Transition State Structure and Energetics of the N$_2$O + X (X = Cl,Br) Reactions

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The structural and vibrational properties of the transition state of the N$_2$O + X (X = Cl,Br) reactions have been characterized by ab initio methods using density functional theory. We have employed Becke's hybrid functional (B3LYP), and transition state optimizations were performed with 6-31G(d), 6-311G(2d,2p), 6-311+G(3d,2p), and 6-311+G(3df,2p) basis sets. For the chlorine atom reaction the coupled-cluster method (CCSD(T)) with 6-31G(d) basis set was also used. All calculations resulted in transition state structures with a planar cis arrangement of atoms for both reactions. The geometrical parameters of transition states at B3LYP are very similar, and the reaction coordinates involve mainly the breaking of the N−O bond. At CCSD(T)/6-31G(d) level a contribution of the O−Cl forming bond is also observed in the reaction coordinate. In addition, several highly accurate ab initio composite methods of Gaussian-n (G1, G2, G3), their variations (G2(MP2), G3//B3LYP), and complete basis set (CBS-Q, CBS-Q//B3LYP) series of models were applied to compute reaction energetics. All model chemistries predict exothermic reactions. The G3 and G2 methods result in the smallest deviations from experiment, 1.8 and 0 kcal mol^{-1}, for the enthalpies of reaction for N$_2$O reaction with chlorine and bromine, respectively. The G3//B3LYP and G1 methods perform best among the composite methods in predicting energies of the transition state, with a deviation of 1.9 and 3.0 kcal mol^{-1}, respectively, in the activation energies for the above processes. However, the B3LYP/6-311+G(3df,2p) method gives smaller deviations of 0.4 and −1.0 kcal mol^{-1}, respectively. The performance of the methodologies applied in predicting transition state energies was analyzed.

I. INTRODUCTION

Chlorine- and bromine-containing nitrogen compounds have been well established as important atmospheric species associated with processes that affect the stratospheric ozone abundance.[1,2] Accurate energetic profiles of any particular elementary reactions related to such species is thus very desirable and advantageous.

For reliable theoretical thermochemical predictions a number of highly accurate ab initio approaches have been developed in recent years which are able to calculate molecular energies to chemical accuracy (1−2 kcal mol^{-1}). The first two in a series of models for computational thermochemistry are the Gaussian-1 (G1) and Gaussian-2 (G2) theories introduced by Pople et al.,[3,4] followed by Gaussian-3 (G3) models of theory.[5] All these models are a composite procedure on a sequence of well-defined ab initio calculations, and the total energy is obtained by combining the results of the different level calculations to overcome uncertainties resulting from the influence of basis set size and electron correlation. Several modifications of these methods have been proposed in which one or more steps have been changed, with the goal of decreasing computational cost or improving the accuracy. The most practical variants of the latter two models are referred to as G2(MP2)[6] and G3//B3LYP,[7] respectively. Another family of model chemistries is the complete basis set (CBS) methods developed by Petersson et al.[8−10] These methods are based on a basis set extrapolation for accurate estimates of total correlation energies.

Unfortunately, these compound methods were not designed specifically for transition state energy calculations. In contrast to equilibrium structures, they are not well tested for chemical dynamics calculations, especially for barrier heights. Their performance for transition states is limited to a small set of transition states containing first- and second-row elements. In the first study G1 and G2 theories were applied in the rearrangement and dissociative reactions of the methanol radical cation,[11] with G2 achieving an accuracy of 4.1 kcal for transition state relative energies. Durant et al.[12] have examined G2 methodology for classical barrier heights on the set of 12 atom−diatom reactions and compared them with previous results of experiment or multireference configuration interaction studies. An average deviation of 1.5 kcal mol^{-1} was found. Further, improved performance in predicting transition state energies was obtained by modifying the G2 method by introducing QCISD/6-311G(d,p) geometries and frequencies instead of MP2/6-31G(d) geometries and scaled HF/6-31G(d) frequencies. Jungkamp et al.[13] reported a modified version of CBS-4 and CBS-q models to predict transition state energies for reactions previously addressed by Durant et al. and for hydrogen transfer between C$_2$H$_4$ and C$_2$H$_5$ as an additional system. B3LYP functional with basis set size ranging from 3-21G(d,p) to 6-311G(d,p) replaced the HF/3-21G(d) geometries and zero-point vibrational frequencies in the original methods. As an extension of the compound G2 and CBS models Petersson proposed an

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IRCMax method[14,15] for the characterization of transition state, which gives rms errors in the classical barrier heights for a 10 atom exchange reaction less than 1.3 kcal mol^{-1}.

The purpose of the present study is to characterize the transition state at high level wave function and density functional theory for the reactions

$$N_2O(^1\Sigma^+) + X(^2P) \rightarrow N_2(^1\Sigma^+) + OX(X^2\Pi) \ X = Cl, Br$$
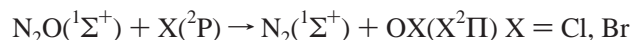
in order to provide accurate geometrical and vibrational parameters, barrier height, and reaction energetics. Further, several compound methods were applied to prove the accuracy of these methods for predicting transition state barrier heights and reaction energies. Theoretical methods used in the current study are detailed in the next section, with results and discussion presented in the following section. Conclusions are summarized in the final section.

II. COMPUTATIONAL METHODS

All calculations in this paper were performed with the GAUSSIAN 98 program.[16] The transition state structures of both reactions were obtained using transition state optimization by the eigenvalue-following (EF) method[17] using Becke three-parameter nonlocal exchange functional[18] with the nonlocal correlation of Lee, Yang, and Parr (B3LYP)[19,20] with standard basis sets 6-31G(d), 6-311G(2d,2p), 6-311+G(3d,2p), and 6-311+G(3df,2p), as implemented in the program.[6] For the chlorine atom reaction the single and double excitation coupled-cluster method, including a perturbation estimate of the effects of connected triple excitations (CCSD(T))[21,22,23] with 6-31G(d) basis set, was also employed. The harmonic frequencies of the transition state were computed analytically and numerically at B3LYP and CCSD(T) levels, respectively, with all mentioned basis sets to characterize it as a first-order saddle point and to determine zero-point vibrational energy (ZPE). As recommended by Scott and Radom[24] the ZPE scaling factor of 0.9806 for B3LYP/6-31G(d) was used. Unfortunately, their comprehensive study on scaling factor did not include the other basis sets or the coupled-cluster method, so these ZPE values were taken without scaling factor.[25]

Particular compound methods for calculating accurate energies have been discussed in detail in the original references cited, so only a brief summary of the steps will be given. The G1, G2, and G3 models use structure optimized at MP2(full)/6-31G(d) level and HF/6-31G(d) scaled ZPE. G1 theory involves approximating the QCISD(T)/6-311+(2df,p) energy using MP4 and QCISD(T) energies calculated with the 6-311G(d,p) basis set and MP4 energies calculated with 6-311+G(d,p) and 6-311(2df,2p) basis sets. The remaining deficiencies in the basis set are included by empirically estimating the term which depends on the number of paired as well as unpaired electrons. The G2 model approximates QCISD(T)/6-311+(3df,2p) calculations by combining MP4 and MP2 energies calculated with the 6-311G(d,p), 6-311+G(d,p), and 6-311G(2df,p) basis sets, MP2/6-311+G(3df,2p) and QCISD(T)/ 6-311G(d,p) energies. A higher level correction, based on the number of pairs of valence electrons, is used to account for residual basis set errors. G3 theory achieves significantly improved accuracy and requires less computational time relative to G2

theory. MP4 and QCISD(T) single point calculations in G3 theory are based on the 6-31G(d) basis set, instead of the 6-311G(d,p) basis set as in G2 theory. MP2 single point calculations use the G3large basis set, which is a modification of the 6-311+G(3df,2p) basis set used in G2 theory. A spin−orbit correction is added to the energies of atomic species, and a correction for core correlation is added. The higher level correction for molecules and for atoms is separated. The G2(MP2) method is a variant of G2, which uses MP2 instead of the MP4 level for basis set extension corrections. In the G3//B3LYP variant of the G3 method, B3LYP/6-31G(d) geometry and scaled ZPE value replaced MP2(full)/6-31G(d) geometry and HF/6-31G(d) scaled ZPE. The CBS-Q model[26] uses geometry derived from the second-order Møller−Plesset (MP2/6-31G(d)) theory[27] and zero-point energy computed by the Hartree−Fock (HF/6-31G(d)) theory.[27] The MP2 calculation with a larger basis set and a CBS extrapolation ensure the energy corrections through second-order, and the two additional calculations at the QCISD(T)/6-31+G(d) and the MP4(SDQ)/6-31+G(d,p) levels are used to approximate higher orders of contributions. There are also empirical corrections for spin contamination and a size-consistent higher-order correction. The CBS-Q//B3LYP[28] method is a modified CBS-Q model which uses B3LYP hybrid density functional geometries and frequencies.

III. RESULTS AND DISCUSSION

Transition States. We present here the results of the B3LYP hybrid DFT method and the coupled cluster ab initio calculations, which show them to be extremely reliable methods for geometry prediction. The optimized geometries of the transition states for the reactions of nitrous oxide with chlorine and bromine atoms which take place on the ^{2}A$^\prime$ surface are listed in Table 1, while their frequencies are summarized in Table 2. For comparison, the HF/-631G(d) and MP2/-631G(d) results from our previous studies[29,30] are included. It can be seen from Table 1 that calculations based on B3LYP theory using four different basis sets produced consistent values, with an uncertainty of less than 2% in predicting the structure of the transition state. The variation of the calculated bond lengths with the basis set also shows that the small basis sets, such as 6-31G(d), are quite adequate to describe both transition states. Inclusion of higher order diffuse functions and polarization functions causes very small oscillations in geometrical parameters which are insignificantly greater for the transition state of the chlorine reaction. These observations are more evident from Figures 1 and 2 where the position of transition states for individual levels of calculation are indicated on the intrinsic reaction coordinate (IRC) for the chlorine and bromine reactions, respectively. It should be mentioned that the IRC, resulting from different levels of calculation, are close to each other, and thus only B3LYP/6-31G(d) IRC is drawn. The energy profile of reactions will be discussed later. Here we just comment that, as expected, the HF and the MP2 methods very poorly describe the energy variation along the reaction path, but both methods provide the position of the transition states reasonably well.

With regard to the vibrational frequencies also the B3LYP level appears to be reliable for these species. Variation in basis set produces quite consistent results, except for the

Table 1. Transition State Geometries[b]

		B3LYP/ 6-31G(d)	B3LYP/ 6-311G(2d,2p)	B3LYP/ 6-311+G(3d,2p)	B3LYP/ 6-311+G(3df,2p)	CCSD(T)/ 6-31G(d)	HF/ 6-31G(d)[a]	MP2/ 6-31G(d)[a]
NNO−Cl ($^2A'$)	R(NN)	1.155	1.138	1.143	1.142	1.163	1.167	1.118
	R(NO)	1.404	1.410	1.385	1.384	1.365	1.330	1.365
	R(OCl)	1.824	1.840	1.832	1.818	1.895	1.866	1.800
	∠NNO	131.4	133.3	133.2	133.3	136.7	126.5	149.6
	∠NOCl	116.2	116.4	116.1	116.2	114.8	115.5	118.4
NNO−Br ($^2A'$)	R(NN)	1.152	1.136	1.138	1.138		1.166	1.119
	R(NO)	1.435	1.431	1.426	1.417		1.338	1.367
	R(OBr)	1.942	1.958	1.950	1.935		1.965	1.916
	∠NNO	129.8	132.4	131.8	132.0		125.4	147.3
	∠NOBr	116.3	117.1	117.2	117.2		116.6	117.3

[a] For NNO−Cl from ref 29, while for NNO−Br from ref 30. [b] Bond lengths in Å, bond angles in degrees.
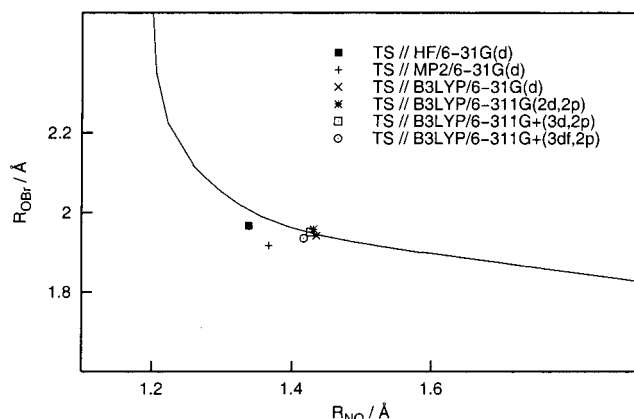
Table 2. Transition State Frequencies (cm^{-1})

	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(2d,2p)	B3LYP/ 6-311+G(3d,2p)	B3LYP/ 6-311+G(3df,2p)	CCSD(T)/ 6-31G(d)	HF/ 6-31G(d)[a]	MP2/ 6-31G(d)[a]
NNO−Cl ($^2A'$)	527i	643i	568i	572i	740i	632i	1354i
	1874	1880	1857	1869	1868	1515	2888
	638	617	646	652	669	815	765
	525	511	524	529	518	588	679
	332	330	344	345	371	338	401
	173	154	172	174	175	242	171
NNO−Br ($^2A'$)	560i	640i	610i	583i		511i	1186i
	1892	1895	1886	1884		1521	2891
	588	576	584	594		785	731
	463	446	457	464		571	628
	292	302	295	301		320	371
	148	131	136	141		224	158

[a] For NNO−Cl from ref 29, while for NNO−Br from ref 30.
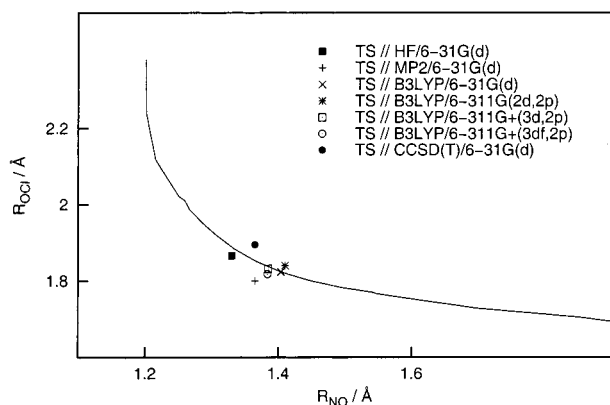
Figure 1. The B3LYP/6-31G(d) IRC for the reaction N$_2$O + Cl → N$_2$ + OCl. The positions of the TS along IRC at different levels of theory are indicated.

Figure 2. The B3LYP/6-31G(d) IRC for the reaction N$_2$O + Br → N$_2$ + OBr. The positions of the TS along IRC at different levels of theory are indicated.

decomposition and N−O−X bending frequencies where the difference in values is rather more pronounced. The N−N stretching frequency is nearly independent of basis set. The frequencies of other modes are within 4.5% and 3.5% for chlorine and bromine reactions, respectively. The decomposition mode, i.e., the imaginary frequency, corresponds to the N−O stretching frequency. From inspection of normal mode animation it can be concluded that normal modes are mainly decoupled from each other, and the assignment is thus relatively unambiguous. The CCSD(T)/6-31G(d) real frequencies of the transition state for the chlorine reaction are very close to B3LYP/6-311+G(3df,2p) values, while the imaginary one is about 170 cm^{-1} higher. It should be noted that here the contribution of the O−Cl stretch vibrational frequency to the decomposition mode is observable. It is

worth mentioning that the frequencies obtained here are more reliable than those of HF and MP2 levels reported in our previous work.[29,30] Since the reaction coordinate for the HF transition states is predominantly associated with the formation of the O-halogen bond, the reaction coordinate of the MP2 transition state is characterized by the largest imaginary frequencies, indicative of the narrowest barrier, and primarily involves N−O bond breaking.

Reaction Enthalpies. The reaction enthalpies, $\Delta H_{298}°$, calculated as the difference in total energy between products and reactants by subtracting the changes in ZPE and in thermal correction (TC) for both reactions, are given in Table 3. Note that the scale factor of 0.8930[24] was used in
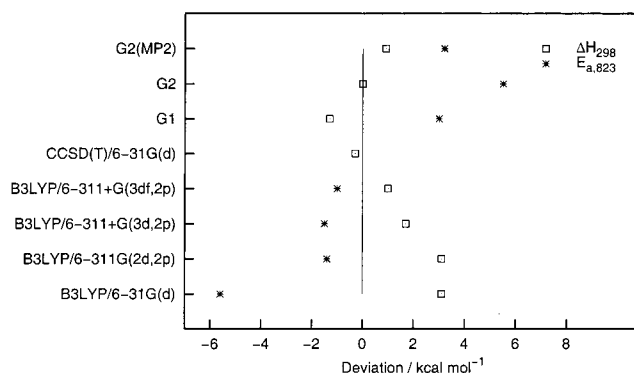
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Table 3. Calculated Enthalpies of Reaction, ΔH_{298}^0 (kcal mol^{-1})

method/basis set	N_2O + Cl → N_2 + OCl	N_2O + Br → N_2 + OBr
B3LYP/6-31G(d)	−14.3	−13.1
B3LYP/6-311G(2d,2p)	−16.6	−13.1
B3LYP/6-311+G(3d,2p)	−20.4	−14.5
B3LYP/6-311+G(3df,2p)	−21.1	−15.2
CCSD(T)/6-31G(d)	−19.8	−16.5
G1	−21.9	−17.5
G2	−21.5	−16.2
G2(MP2)	−21.2	−15.3
G3	−22.4	
G3//B3LYP	−21.0	
CBS-Q	−22.3	
CBS-Q//B3LYP	−21.6	
experiment	−24.0[a]	
	−25.1[b]	
	−24.4[c]	−16.3[c]
	−24.2[d]	−16.2[d]

[a] Reference 32. [b] Reference 33. [c] References 34 and 35. [d] Reference 36.
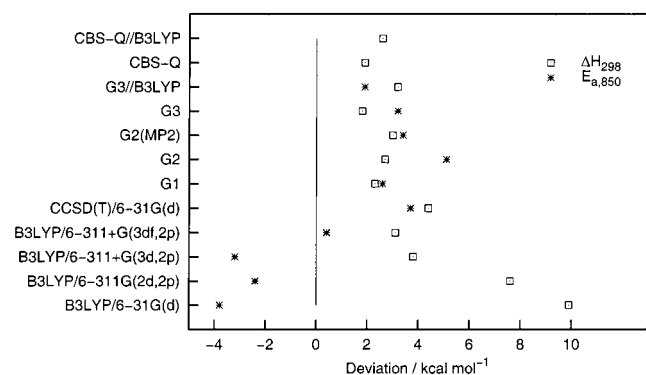
Figure 3. Deviations of reaction enthalpies and activation energies for the reaction N_2O + Cl → N_2 + OCl calculated by selected theories from experiment.

Figure 4. Deviations of reaction enthalpies and activation energies for the reaction N_2O + Br → N_2 + OBr calculated by selected theories from experiment.

calculations of ZPE and TC at the B3LYP/6-31G(d) level, and for all other calculations no scale factor was used. Next to the B3LYP and CCSD(T) levels of calculations the reaction enthalpies are calculated also with G1, G2, and G2(MP2) composite ab initio methods. For the chlorine reaction, G3, G3//B3LYP, CBS-Q, and CBS-Q//B3LYP are reported, while these, due to the lack of the basis set termed G3large[5] and CBS extrapolation[31] for bromine as third-row elements, cannot be applied. The experimental exothermicity of the chlorine reaction is reported to be 24.0 kcal mol^{-1}.[32] A value of 25.1 kcal mol^{-1} is obtained when the reaction enthalpy is calculated from the experimental standard heat of formation using the data for N_2O and OCl as included in the G2 test set.[33] The most recent heat of formation from JANAF Thermochemical Tables[34,35] yields 24.4 kcal mol^{-1} for $\Delta H_{298}°$, and a value of 24.2 kcal mol^{-1} is obtained using the IVTANTERMO Database.[36] Only the latter two sources include the OBr standard heat of formation, and the value of $\Delta H_{298}°$ obtained are 16.3 and 16.2 kcal mol^{-1}. An inspection of Table 3 shows that both traditional and compound methods predicted exothermic reactions. The deviation between calculated and experimental reaction enthalpy is illustrated in Figures 3 and 4 by open squares for chlorine and bromine reactions, respectively. The calculated results are compared to 24.2 and 16.2 kcal mol^{-1}, respectively.

The compound methods employed overestimate the reaction enthalpy for the chlorine reaction by 2.5 kcal mol^{-1} on average. G3 and CBS-Q reaction enthalpies most closely approach the experimental value, being higher by 1.8 and 1.9 kcal mol^{-1}, respectively. The G3//B3LYP deviation of 3.2 kcal mol^{-1} is the highest of all the applied compound methods, while the G2(MP2) deviation is only slightly lower. The deviations of the latter two compound methods are comparable to that of the B3LYP/6-311+G(3df,2p) method. As expected the other level of calculations are less reliable in predicting enthalpy of chlorine reaction.

From Figure 4 it is evident that the G2 reaction enthalpy for the bromine reaction is the same as the experimental value. The G1 method underestimates the reaction enthalpy by 1.3 kcal mol^{-1}, while G2(MP2) overestimates it by 0.9 kcal mol^{-1}. The CCSD(T)/6-31G(d) method is very accurate for this case. The reaction enthalpy computed at the B3LYP/6-311+G(3df,2p) level is comparable with that of the G2(MP2) method. For the B3LYP level of theory the deviations were calculated to be 1.7, 3.1, and 3.1 kcal mol^{-1} for the 6-311+G(3d,2p), 6-311G(2d,2p), and 6-31G(d) basis sets, respectively. Considering the deviation of calculated values from experimental ones, it can be concluded that the B3LYP/6-31G(d) method predicts the reaction enthalpy as well as the G3//B3LYP method does for chlorine reaction.

Barrier Heights. The calculated barrier heights, $\Delta E_0^{\ddagger}$, for both reactions are summarized in Table 4. They are calculated as the difference of the total energies of transition states and the reactants, with the ZPE accounted for. Further, enthalpies of activation, $\Delta H_{298}^{\ddagger}$, and activation energies, $E_{a,T}$, are presented in this table. $E_{a,T}$ was evaluated from $\Delta H_T^{\ddagger}$ (not involved in this table) for an ideal bimolecular gas-phase reaction according to the well-known relation.[37] As far as we know the only experimental activation energies for nitrous oxide reaction with chlorine and bromine atoms were evaluated from the Ahrrenius plots obtained from kinetic measurements performed in the temperature range 773−923 K[29] and 773−873 K,[38] respectively. Thus, for the adequate comparison the activation energy for chlorine reaction was calculated for 850 K and that of bromine for 823 K. The levels employed in the calculations are apparent from the table.

In Figures 3 and 4 we can see the deviation of calculated and experimental activation energies (denoted by an asterisk) for the chlorine and bromine reactions, respectively. From Figure 3 it is evident that the B3LYP/6-311+G(3df,2p)

Table 4. Calculated Barrier Heights, ΔE_0 (kcal mol^{-1}), Enthalpies of Activation, ΔH_{298} (kcal mol^{-1}), and Activation Energies, $E_{A,T}$ (kcal mol^{-1}), for Comparison with Experiment

	NNO−Cl (^{2}A′)			NNO−Br (^{2}A′)		
method/basis set	$\Delta E_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$E_{a,850}$	$\Delta E_0^{\ddagger}$	$\Delta H_{298}^{\ddagger}$	$E_{a,823}$
B3LYP/6-31G(d)	26.3	25.8	28.7	24.1	23.7	26.7
B3LYP/6-311G(2d,2p)	27.6	27.1	30.1	28.4	27.9	30.9
B3LYP/6-311+G(3d,2p)	26.9	26.4	29.3	28.3	27.8	30.8
B3LYP/6-311+G(3df,2p)	30.5	30.0	32.9	28.8	28.4	31.3
CCSD(T)/6-31G(d)	33.9	33.3	36.2			
G1	32.6	32.0	35.1	32.8	32.3	35.3
G2	35.1	34.6	37.6	35.3	34.7	37.8
G2(MP2)	33.4	32.8	35.9	34.5	33.5	36.5
G3	33.2	32.6	35.7			
G3//B3LYP	32.0	31.5	34.4			
experiment	32.5 ± 1.9^a			32.3 ± 0.9^b		

^{a} Reference 29. ^{b} Reference 38.

method most successfully predicts the activation energy for the chlorine reaction, the deviation being only 0.4 kcal mol^{-1}. Next is the G3//B3LYP method, the activation energy being 1.9 kcal mol^{-1} higher than experimental. The activation energy is poorly reproduced by the G2 method, with a deviation of 5.1 kcal mol^{-1} larger by a factor of 2 than that of the G1 method. G3 and G2(MP2) results are qualitatively between G3//B3LYP and G2.

Figure 4 shows that the B3LYP/6-311+G(3df,2p) method is again the most successful in predicting the activation energy of the bromine reaction. The calculated value underestimates the experimental value by 1.0 kcal mol^{-1}. The underestimation of B3LYP/6-311+G(3d,2p) and B3LYP/6-311G(2d,2p) results is only slightly greater, while that of B3LYP/6-31G(d) approaches to 5.6 kcal mol^{-1}. All three compound methods overestimate the activation energy with deviations of 3.0, 3.2, and 5.5 kcal mol^{-1} for the G1, G2, and G2(MP2) methods, respectively. Thus, G1 and G2 appear to be nearly equivalent in providing the transition state energy for N$_2$O reaction with bromine atom; however, both significantly overestimate the experimental result. Duran[12] has also shown that the G2 method can have errors as large as 2.6 kcal in predicting classical barrier heights for an open-shell transition state.

IV. CONCLUDING REMARKS

We have carried out an ab initio study on the transition states involved in the N$_2$O reaction with chlorine and bromine atoms. All calculations applied resulted in a transition state structure with a planar cis arrangement of atoms. With B3LYP theory, the position of the transition state along the reaction coordinate does not change significantly with an increased basis set, the oscillations in geometrical parameters being below 2%. The motion along the reaction coordinate is primarily associated with the N−O stretching vibration. The reactive region of bond breaking and bond forming is approximately from $s = -0.3$ to 0.1 amu$^{1/2}$ Bohr for chlorine and from $s = -0.5$ to 0.5 amu$^{1/2}$ Bohr for bromine reactions. CCSD(T)/6-31G(d) level for the chlorine reaction predicts somewhat longer O−Cl bond and shorter N−O bond compared to the B3LYP series and also an appreciable contribution of the O−Cl stretch vibration to the reaction coordinate.

In addition to density functional and coupled cluster methods, several highly accurate ab initio composite methods

were applied to compute reaction energetics. These composite methods, in contrast to those for equilibrium structures, are not yet widespread for chemical dynamics calculations, especially for barrier heights, where their performance for transition states is limited to a small set of transition states containing predominantly first-row elements. In the present work we have proved their adequacy for transition states with second- and third-row atoms. There is no uniform conclusion concerning the preferred method for the reaction enthalpy or for the activation energy of either reaction. For the reactions under consideration, the following conclusions may be summarized. All model chemistries applied in the study predict both reactions as exothermic process. The G3 and G2 methods provide the smallest deviations of the calculated from experimental enthalpies of reaction, i.e., 1.8 and zero kcal mol^{-1}, for the N$_2$O reaction with chlorine and bromine, respectively. The B3LYP/6-311+G(3df,2p) method performs well in predicting energies of the transition state, with a deviation of 0.4 and −1.0 kcal mol^{-1} in the barrier height for N$_2$O reaction with chlorine and bromine, respectively. For the chlorine reaction, the G1 method is found to be the most reliable of all the methods applied in predicting both the reaction enthalpy and activation energy. For the bromine reaction the B3LYP/6-311+G(3df,2p) method is the preferred one of the seven applied in evaluating the reaction enthalpy and activation energy. An overview of the performance for the applied compound methods shows that average deviations of 2.5 and 3.2 kcal mol^{-1} are found for reaction enthalpy and activation energy, respectively, in the chlorine reaction, while those in the case of bromine atoms are 0.7 and 3.9 kcal mol^{-1}, respectively.

The study will be extended using multireference CI methods as implemented in the DIESEL program,[39] and due to the complexity of these methods the work will be presented in a separate paper.

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