Comparison of Various Quantum Chemistry Methods for the Computation of Equilibrium Constants

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Ab initio as well as density functional computations have been carried out to test their ability to reproduce experimental equilibrium constants. Three kinds of equilibriums in the gaseous phase have been studied: equilibriums involving nitrogenized compounds or methanol or chlorinated compounds. The basis set effect is also examined. In this work, we show that hybrid HF-DFT and G2 methods seem to be the best adapted to compute this thermodynamic parameter.

I. Introduction

The knowledge of equilibrium constants is important in the study of chemical reaction mechanisms. In addition to allowing the prediction of the composition of a mixture, the equilibrium constant is also connected to rate constants in two ways: (1) the existence of equilibrium between stable species in multiple-step processes and (2) the equilibrium between reactants and activated complexes in transition state theory.[1]

Experimentally, the equilibrium constant determination is not always easy, particularly for equilibrium observable only at high pressure. Indeed, even in recent years, there are relatively few experimental studies of gaseous equilibrium.[2−15] Thus, to provide theoretical equilibrium constants is of great interest for experimenters. This kind of calculation requires both energetic and entropic effect determinations.

To our knowledge, in the gaseous phase, there are no theoretical studies concerning this kind of parameter (equilibrium constant or Gibbs free energy), comparing various recent quantum chemistry methods with experimental results. Indeed, most theoretical papers concerning thermodynamics predictions from quantum results present only ΔH results, more often than not ΔH at 0 K (i.e., ΔE only with ZPE correction).[16−23] Nevertheless, the equilibrium constant is a practical indicator to test theoretical methods because it is very sensitive both to the energy quality and to geometrical parameters and also because the electronic structure of each compound that takes part in the equilibrium is extremely different from the others. Moreover, the ability of theoretical methods to give good equilibrium constants is important to study next the nonideality effect of gases at high pressure.[24]

In this work, we have examined 12 equilibriums in the gaseous phase, divided in three groups, computing the constants with ab initio (HF, MPn, G2, BAC-MP4) and density functional (local and nonlocal level as well as hybrid HF-DFT) methods.

II. Computational Details

HF and post-HF computations (MPn, G2) have been done with the Gaussian 94 program.[25] Density functional computations have been carried out with Gaussian 94[25] and deMon-KS 3.2[26] packages. BAC-MP4 computations, which take as a starting point the MP4/6-31G**//HF/6-31G* values of the energies, have been carried out with the program of Melius.[27]

In density functional computations with deMon, we have used only the TZVP basis set (equivalent to a 6-311G** Gaussian set), which is the following: (41/1) for hydrogen; (7111/411/1) for carbon, nitrogen, and oxygen.[28] The auxiliary basis sets, used in the fitting of the charge density and the exchange-correlation potential, were (4; 4) for H and (4, 4; 4, 4) for C, N, and O. The charge density was fitted analytically, whereas the exchange-correlation potential was fitted numerically on a grid, as proposed in deMon. The FINE grid was employed. In calculations using the local density approximation, the Vosko, Wilk, and Nusair[29] parametrization of the correlation energy in the homogeneous electron gas was used. These calculations will be labeled VWN. Nonlocal corrections to the exchange-correlation potential were included self-consistently using density gradient corrections. Three functionals have been employed: PP, BP, and BLAP. In calculations labeled PP, the approximations proposed by Perdew[30,31] for the exchange and correlation parts were used. In computations labeled BP, the functional of Becke[32] for the exchange and that of Perdew[31] for correlation were employed. Concerning the last labeled BLAP, the functional of Becke[32] and that of Proynov et al.[33] for correlation were used. All the geometries obtained with deMon were fully optimized using the Versluis−Ziegler correction.[34]

In computations using Gaussian 94, for two equilibriums, several basis sets have been employed: 6-31G**,[35−39] 6-311G**,[40,41] 6-311++G**,[40−42] cc-pVTZ,[43−45] and AUG-cc-pVTZ (cc-pVTZ with diffuse functions).[43−45] Otherwise, we have used 6-311G**. DFT calculations with Gaussian 94 have been carried out using the BLYP[32,46,47] functional. For HF-DFT computations, we have used B3LYP,[46−48] B3PW91,[48,49] and B3P86[48,31] functionals.

All energy as well as frequency computations have been done with the geometry obtained by a full optimization in the same basis set. Frequencies are obtained analytically with Gaussian and numerically with deMon.

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TABLE 1: Comparison of Theoretical and Experimental log $K_{eq} = f(T)$ for $NO_2 \rightleftharpoons NO + {}^1/_2O_2$[a]

	T (K)								
	499.0	521.9	577.0	626.5	699.9	733.3	792.4	799.9	825.4
HF[b]	11.26	10.94	10.27	9.78	9.17	8.93	8.56	8.52	8.38
MP2(full)	−3.36	−3.04	−2.37	−1.87	−1.26	−1.02	−0.64	−0.60	−0.46
MP4(SDTQ)[c]	−2.98	−2.68	−2.05	−1.57	−0.99	−0.76	−0.41	−0.36	−0.23
BAC-MP4[d]	−2.71	−2.43	−1.86	−1.41	−0.88	−0.67	−0.35	−0.31	−0.18
G2	−2.98	−2.68	−2.08	−1.62	−1.06	−0.85	−0.51	−0.47	−0.34
VWN	−12.27	−11.57	−10.12	−9.03	−7.70	−7.17	−6.37	−6.27	−5.96
BP	−6.61	−6.16	−5.22	−4.53	−3.67	−3.33	−2.81	−2.75	−2.55
PP	−6.48	−6.04	−5.12	−4.43	−3.58	−3.25	−2.74	−2.68	−2.48
BLAP	−5.08	−4.69	−3.90	−3.30	−2.57	−2.29	−1.84	−1.79	−1.62
BLYP	−4.83	−4.46	−3.68	−3.10	−2.39	−2.12	−1.69	−1.64	−1.47
B3P86	−4.26	−3.91	−3.19	−2.64	−1.98	−1.72	−1.32	−1.27	−1.11
B3PW91	−3.60	−3.28	−2.61	−2.12	−1.51	−1.27	−0.90	−0.86	−0.71
B3LYP	−2.55	−2.28	−1.71	−1.29	−0.76	−0.56	−0.24	−0.20	−0.09
exptl[e]	−2.11	−1.85	−1.29	−0.878	−0.371	−0.179	0.125	0.164	0.285

[a] Geometries are fully optimized in each method using 6-311G*, except for MP4, G2, and BAC-MP4 computations. [b] Frequencies scaled by 0.89. [c] MP4(SDTQ) energy computation on MP2(full) geometry. [d] Interpolated values. [e] From ref 5.

The equilibrium constant K_{eq} (or Δ_rG^0) is provided by a statistical thermodynamic treatment with

$$K_{eq} = \exp -(\Delta_rG^{IG})/(RT)$$

where $\Delta_rG^{IG} = \Delta_rG^0$ for an ideal gas (relative to a reaction with stoichiometric coefficients given and to gaseous species in the standard state) and

$$G = E_{electronic} + ZPE + (H_T - H_0) - TS$$

The H and S thermodynamic properties are obtained using the molecular partition function (see ref 50 for a review). This treatment was carried out with our thermochemistry package[51] (except for G2 and BAC-MP4). This package can compute directly, from the electronic energy, frequencies and moments of inertia for reactants and products (or transition state), the equilibrium constant or the rate constant for a set of temperatures. For BAC-MP4 computations, the program providing results only for certain temperatures, we have interpolated these values to temperatures in which we are concerned. Subsequently in the discussion, we will use the ratio α defined as (K_{exptl}/K_{theor}).

III. Results and Discussion

Equilibriums studied in this work can be divided in three groups: equilibriums involving nitrogenized compounds or methanol or chlorinated compounds.

1. Nitrogenized Compounds. Nitrogen oxides are involved in many reactions, being the concern of both tropospheric (air pollution) and stratospheric (ozone layer destruction) chemistry.[52−54] Moreover, some experimental data are available in the litterature for gas-phase equilibrium with NO_x and N_xO_y systems.[4−8,12,13] In addition to nitrogen oxides, we have examined also the NH_3 formation. First, since experimental temperature dependence of the equilibrium constant is available,[5] we begin this study with the equilibrium between NO and NO_2.

$$NO_2 \rightleftharpoons NO + {}^1/_2O_2$$

In Table 1, we compare the theoretical log K_{eq} obtained with various methods with the experimental one for several temperatures. Unless otherwise stated, all geometries are optimized with each method using the 6-311G* basis set. These results are plotted in Figure 1. We can see immediately that HF equilibrium constants are very poor (α ≃ 10^{-13} for T = 499 K). Even worse, the variation with T is opposite because the temperature for which $\Delta_rG^0 = 0$ is shifted a lot. This is not surprising, and this is due to a poor representation of both geometries and energies. In particular, it has been already pointed out that NO and NO_2 structures are not well-described by UHF calculations.[55] MP2 and MP4 computations improve drastically the value (α ≃ 18 and α ≃ 7.5, respectively). BAC-MP4 is slightly better (α ≃ 4), and G2 results are very similar to those of MP4.

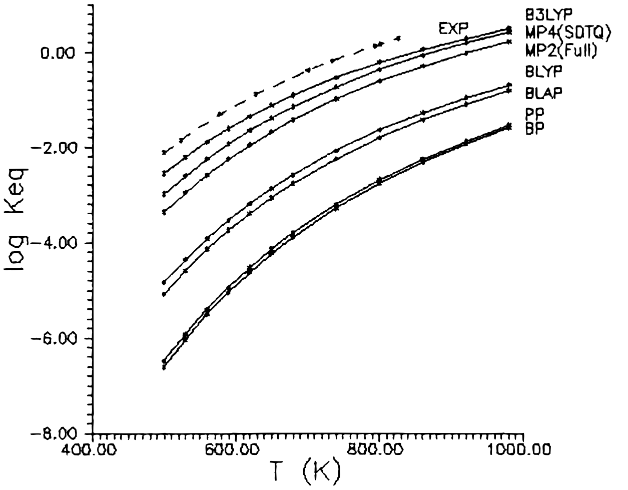

Figure 1. Comparison of theoretical and experimental log $K_{eq} = f(T)$ for $NO_2 \rightleftharpoons NO + {}^1/_2O_2$.

Concerning DFT methods, local results (VWN) are as poor as those of HF, with α ≃ 10^{10}. The use of gradient corrections improve more or less, depending on which potential is employed. For deMon computations (BP, PP, and BLAP), the more recent potential BLAP is the best one (α ≃1000). But, BLYP provides the best DFT value with α ≃ 525, which remains worse than MPn results. We have to specify here that differences between deMon (VWN, BP, PP, and BLAP) and Gaussian (BLYP) results are not due to differences in basis set but really to the potential only (BP values obtained with Gaussian are similar to those of BP deMon). Anyway, the best values set is obtained with the hybrid HF-DFT using B3LYP potential (α ≃ 2.8), twice as good as MP4.

In order to improve these best results, we have used various basis sets with B3LYP. Table 2 shows the basis set effect using B3LYP. In this case, this effect is relatively small. It seems

TABLE 2: Basis Set Effect on Theoretical log $K_{eq} = f(T)$, Using B3LYP, for $NO_2 \rightleftharpoons NO + {}^1/_2O_2$

T (K)	6-31G*	6-31+G*	6-311G*	6-311+G*	cc-pVTZ	AUG-cc-pVTZ	exptl[a]
499.0	−2.68	−2.84	−2.5S	−2.61	−2.92	−2.91	−2.11
521.9	−2.40	−2.55	−2.28	−2.33	−2.63	−2.62	−1.85
577.0	−1.82	−1.95	−1.71	−1.76	−2.02	−2.02	−1.29
626.5	−1.38	−1.51	−1.29	−1.33	−1.57	−1.57	−0.878
699.9	−0.85	−0.96	−0.76	−0.80	−1.02	−1.02	−0.371
733.3	−0.64	−0.75	−0.56	−0.60	−0.81	−0.80	−0.179
792.4	−0.32	−0.42	−0.24	−0.28	−0.47	−0.46	0.125
799.9	−0.28	−0.38	−0.20	−0.24	−0.43	−0.43	0.164
825.4	−0.16	−0.26	−0.09	−0.12	−0.30	−0.30	0.285

[a] From ref 5.

TABLE 3: Comparison of Theoretical and Experimental ln $K_{eq} = f(T)$ for ${}^1/_2N_2 + {}^3/_2H_2 \rightleftharpoons NH_3$ Using the 6-311G Basis Set**

	T (K)									
	150	200	250	300	350	400	450	500	550	600
HF[a]	13.96	7.90	4.11	1.49	−0.45	−1.96	−3.16	−4.14	−4.97	−5.67
MP2(full)	0.31	−2.34	−4.09	−5.35	−6.32	−7.10	−7.73	−8.27	−8.73	−9.13
MP4(SDTQ)[b]	−4.34	−5.84	−6.88	−7.68	−8.32	−8.84	−9.28	−9.67	−10.00	−10.29
BAC-MP4	24.68	15.93	10.55	6.86	4.14	2.07	0.41	−0.92	−2.05	−2.99
G2	20.11	12.52	7.81	4.57	2.19	0.36	−1.10	−2.29	−3.29	−4.14
VWN	68.19	48.54	36.60	28.54	22.73	18.32	14.85	12.06	9.75	7.82
BP	27.52	18.05	12.22	8.23	5.32	3.09	1.32	−0.13	−1.32	−2.34
PP	25.10	16.23	10.76	7.02	4.28	2.18	0.51	−0.85	−1.98	−2.94
BLAP	10.51	5.30	2.02	−0.26	−1.95	−3.27	−4.33	−5.20	−5.93	−6.56
BLAP3	13.24	7.35	3.66	1.11	−0.78	−2.25	−3.42	−4.38	−5.19	−5.88
BLYP	6.84	2.55	−0.17	−2.08	−3.52	−4.64	−5.55	−6.30	−6.93	−7.48
B3P86	33.89	22.84	16.06	11.44	8.07	5.50	3.46	1.81	0.44	−0.72
B3PW91	28.04	18.45	12.54	8.51	5.56	3.30	1.51	0.05	−1.16	−2.19
B3LYP	18.96	11.64	7.10	3.98	1.68	−0.10	−1.51	−2.67	−3.63	−4.45
exptl[c]	24.2	15.5	10.2	6.5	3.9	1.8	0.2	−1.1	−2.3	−3.2

[a] Frequencies scaled by 0.89. [b] MP4(SDTQ) energy computation on MP2(full) geometry. [c] From ref 50.

TABLE 4: Basis Set Effect on Theoretical ln $K_{eq} = f(T)$, Using B3LYP, for ${}^1/_2N_2 + {}^3/_2H_2 \rightleftharpoons NH_3$

T (K)	6-31G**	6-31++G**	6-311G**	6-311++G**	cc-pVTZ	AUG-cc-pVTZ	exptl[a]
150	17.40	29.70	18.96	29.21	22.93	29.38	24.2
200	10.47	19.70	11.64	19.33	14.62	19.46	15.5
250	6.17	13.55	7.10	13.25	9.48	13.35	10.2
300	3.20	9.35	3.98	9.10	5.96	9.19	6.5
350	1.01	6.28	1.68	6.07	3.38	6.15	3.9
400	−0.68	3.94	−0.10	3.75	1.40	3.82	1.8
450	−2.03	2.08	−1.51	1.91	−0.18	1.97	0.2
500	−3.13	0.56	−2.67	0.42	−1.47	0.47	−1.1
550	−4.06	−0.69	−3.63	−0.83	−2.54	−0.78	−2.3
600	−4.84	−1.75	−4.45	−1.88	−3.45	−1.83	−3.2

[a] From ref 50.

that 6-31G* is the minimal basis set to employ (the 3-21G value being poor), the best equilibrium constant being obtained with 6-311G*. Moreover, diffuse functions change the value a little and do not improve it.

$${}^1/_2N_2 + {}^3/_2H_2 \rightleftharpoons NH_3$$

In order to confirm the tendency observed for the above reaction, we have done the same study for the NH_3 formation equilibrium. In Table 3, we compare first the theoretical ln K_{eq} obtained with several methods to the experimental one. HF gives also poor values ($\alpha \simeq 28\,000$). This time, surprisingly, MP2 and MP4 values are worse. In fact, since reactants and products are very different systems and because there are coefficients applied to the energy, the least error on the absolute energy is highly amplified. Besides, the problem is largely corrected by the BAC-MP4 method ($\alpha \simeq 0.6$), which is precisely tabulated for this kind of compound and reaction (formation). To a lesser degree, G2 improves also significantly MPn results. Concerning the DFT method, local results (VWN) are very poor like previously. Nonlocal computations yield more or less correct equilibrium constants. Unlike the first equilibrium, BP and PP provide the best values. Finally, concerning the HF-DFT method, B3LYP results are again among the best, like B3PW91.

Here, the basis effect is more pronounced (see Table 4). Diffuse functions have a large influence and provide similar results whatever the basis size may be. With B3LYP, the best result is obtained using the cc-pVTZ basis set.

$${}^1/_2N_2 + {}^1/_2O_2 \rightleftharpoons NO \quad \text{and} \quad {}^1/_2N_2 + O_2 \rightleftharpoons NO_2$$

Results for these two equilibriums are presented in Table 5. Curiously, for NO formation, all methods (except MPn) provide very good values, even HF results. According to comments for the two previous equilibriums, this good HF behavior is an accident. Nevertheless, the HF-DFT methods (B3LYP, B3PW91, and B3P86) remain the best. For NO_2 formation, we observe the same tendency as for the first two equilibriums: MPn improves the HF results a lot, B3LYP and BAC-MP4 give the

TABLE 5: Comparison of Theoretical and Experimental ln $K_{eq} = f(T)$ for NO and NO_2 Formation Using the 6-311G* Basis Set

	T (K)				
	298.15	500	1000	2000	3000
	$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$				
HF[a]	−33.72	−19.76	−9.46	−4.29	−2.57
MP2(full)	−46.59	−27.47	−13.43	−6.53	−4.29
MP4(SDTQ)[b]	−42.13	−24.81	−12.10	−5.87	−3.84
BAC-MP4	−35.56	−20.86	−10.02	−4.56	−2.74
G2	−31.40	−18.38	−8.76	−3.94	−2.33
VWN	−36.52	−21.44	−10.31	−4.74	−2.88
BP	−35.06	−20.57	−9.87	−4.52	−2.73
PP	−34.88	−20.47	−9.82	−4.50	−2.72
BLAP	−35.97	−21.11	−10.15	−4.66	−2.83
BLYP	−34.91	−20.48	−9.83	−4.50	−2.72
B3P86	−34.45	−20.21	−9.69	−4.43	−2.67
B3PW91	−34.64	−20.32	−9.74	−4.45	−2.69
B3LYP	−34.68	−20.34	−9.76	−4.46	−2.70
exptl[c]	−34.6	−20.0	−9.3	−3.9	−2.1
	$\frac{1}{2}N_2 + O_2 \rightleftharpoons NO_2$				
HF[a]	−71.04				
MP2(full)	−27.60				
MP4(SDTQ)[b]	−24.59				
BAC-MP4	−19.45				
G2	−14.31				
VWN	16.39				
BP	−4.00				
PP	−4.32				
BLAP	−10.83				
BLYP	−10.73				
B3P86	−12.41				
B3PW91	−15.14				
B3LYP	−19.23				
exptl[d]	−20.67				

[a] Frequencies scaled by 0.89. [b] MP4(SDTQ) energy computation on MP2(full) geometry. [c] From ref 50. [d] From ref 56.

TABLE 6: Comparison of Theoretical and Experimental ln $K_{eq} = f(T)$ for $N_2O_3 \rightleftharpoons NO + NO_2$ Using the 6-311G* Basis Set

	T (K)				
	278.15	288.15	298.15	308.15	318.15
HF[a]	69.47	67.67	65.99	64.42	62.94
MP2(full)	−9.30	−8.39	−7.54	−6.75	−6.01
MP4(SDTQ)[b]	−11.47	−10.48	−9.57	−8.71	−7.90
BAC-MP4[c]	11.33	11.61	11.86	12.09	12.32
G2MP2	−0.22	0.41	1.01	1.56	2.08
VWN	−40.93	−38.89	−36.98	−35.20	−33.54
BP	−14.45	−13.36	−12.33	−11.38	−10.48
PP	−16.89	−15.70	−14.59	−13.56	−12.59
BLAP	−10.72	−9.76	−8.87	−8.03	−7.25
BLYP	−10.12	−9.17	−8.29	−7.47	−6.70
B3P86	−1.45	−0.78	−0.16	0.42	0.96
B3PW91	2.83	3.34	3.82	4.27	4.69
B3LYP	3.82	4.30	4.74	5.16	5.55
exptl[d]	−0.52	0.08	0.65	1.13	1.65

[a] Frequencies scaled by 0.89. [b] MP4(SDTQ) energy computation on MP2(full) geometry. [c] Interpolated values. [d] From ref 57.

best equilibrium constants, and, this time, G2 does not provide very good values but remains about the same as HF-DFT results.

TABLE 7: Comparison of Theoretical and Experimental ln $K_{eq} = f(T)$ for $N_2O_4 \rightleftharpoons 2NO_2$ Using the 6-311G* Basis Set

	T (K)		
	298.1	308.1	318.1
HF[a]	50.67	49.65	48.69
MP2(full)	−18.40	−17.20	−16.08
MP4(SDTQ)[b]	−15.94	−14.82	−13.77
BAC-MP4[c]	0.76	1.40	2.00
G2MP2	−4.27	−3.45	−2.68
VWN	−40.90	−38.92	−37.07
BP	−12.31	−11.28	−10.31
PP	−14.44	−13.34	−12.31
BLAP	−7.50	−6.63	−5.82
BLYP	−9.07	−8.15	−7.28
B3P86	−6.93	−6.05	−5.23
B3PW91	−2.64	−1.90	−1.21
B3LYP	−0.72	−0.04	0.59
exptl[d]	−2.00	−1.20	−0.47

[a] Frequencies scaled by 0.89. [b] MP4(SDTQ) energy computation on MP2(full) geometry. [c] Interpolated values. [d] From ref 4.

$N_2O_3 \rightleftharpoons NO + NO_2$ and $N_2O_4 \rightleftharpoons 2NO_2$

N_2O_3 and N_2O_4 are, respectively, a NO−NO_2 complex and $(NO_2)_2$ dimer. They are both characterized by a long N−N bond length (≃1.8 Å). Tables 6 and 7 show the dissociation equilibrium constants of these species. The same main tendencies are observed. MPn methods improve drastically HF results. BAC-MP4 is not as good as before, but this is certainly due to a poor geometry of the complexes at the HF level.[55] BLYP and BLAP are the best DFT potentials. Good values are obtained with the HF-DFT method. But, this time, B3LYP does not provide the best value, which is obtained with B3P86 (for N_2O_3) and B3PW91 (for N_2O_4). Concerning the G2 method, we present here only G2MP2 results because G2 computations require large space disk, which is not available on our computers. G2MP2 values are very good for N_2O_3 (better than HF-DFT) and correct for N_2O_4 (about the same as HF-DFT results).

2. Methanol. The industrial methanol synthesis is based on the equilibrium $CO + 2H_2 \rightleftharpoons CH_3OH$ (1), carried out at high pressure (≃300 atm) to improve the efficiency of reaction. In order to reach experimentally this equilibrium constant, experimenters have measured it either directly ($P \simeq 1-100$ atm)[2,3] or measured constants of two equilibriums involving methanol: $2CH_3OH \rightleftharpoons 2H_2 + HCOOCH_3$ (2) and $HCOOCH_3 \rightleftharpoons CH_3OH + CO$ (3), which are studied at atmospheric pressure.[3,58]

Experimental values being available and to confirm the tendency observed for nitrogenized compounds (behavior of HF-DFT method in particular), we have computed equilibrium constants for these three equilibriums. But, according to results above, we have retained only the most interesting methods: MPn, G2, BAC-MP4, DFT (BLAP and BLYP), and HF-DFT (B3P86, B3PW91, and B3LYP).

Our results are presented in Table 8. HF-DFT and G2 methods provide again good values (at best with a factor of 10), except for the third equilibrium in which, incomprehensibly, BLAP ($\alpha \simeq 22$) and MP2 ($\alpha \simeq 0.05$) are among the best (the G2 result being excellent), ahead of BAC-MP4 ($\alpha \simeq 0.01$) and B3LYP ($\alpha \simeq 388$). This is all the more surprising because equilibrium 3 is nothing else than a simple combination between equilibriums 1 and 2. This is partially probably due to errors on the two first equilibriums, which cumulatively combine. However, according to Lacy et al.[3], there is a larger significative experimental uncertainty on the third equilibrium's K_{eq} than on the two first. Therefore, this is very difficult for us to conclude here. We can note that BAC-MP4 is excellent ($\alpha \simeq 0.8$) only for the first equilibrium.

3. Chlorine Oxides. To end this study, we have considered a last group of compounds that contain a kind of atom having more electrons than C, N, and O: chlorine oxides. We have chosen the three chlorine oxides (ClO, ClO_2, and Cl_2O), which

TABLE 8: Comparison of Theoretical and Experimental ln K_{eq} for Equilibriums Involving Methanol Using the 6-311G Basis Set**

T (K)	MP2(full)	MP4(SDTQ)[a]	BAC-MP4[b]	G2	BLAP	BLYP	B3P86	B3PW91	B3LYP	exptl
$CO + 2H_2 \rightleftharpoons CH_3OH$ (1)										
573.15	−15.81	−19.90	−7.12	−10.42	−14.37	−14.53	−2.48	−5.10	19.75	7.34[c]
$2CH_3OH \rightleftharpoons 2H_2 + HCOOCH_3$ (2)										
500.15	4.45	6.10	−6.25	0.72	7.27	9.97	0.37	1.43	3.95	−1.94[d]
$HCOOCH_3 \rightleftharpoons CH_3OH + CO$ (3)										
347.15	5.37	9.75	6.65	2.01	−0.82	−4.30	−10.55	−7.761	−3.69	2.27[d]

[a] MP4(SDTQ) energy computation on MP2(full) geometry. [b] Interpolated values. [c] From ref 2. [d] From ref 58.

TABLE 9: Comparison of Theoretical and Experimental ln K_{eq} for Chlorine Oxide Formation at 298.15 K Using the 6-311G* Basis Set

MP2(full)	MP4(SDTQ)[a]	BAC-MP4	G2	BLYP	B3P86	B3PW91	B3LYP	exptl[b]
$^1/_2Cl_2 + ^1/_2O_2 \rightleftharpoons C1O$								
−63.62	−56.84	−48.23	−40.36	−45.78	−48.09	−48.30	−46.94	−39.54
$^1/_2Cl_2 + O_2 \rightleftharpoons ClO_2$								
<(−99)	<(−99)	−67.97	−48.47	−83.38	−92.29	−95.86	−98.86	−48.57
$Cl_2 + ^1/_2O_2 \rightleftharpoons Cl_2O$								
−46.86	−45.68	−39.67	−33.08	−38.18	−38.77	−47.25	−44.78	−39.46

[a] MP4(SDTQ) energy computation on MP2(full) geometry. [b] From ref 56.

TABLE 10: Basis Set Effect on Theoretical ln K_{eq}, Using B3LYP, for Chlorine Oxide Formation at 298.15 K

formation of	6-311G*	6-311+G*	cc-pVTZ	AUG-cc-pVTZ	exptl[a]
ClO	−46.94	−43.51	−41.10	−39.72	−39.54
ClO_2	−98.86	−92.41	−69.00	−65.46	−48.57
Cl_2O	−44.78	−43.79	−42.55	−42.12	−39.46

[a] From ref 56.

are gaseous at 298.15 K, to examine their formation reaction. These results are reported in Table 9.

For ClO formation, we obtain the best equilibrium constant with G2 (α ≃ 2.3), then with BLYP (α ≃ 513) followed by B3LYP (α ≃ 1636), these deviations being much larger than those achieved for the two previous groups of compounds. Concerning the second equilibrium (ClO_2 formation), theoretical results are extremely poor, except the G2 value, which is excellent (α ≃ 0.9). On the contrary, for Cl_2O formation, BAC-MP4 (α ≃ 1.2), B3P86 (α ≃ 0.5), and BLYP (α ≃ 0.3) results are very good and the G2 value is among the worst (α ≃ 0.002).

To try to improve these results (particularly for $Cl0_2$), we show in Table 10 the basis size effect in B3LYP for the three equilibriums. We can see immediately that, for this kind of system, the basis size have a large influence. In all cases, the values obtained in 6-311G* are significantly improved, especially for the ClO_2 formation for which the change is considerable. This is due, to some extent, to a better geometry obtained with a larger basis set. Considering this amelioration, we can hope, increasing the basis set size (cc-pVQZ ...), to improve further the theoretical equilibrium constant for ClO_2 formation.

IV. Conclusions

In this work, we have tested the ability of ab initio and DFT methods to compute equilibrium constants for reactions in gaseous phase. We have shown HF, as expected, is inadequate to obtain correct values. MPn and DFT are rather irregular in the quality yielded. BAC-MP4 gives rather good values, but only if it deals with compounds for which the geometry is well-represented at the HF level. Otherwise, as noted for N_2O_3 and N_2O_4 dissociation, results are poor. HF-DFT and G2 methods are noticeable, providing good equilibrium constants, in most cases, in qualitative agreement with experiment (generally with a factor less than 100).

Basis size does not have a large influence, except for compounds including atoms heavier than C, N, O, ... (Cl, for example). It seems we have to use 6-311G** basis set at least.

However, a good result can be obtained exceptionally with a low level of calculation. This is due to the fact that some errors can be compensated (size-consistency, stoichiometric coefficients, correlation effect, ...). But, to obtain a constancy in series, it is better to use a high level of computation, even (at present) if the experimental value is not well-reproduced.

Therefore, the quantitative theoretical value is not still attainable, but, now, we make use of methods (HF-DFT and G2 in particular) capable of supplying the order of scale for equilibrium constants.

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