (eq 1), which depends on the internal rotation partition functions. The latter can be expressed in terms of the reduced moment of inertia (I') of the two tops (A and B) involved in each rotation:

$$I' = I_A I_B / (I_A + I_B) \quad (2)$$

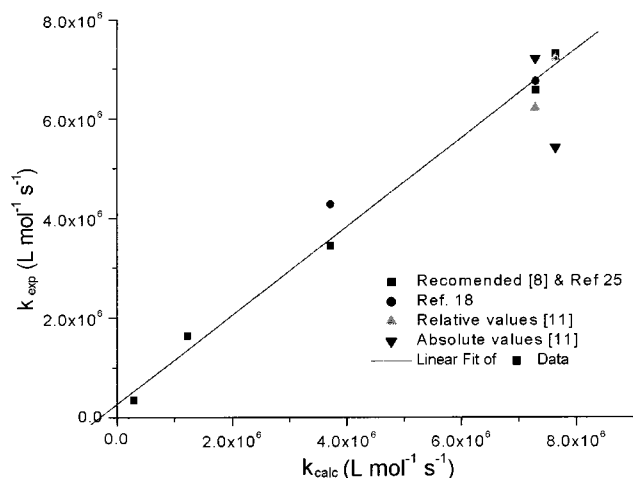
I_A and I_B represent the moments of inertia of tops A and B about a common axis of internal rotation. The partition function of each internal rotation, according to the free rotor model, can be calculated as:

$$Q_{\text{free rotor}} = (8\pi^3 I' k_B T)^{1/2} / \sigma_{\text{int}} h \quad (3)$$

σ_{int} is the internal (or effective) symmetry number of the internal rotation, k_B is the Boltzmann constant, and h is the Planck constant.

Table 3. Partition Functions Ratios (Q^\ddagger/Q_r), Preexponential Factors (A), Tunneling Effects (κ), and Rate Constants (k)

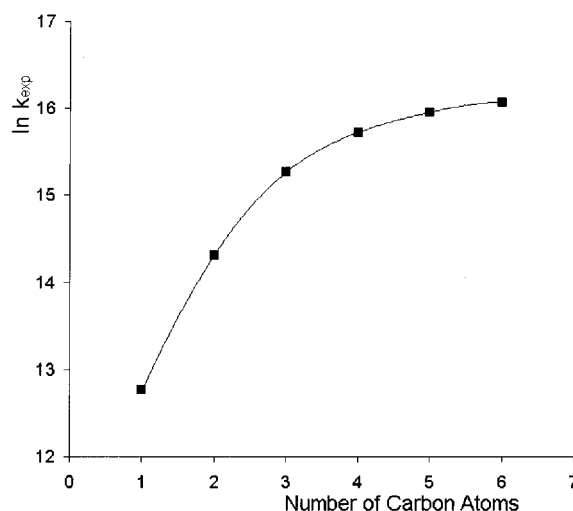
	Q^\ddagger/Q_r		A (mol·L ⁻¹ ·s ⁻¹)		κ	k (mol·L ⁻¹ ·s ⁻¹)	
	Gauss	corr.	calcd	exptl		calcd	exptl
formaldehyde	8.93×10^{-7}	1.56×10^{-4}	9.67×10^8	1.20×10^9	1.06	2.73×10^5	3.49×10^5 [ref 8]
acetaldehyde	1.42×10^{-6}	6.07×10^{-5}	3.79×10^8	8.43×10^8	1.02	1.19×10^6	1.64×10^6 [ref 23]
propanal	4.27×10^{-7}	6.98×10^{-5}	4.34×10^8	NA	1.00	3.71×10^6	3.44×10^6 [ref 25] 4.27×10^6 [ref 18]
<i>n</i> -butanal	5.31×10^{-7}	1.09×10^{-4}	6.79×10^8	7.2×10^8	1.00	7.29×10^6	6.56×10^6 [ref 25] 6.74×10^6 [ref 18] 6.02×10^6 [ref 11] 7.2×10^6 [ref 11]
isobutanal	9.57×10^{-8}	5.30×10^{-5}	3.29×10^8	1.74×10^9	1.00	7.64×10^6	7.29×10^6 [ref 25] 7.2×10^6 [ref 11] 5.41×10^6 [ref 11]

**Figure 6.** Correlation of calculated vs experimental rate constants for the aldehyde-NO₃ reaction.

The most important rotations in transition states include the aldehydic group in one top and the NO₃ in the other. The reduced moment of inertia is always less than the intrinsic moment of inertia of any of the tops, and the I' upper limit is equal to the smallest of them. In the formaldehyde-NO₃ transition state the NO₃ is the heaviest top, but in propanal-NO₃ both tops have similar moments of inertia, and in *n*-butanal and isobutanal the aldehyde group is the heaviest top. This suggests that the partition functions of equivalent internal rotations vary significantly from one aldehyde to another. For example, the partition function corresponding to the rotation around one of the axes formed in the transition structure changes from 21.60 in formaldehyde to 41.55 in propanal and 52.02 in *n*-butanal.

As the size of the aldehydes increases I_A becomes much larger than I_B and in the limit the I' is equal to the moment of inertia of the lighter top (NO₃). Accordingly, if the increase in the rate constant in the aldehydic series arises from the increase of the reduced moment of inertia, a plot of the k values versus the size of the aldehyde should present an asymptotic tendency. To confirm this hypothesis we have plotted experimental rate coefficients^{8,18,23} versus the number of carbon atoms (Figure 7). To avoid mixing different factors we have excluded isobutanal. The figure clearly shows the expected trend for aldehydes up to six carbon atoms. According to the shape of this figure the values of the rate constants corresponding to *n*-aldehydes with six or more carbon atoms should be roughly the same.

The aldehyde + OH reaction does not have the same behavior because the OH moiety is the lighter top in all the internal rotations. Therefore the reduced moment of inertia of any

**Figure 7.** Plot of logarithm of experimental rate constant vs number of carbon atoms in aldehyde-NO₃ reactions: C1 [ref 8], C2 [ref 23], and C3-6 [ref 18].

rotation involving the OH group and any aldehyde will be very similar to the OH intrinsic moment of inertia. Indeed, very small differences are found in the internal rotation partition function of transition states of OH reaction with different aldehydes.²¹ Consequently the rate coefficients of the aldehyde + OH and aldehyde + NO₃ reactions cannot correlate.

There is still an open question about the difference in behavior between the aldehyde + NO₃ reactions and the alkane + NO₃ reactions. The modeling of the latter is in progress, and it can be suggested that in this reaction the transition vector is typical of a hydrogen abstraction, the activation energies are higher than in the NO₃ + aldehyde reaction, and therefore the tunneling effect is considerable. The tunneling increases as the activation energy increases, thus in the series methane, ethane, propane, and isobutane it decreases, whereas the free rotation partition functions increase. Both factors cancel each other to some extent, and a typical increase of the rate coefficient is observed. In addition, for the alkane + NO₃ reactions the influence of substituents is more important than in the corresponding reaction of aldehydes, since the substituent is directly bonded to the carbon atom from which the hydrogen is abstracted. Therefore, for the alkane + NO₃ reactions, the changes in activation energies are much more important than the changes in the preexponential factor.

Unfortunately, to our knowledge, there are not enough experimental data to compare the calculated activation energies of the aldehyde + NO₃, the aldehyde + OH, and the alkane + OH reactions. This lack of data also obstructs the testing of the correlation among the activation energies of these three reac-

tions. In the literature it has been established that there is no correlation among their rate coefficients,³² but in our opinion their activation energies should correlate.

From the results shown above, we suggest that the reason for the “abnormal” increase of the rate coefficients in the aldehyde + NO₃ reaction is the increase in the preexponential factor. The latter is a consequence of the larger influence of the internal rotations when the size of the aldehyde increases.

In addition to the explanation for the “abnormal” increase in rate constants for the aldehyde + NO₃ reaction, there is another fact that always contributes to increase the *k*, the nature of the alkyl group linked to the carbonyl group: the larger or more branched is the alkyl group, the more favored is the abstraction. The activation energies, which are independent of the partition functions, thus increase in the series formaldehyde, acetaldehyde, propanal, and isobutanol (Table 2).

Analyzing the rate constant of the reaction of any aldehyde with NO₃, both of the above-discussed effects should be considered: the decrease in the activation energy due to the branching of the alkyl substituent and the increase in partition functions with the size of the aldehyde. Isobutanol has lower activation energy and a smaller partition function than the *n*-butanol. One effect partially cancels the other and both rate constant results are similar, but that of isobutanol is slightly larger, because the nature of the alkyl group seems to be more relevant than the increase of the partition function. We have not modeled the reactions of 2,2-dimethylpropanal and 3,3-dimethylbutanal with NO₃, but according to the trends found in this work, we could explain why the rate constant of the former is larger than that of the latter (1.38×10^7 and 1.21×10^7 L·mol⁻¹·s⁻¹, respectively.²⁵). This is probably because the carbonyl group of 2,2-dimethylpropanal is linked to a tertiary alkyl group while in the 3,3-dimethylbutanal it is linked to a primary alkyl group. If the nature of the alkyl group is not taken into account the opposite order in their rate constants should be expected, but according to our results the increase in the partition functions is not enough to overcome the effect of the different substituents.

The calculated and experimental Arrhenius parameters are not conceptually equivalent. According to CTST and using statistical mechanics and quantum-mechanical calculations, the theoretical expression to calculate *k*, for a bimolecular reaction between two nonlinear molecules, has the form:

$$k = \kappa A' T^{-2} e^{E_a'/RT} \quad (4)$$

whereas the experimental equation is of the form:

$$k = \kappa A e^{E_a/RT} \quad (5)$$

Therefore there should be a slight difference between *A* and *A'*, and between *E_a* and *E_a'*; this is the calculated activation energy at 298.15 K and is expected to be lower than the experimental value. Since the activation energy changes with temperature, at 0 K the calculated activation energy could appreciably differ from the one calculated at 298.15 K and also from the experimental value. Our calculations show that, in the case of the aldehyde–NO₃ reactions, the activation energy increases with temperature (Table 2).

There are only a few experimental Arrhenius parameters of the studied reaction. For acetaldehyde there are two recommended results, which are very close.^{8,22} For formaldehyde the only reported value is an estimation made by Atkinson.⁸ More recently Arrhenius parameters for isobutanol and *n*-butanol have been published.¹¹ Although the calculated results are expected

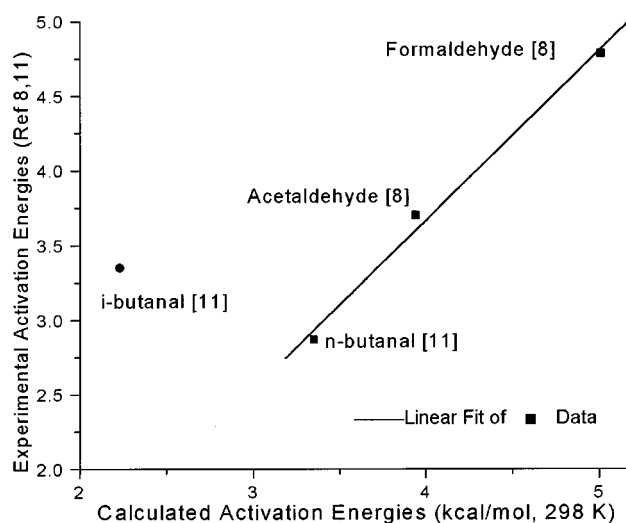


Figure 8. Correlation of calculated vs experimental activation energies for the aldehyde–NO₃ reaction.

to be slightly different than the experimental ones, the correspondence obtained in the present paper is excellent (Figure 8): the activation energy for acetaldehyde differs only by 6% with respect to ref 8 and 4% with respect to ref 22. In the cases of formaldehyde and *n*-butanol the differences are 5%⁸ and 13%,¹¹ respectively. The calculated activation energies are always higher than the experimental ones. The largest difference is observed for isobutanol (21%),¹¹ and it is also the only case for which the experimental activation energy is lower than the calculated one.

According to chemical intuition it is evident that the inductive effect of methyl groups in the α-carbon atoms should favor the –CHO hydrogen abstraction. Therefore the activation energies should increase along the series isobutanol, propanal, acetaldehyde, and formaldehyde, in agreement with the results of the present work. Indeed, the calculated activation energies are 2.65, 3.38, 3.94, and 5.01 kcal/mol, respectively. The activation energy of *n*-butanol is expected to lie between the ones of propanal and isobutanol and closer to the first. The calculated value is 3.35 kcal/mol, in agreement with the expected behavior. From a structural point of view there is no plausible explanation for the findings of Ullerstam et al.¹¹ that the activation energy of isobutanol is higher than that of *n*-butanol. Taking into account the fact that their activation energy was calculated from absolute rate coefficients, which have a discrepancy of 25% with respect to the relative rate coefficient of the same authors, in the same paper, and that our rate coefficient is in excellent agreement with their relative rate coefficient and with the independent results of D’Anna and Nielsen,²⁵ we conclude that the abnormally high activation energy seems to be an artifact of the experiment.

Conclusions

The NO₃ hydrogen abstraction reactions from aldehydes can be considered as an elementary process. The formation of an intermediate adduct is ruled out by the current results, especially taking into account that there is no experimental evidence of its existence. There is no need to introduce the formation of the adduct to explain the observed results.

The activation energies for the abstraction of hydrogen atoms other than the aldehydic one are large enough to assume that the channel of the –CHO hydrogen abstraction is highly predominant and probably unique. Both Cβ and Cα position are predicted as deactivated in comparison to aldehydic H.

The calculated activation energies agree well with the available experimental results. Therefore the results of the present work can be used as a good approach to the real values, in those cases in which they have not been measured. The calculated values of the activation energies can also be used to discriminate among discrepant experimental results.

The atypical behavior of the hydrogen abstraction reactions by the NO_3 radical in aldehydes is a consequence of the increase of entropy and hence of the partition functions in the transition states due to the internal rotations. This behavior does not occur in the corresponding hydrogen abstraction by the OH radical because the moment of inertia of the OH top is always the smallest.

It seems that the Arrhenius parameters and the absolute rate constant of isobutanal should be revised.

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