J. Braz. Chem. Soc., Vol. 16, No. 2, 190-196, 2005.
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0103 - 5053 $6.00+0.00

Article

Evaluation of Reaction Thermochemistry Using DFT Calculated Molecular Properties: Application to *trans*-HONO (X^1A') $\rightarrow$ HO(X^2P) + NO(X^2P)

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Cálculos B3LYP usando bases até 6-311G(3d2f,3p2d) foram utilizados para a previsão acurada de propriedades termoquímicas relacionadas à reação de dissociação *trans*-HONO(X^1A') $\rightarrow$ HO(X^2P) + NO(X^2 P). Um estudo sistemático da influência da base foi realizado e resultados B3LYP foram comparados a dados experimentais e a outros resultados teóricos, calculados usando os métodos G2, G2MP2, CBS e métodos *ab initio* CCSD(T) e QCISD. Os resultados obtidos sugerem que para este tipo de processo unimolecular: cálculos B3LYP geram resultados mais acurados para entalpia de dissociação que outros métodos convencionais e o melhor acordo com dados experimentais foi obtido a partir de cálculos em nível B3LYP/6-311G(3d2f,3p2d): 49.2 kcal mol^{-1} (experimental) e 49.0 kcal mol^{-1} (calculado). Ainda, diferenças de entropia e de energia livre de Gibbs foram calculadas e constantes de equilíbrio foram determinadas segundo a expressão: $Keq(T) = 1.16 \times 10^{28} \times exp(-48.34/RT)$, para a faixa de temperatura 200 – 500 K.

B3LYP calculations using basis sets up to 6-311G(3d2f,3p2d) have been employed to predict accurate thermochemical properties related to the bond dissociation reaction *trans*-HONO(X^1A') $\rightarrow$ HO(X^2P) + NO(X^2 P). A systematic study of the influence of the basis set was performed and results were compared with experimental data and with other calculated results, obtained using standard Gaussian methods (G2 and G2MP2), complete basis set extrapolation methods (CBS) and *ab initio* calculations (CCSD(T) and QCISD). The results suggest that, for this kind of unimolecular process: B3LYP calculations produce bond dissociation enthalpies that are more accurate than standard *ab initio* methods and) the best agreement with the experimental enthalpy has been found with B3LYP/6-311G(3d2f,3p2d) calculations: 49.2 kcal mol^{-1} and 49.0 kcal mol^{-1}, respectively. Also, entropy and Gibbs free energy have been calculated and equilibrium constants have been determined as $Keq(T) = 1.16 \times 10^{28} \times exp(-48.34/RT)$, for the temperature range 200 – 500 K.

Keywords: nitrous acid, thermochemical properties, density functional theory, equilibrium constants

Introduction

The theoretical thermochemical calculation of homolytic bond dissociation reactions is an important application of quantum chemistry methods. These determinations are relevant to the understanding of the outcome of radical reactions and to analyze the mechanism of chemical reactions in general. Due to the rapid progress in computational methods, highly sophisticated calculations can be performed, with minor errors in comparison to experimental data. Several methods have been widely used for bond dissociation energies (BDE) and thermochemical data calculations. Gaussian family of methods (G1, G2, G2MP2, G3) and the complete basis set extrapolation (CBS) approach have been used to predict reaction enthalpies and thermochemical properties (enthalpies of formation, for instance).[1-5] Generalized valence bond theory, in the perfect pairing approximation, in connection with a local spin density correlation functional (GVB-PP/LSDC) was also recommended for the accurate calculation of BDE and correct description of the potential hypersurface along the dissociation coordinate.[6] Other levels of theory like coupled-cluster techniques have also been used since they include certain excitations to infinite order and are generally more accurate than finite order perturbation methods, such as MP4.[7]

All the methods cited above are computationally very expensive. An alternative to these high cost calculations is

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the use of density functional (DFT) methods. Jursic *et al.* have demonstrated that density functional methods are as accurate as quadratic complete basis set *ab initio* methods in calculating BDE and a comparison among CBS, Gaussian and DFT methods showed the power of DFT methods to compute reliable BDE and enthalpies of formation.[8-18] Moreover, Ventura and coworkers have successfully determined thermochemical properties of species, for which bonding patterns are difficult to describe with traditional *ab initio* techniques, using DFT methods.[19-23] For example, DFT was shown to rival or surpass CCSD(T) calculations in the study of fluorine oxides and sulfines.[24] In our laboratory, we have also demonstrated that DFT techniques can be used in the calculations of barrier heights of reactions with a first order saddle point leading to results as accurate as those obtained with conventional *ab initio* methods.[25-27]

In this work we have applied DFT methods for the evaluation of the thermochemical properties of the bond dissociation reaction *trans*-HONO(X^1A') → HO(X^2P) + NO(X^2P). This reaction is of great interest in atmospheric chemistry, since HONO is one of the main sources of OH radical at troposphere. The experimental enthalpy of this reaction is 49.2 kcal mol^{-1} at 298.15K, based on NIST standard tables, available on-line.[28] Photochemical data for this reaction can also be found in the literature: the threshold wavelength for HONO + hυ → OH + NO dissociation is 591 nm.[29] A theoretical evaluation of this reaction has been reported by Nguyen *et al.*: B3LYP/6-311++G(3df,2p)//B3LYP/6-31G** and CCSD(T)/6-311++G(3df,2p)//CCSD(T)/6-31G** levels have been used to calculate the energy difference, including the zero point energy, for OH + NO → *trans*-HONO, and obtained –45.9 and –45.7 kcal mol^{-1}, respectively.[30] These values are, respectively, 3.3 and 3.5 kcal mol^{-1} lower than the experimental energy. Although it may be considered an acceptable error (7%), for this kind of system, it leads to very large errors on the calculated values of related properties, as rate coefficients and equilibrium constants.

Jursic has recently reported a DFT study of the HONO potential energy surface, in which enthalpies of formation were calculated and used to estimate energy differences (including barrier energies and BDE).[31] The best result reported for *trans*-HONO → HO + NO is 47.4 kcal mol^{-1}, computed at B3LYP/6-311G(3df,3pd), at 0 K. No thermal corrections were included to account for the energy difference from 0 to room temperature, which makes the interpretation of this BDE value difficult. Considering the thermal correction of an ideal gas, the value 47.4 kcal mol^{-1}, added to RT, results in 48.0 kcal mol^{-1}, which is 1.2 kcal mol^{-1} lower than the reported experimental value at 298.15 K.

The main goal of this work is to explore a particular DFT method for the determination of thermochemical properties of this reaction, at 298.15 K. The hybrid functional B3LYP has been chosen. A systematic study of the basis set has also been performed here, and results are discussed on the basis of the agreement with experimental enthalpy data. Other thermochemical properties, like entropy, Gibbs free energy and equilibrium constants have also been evaluated as a function of temperature.

Computational Details

As stated above, B3LYP hybrid functional has been used in conjunction with a series of basis set, which ranges from the smaller 6-31G(d,p) to 6-311G(3d2f,3p2d). The inclusion of diffuse functions has also been considered. In addition, correlation consistent basis sets of Dunning have also been employed. For comparison, selected standard Gaussian family and *ab initio* CBS calculations are reported here, as well as standard *ab initio* methods, CCSD(T) and QCISD.

Geometries of the reactant, *trans*-HONO, and the products, HO(X^2P) and NO(X^2P), have been optimized and vibrational frequencies obtained at the same levels. Enthalpies have been calculated as the energy differences of products and reactant, corrected by zero point energy and a thermal correction term, which was evaluated here by integration of theoretical Cp function over the range from 0 K to the temperature of interest, expression (1):

$$\Delta H(T) = \Delta E_{electronic} + \Delta(ZPE) + \int_0^T \Delta(Cp) \cdot dT \tag{1}$$

Entropy has been evaluated by standard statistical thermodynamic methods.[32] Finally, Gibbs free energy of the reaction has been evaluated by using expression (2):

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) \tag{2}$$

and equilibrium constants were calculated as a function of temperature in the range 200 – 500 K. All thermochemical properties have been evaluated with a computational code developed in our laboratory.

Results and Discussion

As mentioned above, optimized geometries and vibrational frequencies were calculated at B3LYP level, including basis sets, which range from 6-31G(d,p) to 6-311G(3d2f,3p2d). These values are shown in Tables 1a and 1b. Also shown for comparison, are the experimental values and some standard *ab initio* results (CCSD(T) and QCISD). Optimized geometries, vibrational frequencies and electronic energies were used as input parameters for the thermochemical properties evaluations. Computed electronic energy differences, energy differences at 0 K (sum of electronic and vibrational energies) and thermal correction terms (to 298.15 K) are shown in Table 2. Computed thermochemical properties at 298.15 K are shown in Table 3.

Geometry and frequencies

Optimized geometrical parameters are introduced in Table 1a. Vibrational frequencies are introduced in Table 1b. The vibrational modes of *trans*-nitrous acid are defined as υ_1 – OH stretching, υ_2 – N=O stretching; υ_3 – HON bending; υ_4 – O-N stretching; υ_5 – ONO bending and υ_6 – torsion. These structural parameters show good agreement with experimental data.[33-35]

The analysis of geometry data, in Table 1a, shows that: distances and angles values determined using double zeta basis correlates with the number polarization functions, while those determined with triple zeta basis, are less influenced by the inclusion of polarization functions; the errors of calculated values in relation to experimental values do not change when the double zeta basis set is changed to a triple zeta; the inclusion of diffuse function increases the error of the calculated values in relation to experimental data; CCSD(T) results are comparable to B3LYP results, and both show low error value as compared to experimental data; the internal coordinate with the largest mean error is the OH distance: 2% in relation to the experimental value; all other internal coordinates show mean error values lower than 1%.

Similar analysis can be done for vibrational frequencies: the data in Table 1b shows that the values obtained using the triple zeta basis sets show smaller dependence on the inclusion of polarization functions than those obtained using the double zeta basis; the error of the calculated frequencies in relation to the experimental lower when the quality of the basis sets is improved to triple zeta; the inclusion of diffuse functions lowers the error of the

Table 1a. Optimized geometries (Angstroms and degree) calculated at different levels. Experimental values [33-35] also included. Dihedral angle = 180°

		trans-HONO					HO	NO
		HO	ON	NO	HON	ONO		
B3LYP	6-31G(d,p)	0.972	1.427	1.179	102.35	110.62	0.980	1.159
	6-31G(2d,2p)	0.969	1.426	1.172	102.15	110.79	0.977	1.152
	6-31G(3d,3p)	0.970	1.420	1.172	102.73	110.89	0.975	1.151
	6-31G(2df,2p)	0.968	1.422	1.171	102.32	110.83	0.976	1.151
	6-31G(2df,2pd)	0.967	1.422	1.171	101.99	110.90	0.974	1.151
	6-31G(3df,3pd)	0.968	1.419	1.171	102.77	110.95	0.973	1.150
	6-31G(3d2f,3p2d)	0.969	1.419	1.170	102.83	110.93	0.974	1.149
	6-311G(d,p)	0.968	1.433	1.166	102.30	111.02	0.975	1.148
	6-311G(2d,2p)	0.967	1.433	1.166	102.10	110.91	0.974	1.148
	6-311G(3d,3p)	0.967	1.433	1.165	102.39	110.85	0.973	1.147
	6-311G(2df,2p)	0.967	1.430	1.164	102.30	110.97	0.974	1.146
	6-311G(2df,2pd)	0.966	1.429	1.164	102.28	110.99	0.973	1.146
	6-311G(3df,3pd)	0.966	1.430	1.163	102.57	110.95	0.973	1.145
	6-311G(3d2f,3p2d)	0.966	1.431	1.163	102.59	110.95	0.972	1.145
	6-31+G(d,p)	0.973	1.426	1.177	103.11	110.89	0.980	1.158
	6-31++G(d,p)	0.973	1.426	1.177	103.11	110.89	0.980	1.158
	6-31+G(2df,2p)	0.969	1.425	1.169	102.95	111.05	0.976	1.150
	6-311+G(d,p)	0.970	1.433	1.165	102.93	111.17	0.976	1.148
	6-311++G(d,p)	0.970	1.432	1.166	102.96	111.15	0.971	1.159
	6-311+G(2df,2p)	0.968	1.430	1.164	103.00	111.11	0.974	1.146
	cc-pVDZ	0.975	1.430	1.172	101.86	110.76	0.984	1.154
	cc-pVTZ	0.968	1.433	1.164	102.51	110.99	0.975	1.146
	AUG-cc-pVDZ	0.972	1.429	1.173	102.89	110.86	0.979	1.154
	AUG-cc-pVTZ	0.969	1.433	1.163	102.81	111.08	0.975	1.146
QCISD	6-31G(d,p)	0.969	1.425	1.187	102.36	110.17	0.975	1.175
	6-31G(2df,2p)	0.963	1.406	1.174	102.13	110.55	0.969	1.158
CCSD(T)	6-31G(d,p)	0.971	1.434	1.192	101.96	110.14	0.976	1.169
	6-31G(2df,2p)	0.966	1.417	1.180	101.66	110.47	0.970	1.156
Experimental		0.958	1.432	1.170	102.1	110.7	0.970	1.151

Table 1b. Vibrational frequencies (cm^{-1}) calculated at different levels. Experimental values [33-35] also included

		trans-HONO						HO	NO
		v_1	v_2	v_3	v_4	v_5	v_6	v	v
B3LYP	6-31G(d,p)	596.1	631.1	862.2	1305.9	1791.8	3756.8	3696.4	1991.1
	6-31G(2d,2p)	599.9	636.2	853.2	1326.4	1786.1	3769.9	3702.1	1983.3
	6-31G(3d,3p)	596.4	639.0	850.6	1312.5	1785.0	3749.1	3712.2	1987.1
	6-31G(2df,2p)	599.8	641.6	860.3	1320.6	1786.1	3768.7	3701.4	1985.5
	6-31G(2df,2pd)	601.9	641.3	861.1	1320.8	1786.7	3768.1	3702.3	1985.5
	6-31G(3df,3pd)	594.4	641.5	854.1	1306.9	1783.5	3761.2	3720.3	1987.3
	6-31G(3d2f,3p2d)	589.4	641.7	854.5	1307.1	1779.4	3751.1	3711.2	1984.0
	6-311G(d,p)	591.0	618.7	833.9	1297.8	1792.7	3774.8	3704.7	1988.4
	6-311G(2d,2p)	596.4	623.0	839.4	1318.7	1773.1	3778.4	3708.8	1964.8
	6-311G(3d,3p)	590.5	618.5	829.5	1314.7	1788.0	3769.5	3712.3	1980.3
	6-311G(2df,2p)	597.1	624.5	839.1	1312.2	1785.6	3777.9	3706.5	1981.0
	6-311G(2df,2pd)	597.7	624.8	839.7	1312.8	1784.7	3777.6	3707.8	1981.0
	6-311G(3df,3pd)	590.9	622.7	830.0	1305.5	1792.5	3780.6	3723.6	1988.3
	6-311G(3d2f,3p2d)	589.6	622.6	828.7	1304.4	1784.7	3778.6	3727.1	1980.7
	6-31+G(d,p)	585.8	627.4	830.4	1296.3	1782.8	3752.9	3703.8	1980.3
	6-31++G(d,p)	585.8	627.3	830.2	1295.7	1782.8	3752.4	3701.8	1980.3
	6-31+G(2df,2p)	589.8	629.2	827.6	1305.8	1777.3	3767.4	3716.9	1974.3
	6-311+G(d,p)	583.7	613.9	811.3	1292.3	1786.5	3761.8	3708.9	1979.7
	6-311++G(d,p)	583.1	615.5	812.9	1292.3	1784.6	3760.1	3710.5	1980.4
	6-311+G(2df,2p)	585.4	618.7	816.9	1299.5	1775.6	3767.6	3714.8	1970.8
	cc-pVDZ	590.7	623.7	846.4	1294.0	1797.5	3715.0	3628.2	1993.6
	cc-pVTZ	592.0	617.0	826.3	1301.9	1781.6	3761.6	3699.7	1976.5
	AUG-cc-pVDZ	593.4	620.7	821.4	1300.5	1778.6	3744.5	3683.5	1974.1
	AUG-cc-pVTZ	585.3	611.9	811.5	1296.6	1773.6	3748.8	3695.0	1967.8
QCISD	6-31G(d,p)	574.9	644.8	874.9	1337.2	1769.1	3835.5	3778.3	1949.9
	6-31G(2df,2p)	584.6	674.4	904.8	1368.0	1785.4	3841.0	3780.2	1822.5
CCSD(T)	6-31G(d,p)	576.3	621.8	851.7	1315.8	1720.3	3812.2	3761.6	1965.7
	6-31G(2df,2p)	585.9	648.5	874.8	1343.4	1734.7	3807.9	3756.9	2089.9
Experimental		540	593	791	1265	1699	3588	3738	1904

calculated frequencies in relation to experimental data; CCSD(T) results are comparable to the values obtained at B3LYP level; frequency related to the torsion mode is the one with the largest mean error value: 9%; all other frequencies show mean error values lower than 5%.

The bond distances and frequencies calculated for the OH and NO radicals are also in good agreement with experimental data, being the mean errors: 0.6% for O – H distances, 0.4% for N – O distances, 0.9% for the O – H stretching mode frequencies, 4.2% for N – O stretching mode frequencies.

B3LYP enthalpies

Electronic energy differences, energy differences at 0 K (sum of electronic and vibrational energies) and thermal correction terms (to 298.15 K) are shown in Table 2. Thermochemical properties at 298.15 K are shown in Table 3. B3LYP calculated enthalpies at 298.15 K are in excellent agreement with the experimental value and show a maximum deviation of less than 10% when the 6-311+G(d,p) basis set is used (see tables 2 and 3).

As shown in Figure 1, the size of the basis set clearly affects the differences between calculated and experimental values. The increase in the polarization space causes the enthalpy to increase up to 2 kcal mol^{-1}, when going from (d,p) to (3d2f,3p2d) polarization sets. The change from the double to the triple zeta basis sets causes the enthalpy to decrease. The use of the double zeta basis, however, gives results systematically higher than the experimental enthalpy. When the triple zeta is used, calculated results smoothly converge to the experimental value, 49.2 kcal mol^{-1},[28] and reach 49.0 kcal mol^{-1} when the largest 6-311G(3d2f,3p2d) basis set is used.

The decrease in the calculated enthalpy due to the change from double to triple zeta basis set can also be found in the calculations with Dunning correlation consistent basis sets: cc-pVDZ and cc-pVTZ. These basis sets, however, did not prove to be better than the 6-31G and 6-311G basis sets, since the values obtained with cc-

Table 2. Electronic energies (ΔE, hartrees), energy differences at 0 K (ΔU^0, kcal mol^{-1}) and thermal correction terms to the enthalpy (TC^{298}, kcal mol^{-1}) calculated from theoretical data

		ΔE	ΔU^0	TC^{298}
B3LYP	6-31G(d,p)	0.08365220	47.84	1.54
	6-31G(2d,2p)	0.08391409	47.96	1.54
	6-31G(3d,3p)	0.08601158	49.35	1.54
	6-31G(2df,2p)	0.08468885	48.44	1.54
	6-31G(2df,2pd)	0.08470884	48.45	1.54
	6-31G(3df,3pd)	0.08682298	49.86	1.54
	6-31G(3d2f,3p2d)	0.08704205	50.01	1.54
	6-311G(d,p)	0.08053734	45.94	1.53
	6-311G(2d,2p)	0.08232571	47.01	1.53
	6-311G(3d,3p)	0.08235410	47.08	1.53
	6-311G(2df,2p)	0.08283093	47.33	1.53
	6-311G(2df,2pd)	0.08291400	47.39	1.54
	6-311G(3df,3pd)	0.08286010	47.41	1.53
	6-311G(3d2f,3p2d)	0.08286742	47.43	1.53
	6-31+G(d,p)	0.08052084	45.97	1.53
	6-31++G(d,p)	0.08047470	45.94	1.53
	6-31+G(2df,2p)	0.08116766	46.35	1.53
	6-311+G(d,p)	0.07772461	44.26	1.52
	6-311++G(d,p)	0.07769766	44.24	1.52
	6-311+G(2df,2p)	0.08016456	45.76	1.52
	cc-pVDZ	0.08388877	48.00	1.53
	cc-pVTZ	0.08134558	48.10	1.53
	AUG-cc-pVDZ	0.08072263	46.08	1.53
	AUG-cc-pVTZ	0.07995832	45.65	1.52
QCISD	6-31G(d,p)	0.06636469	36.92	1.54
	6-31G(2df,2p)	0.07340651	40.98	1.56
CCSD(T)	6-31G(d,p)	0.07327568	41.45	1.53
	6-31G(2df,2p)	0.07340651	41.56	1.54

pVDZ or cc-pVTZ lie between those obtained with 6-31G(d,p) and 6-31G(2d,2p) or 6-311G(d,p) and 6-311G(2d,2p), respectively.

Some calculations were performed using diffuse functions, but, to our disappointment, the reaction enthalpies were lowered, being the worst result the B3LYP/6-31+G(2df,2p) enthalpy, which is 2.2 kcal mol-1 lower than the B3LYP/6-31G(2df,2p) enthalpy. The correlation consistent basis sets augmented with diffuse functions show the same trend. This behavior may be attributed to the fact that diffuse functions do not describe reactants and products in an equivalent way: radicals' energies are lowered in relation to the reactant molecule energy and give a lower reaction enthalpy. For this reason, the use of diffuse functions is not recommended for the determination of reaction energetic of this kind of process. This is probably the reason why Nguyen *et al.* [30] obtained low values of reaction enthalpy in their study.

A comparison of the enthalpies calculated at B3LYP and the classical G2, G2MP2, CBS-4 and QCBS methods (Table 3) shows that B3LYP results are more accurate than the others, thus proving the efficiency of this method in predicting thermochemical properties for this type of system.

Table 3. Enthalpies (ΔH^{298}, kcal mol^{-1}), Entropies (ΔS^{298}, cal mol^{-1}K^{-1}) and Gibbs free energies (ΔG^{298}, kcal mol^{-1}) calculated at 298.15K from theoretical data. Experimental values[28] included for comparison

		ΔH^{298}	ΔS^{298}	$\Delta G^{298} = \Delta H^{298} - T\Delta S^{298}$
B3LYP	6-31G(d,p)	49.4	34.40	39.1
	6-31G(2d,2p)	49.5	34.39	39.2
	6-31G(3d,3p)	50.9	34.39	40.6
	6-31G(2df,2p)	50.0	34.41	39.7
	6-31G(2df,2pd)	49.9	34.40	39.7
	6-31G(3df,3pd)	51.4	34.39	41.1
	6-31G(3d2f,3p2d)	51.5	34.38	41.3
	6-311G(d,p)	47.5	34.30	37.3
	6-311G(2d,2p)	48.5	34.33	38.3
	6-311G(3d,3p)	48.6	34.30	38.4
	6-311G(2df,2p)	48.9	32.33	38.6
	6-311G(2df,2pd)	48.9	32.33	38.7
	6-311G(3df,3pd)	48.9	32.31	38.7
	6-311G(3d2f,3p2d)	49.0	32.30	38.7
	6-31+G(d,p)	47.4	34.36	37.2
	6-31++G(d,p)	47.4	34.36	37.1
	6-31+G(2df,2p)	47.8	34.34	37.6
	6-311+G(d,p)	45.7	34.28	35.5
	6-311++G(d,p)	45.8	34.28	35.5
	6-311+G(2df,2p)	47.3	32.29	37.1
	cc-pVDZ	49.5	32.37	39.3
	cc-pVTZ	48.0	32.30	37.8
	AUG-cc-pVDZ	47.6	34.34	37.4
	AUG-cc-pVTZ	47.2	34.27	37.0
QCISD	6-31G(d,p)	38.5	34.41	28.2
	6-31G(2df,2p)	42.5	34.48	32.3
CCSD(T)	6-31G(d,p)	43.0	34.31	32.7
	6-31G(2df,2p)	43.1	34.39	32.9
G2		50.4	103.64	19.5
G2MP2		72.3	103.97	41.3
CBS-4		53.3	32.53	43.6
QCBS		50.5	33.88	40.4
Experimental		49.2	34.67	38.9

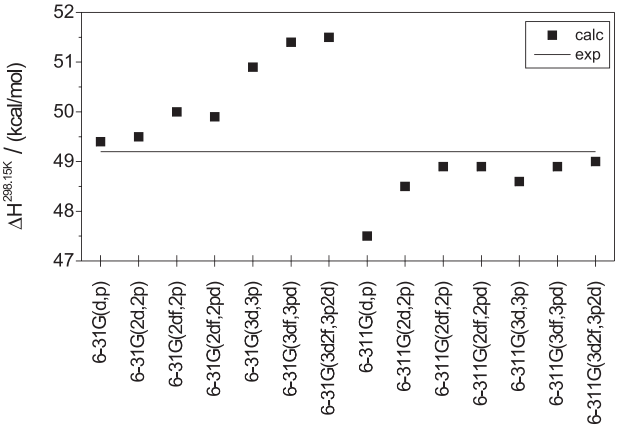

Figure 1. Enthalpy differences calculated at B3LYP levels, using 6-31G and 6-311G basis sets with different polarization spaces. The solid horizontal line is the experimental value.

QCISD/6-31G(d,p) enthalpies are 10.7 kcal mol^{-1} lower than the experimental enthalpy. Calculations with a larger basis set, QCISD/6-31G(2df,2p), increases this value, but the agreement with the experimental value is still poor. The lower values obtained at QCISD level can be explained by the lack of size consistency of the method.

Reaction enthalpies calculated with CCSD(T) method did not show significant dependence with the basis set size. A comparison between B3LYP and CCSD(T) methods shows that the former leads to more accurate results.

Entropies and Gibbs free energies

By comparing the DFT results for entropy with the experimental data, all the calculated values may be observed to lie about 0.3 cal $mol^{-1}K^{-1}$ below the experimental value, which represents 1% deviation. By applying the thermodynamic relation: $\Delta G = \Delta H - T\Delta S$ to our data, Gibbs free energy of the reaction was estimated at 298.15 K (see Table 3). Again, the B3LYP/6-311G(3d2f,3p2d) level gives the best result (38.7 kcal mol^{-1}) in comparison with the experimental value (38.9 kcal mol^{-1}).

Equilibrium constants

The standard statistical thermodynamic equations were used to evaluate enthalpy and entropy over a range of temperature of 200 – 500 K. The B3LYP/6-311G(3d2f,3p2d) data were used to evaluate the thermochemical properties as a function of the temperature and, then, the equilibrium constants in the same temperature range. The results fit the equation:

$$Keq = 2.08 \times 10^{26} \times \exp(-47.94/RT)$$

From the experimental Gibbs free energy as a function of temperature the following expression is obtained over the same temperature range:

$$Keq = 1.97 \times 10^{26} \times \exp(-48.28/RT)$$

Also, a recommended equilibrium constant for the range of temperature from 1100K to 1500K is:

$$Keq = 1.26 \times 10^{26} \times \exp(-47.75/RT)$$

A comparison of our obtained expression with other expression from literature shows that our calculations are in excellent agreement with the available data.

Conclusions

In this paper the thermochemical properties of the bond dissociation reaction *trans*-HONO(X^1A') → HO(X^2P) + NO(X^2P) have been evaluated using theoretical methods in quantum chemistry. A systematic study of the basis set size has been performed using the B3LYP hybrid functional. The results of this study show that the reaction enthalpy calculation is sensitive to the polarization space and that the addition of diffuse functions is not adequate to describe reactants and radical products relatively to each other. Also, for this system, B3LYP calculations have proved to be very efficient in predicting reaction energetics in comparison with highly sophisticated (and computational expansive) *ab initio* and standard Gaussian and CBS families of methods. This conclusion is in agreement with previous results obtained by Jursic,[31] who had determined the enthalpies for this BDE at 0K, from a slightly different formalism.

Gibbs free energies and equilibrium constants were calculated over the temperature range 200 – 500 K, in excellent agreement with experimental data.

Acknowledgements

The authors thank CAPES and CNPq for financial support.

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Received: May 31, 2004
Published on the web: February 21, 2005