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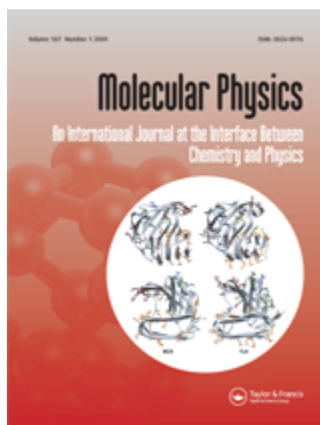
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Computational study of the perhalogenated methyl nitrates CX_3ONO_2 , $CX_xY_{3-x}ONO_2$ (X, Y=F,Cl)

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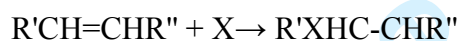
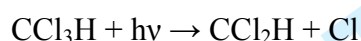
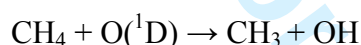
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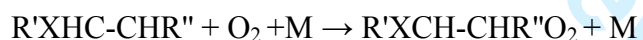
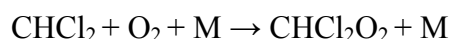
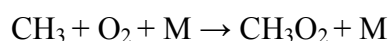
Ab initio and density functional theory methods are employed to study the structures, harmonic frequencies, energetics and thermodynamic properties of the perhalogenated methyl nitrates, CX_3ONO_2 , $CX_xY_{3-x}ONO_2$ (X, Y=F, Cl), which may be formed as secondary reactive intermediates in the coupling of the halogenated methylperoxy radicals with NO. Reaction energies are computed with respect to CX_3O_2+NO , $CX_xY_{3-x}O_2+NO$ and CX_3O+NO_2 , $CX_xY_{3-x}O+NO_2$ radical pair decomposition species. The large heat of formation values calculated indicate the high stabilization achieved upon halogenation of the methyl radical, particularly for the fluorinated compounds. Thus, the halogenated methyl nitrates which appear in the oxidation chain of halomethanes can be thermally deactivated under suitable temperature and pressure conditions and act as reservoir compounds for the halogenated methylperoxy radicals, CX_3O_2 , $CX_xY_{3-x}O_2$ and NO, in the troposphere. The computational investigation also demonstrates the significant structural changes caused by the halogen electron withdrawing effect, compared to the methyl analog, CH_3ONO_2 .

1. Introduction

Organic nitrate chemistry is an area in which the atmospheric cycles of nitrogen and organic carbon are strongly coupled [1, 5]. Alkyl nitrates, RONO_2 , are formed in the troposphere during the oxidation chain of organic pollutants emitted by biogenic and anthropogenic sources [2, 3]. The alkyl radicals produced by photodissociation or oxidation of hydrocarbons and halocarbons [4, 5] or addition of an atmospheric oxidant X ($\text{X}=\text{OH}, \text{Cl}$) to an alkene double bond [6, 7]



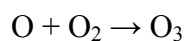
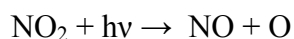
readily pick up an O_2 molecule to form organic peroxy radicals



The usual fate of the alkylperoxy radicals in regions with high nitrogen oxide concentrations is coupling with NO to yield alkoxy radical RO and NO_2



which upon photodissociation, contributes to O_3 production in the troposphere



The secondary channel (1b) however, that leads to the production of trace amounts of alkyl nitrates



has also been identified. The organic nitrates thus formed, may be thermally deactivated under suitable atmospheric conditions and act as reservoir compounds for the halogenated alkylperoxy radicals, CX_3O_2 , $\text{CX}_x\text{Y}_{3-x}\text{O}_2$ and NO. The mechanism for channel (1b) has

been a very interesting problem, not fully clarified yet and the nitrate formation channel although being a minor pathway, has been difficult to quantify so far. The alkyl nitrates are also the association minima in the potential energy surface of the reaction between alkoxy radicals and nitrogen dioxide



Due to the importance of reaction (1) the subject has known numerous experimental investigations [8-13], many of which have investigated the reactions of the halogenated peroxy radicals [14-16] and particularly, the fluorinated ones [17-25]. The branching ratio for RONO_2 formation has been reported to vary systematically with carbon number and increase from <0.014 for ethyl to >0.32 for octyl radicals [5, 24]. It has been also postulated that the size of the alkyl radical and the presence of electron donating and electron withdrawing groups attached to the carbon bearing the peroxy moiety affect positively or negatively the importance of the nitrate formation channel. The more voluminous fluorine atoms in CF_3O_2 for instance, which at the same time exhibit a strong electron-withdrawing effect, enhance the nitrate yield from $\text{CF}_3\text{O}_2 + \text{NO}$ compared to that from $\text{CH}_3\text{O}_2 + \text{NO}$, but on the other hand, this yield was shown to be less than that from $(\text{CH}_3)_3\text{CO}_2 + \text{NO}$ [25]. The computational modeling of the nitrate formation channel has also been the subject of many theoretical efforts focused primarily on the simplest system $\text{CH}_3\text{O}_2 + \text{NO}$. In all theoretical investigations, the mechanism of the reaction was found to involve the formation of both conformers of the nascent association methylperoxy nitrite adduct [26-32]. The two distinct conformeric structures have been characterized with respect to the ONOO dihedral angle as the *cis*-perp and the *trans*-perp configurations, where the perp notation refers to the nearly perpendicular geometry of the carbon atom of the attached methyl group. The two conformers were found to be formed with a nearly equal probability but were calculated to follow different reaction pathways. The *cis*-perp isomer dissociates directly to radical-pair formation, $\text{CH}_3\text{O} + \text{NO}_2$, while the *trans*-perp was

suggested to isomerize to CH_3ONO_2 [32]. The methyl nitrate thus formed, may either dissociate to $\text{CH}_3\text{O}+\text{NO}_2$ too or may be collisionally stabilized to produce the corresponding thermalized species under suitable temperature and pressure conditions in the atmosphere.

Organic nitrates in the laboratory have been synthesized in a variety of ways [1], mainly involving the esterification of the parent alcohol, ROH , in nitric acid solution or the treatment of the corresponding alkyl halide, RX , with silver nitrate. More specialized methods have been used for the preparation of nitrates possessing additional functional groups. The perfluorinated methyl nitrate CF_3ONO_2 has been given considerable attention recently and has been synthesized in the laboratory [33-34]. It is a colourless gas with a boiling point of $-18\pm 3^\circ\text{C}$ and a melting point of -163°C . It decays slowly into carbonyl fluoride, F_2CO , and nitryl fluoride, FNO_2 , at room temperature in the gas phase and at lower temperature in the liquid phase.

In the present work we have carried out the computational investigation of the perhalogenated nitrates of the type CX_3ONO_2 , $\text{CX}_x\text{Y}_{3-x}\text{ONO}_2$ ($\text{X}, \text{Y}=\text{F}, \text{Cl}$). Geometries, harmonic vibrational frequencies, electronic energies and heat of formation values are determined. The result of the halogen electron-withdrawing tendency on the structural features and the stabilization of the nitrates in comparison with the methyl analog, CH_3ONO_2 , is discussed. Finally, the relative energies with respect to $\text{CX}_3\text{O}_2+\text{NO}$, $\text{CX}_x\text{Y}_{3-x}\text{O}_2+\text{NO}$ and $\text{CX}_3\text{O}+\text{NO}_2$, $\text{CX}_x\text{Y}_{3-x}\text{O}+\text{NO}_2$ radical pair reactant and decomposition species are also computed.

2. Computational Details

The optimization of the structures of the perhalogenated methyl nitrates including methyl nitrate, CH_3ONO_2 , have been performed using ab initio and density functional theory techniques. The (U)MP2 [35] and the (U)B3LYP [36-37] methods combined with

the 6-311++G(d,p) basis set were used for the optimization of the equilibrium structures and the vibrational frequency characterization.

The electronic energies and the relative energies with respect to CX_3O_2+NO , $CX_xY_{3-x}O_2+NO$ and CX_3O+NO_2 , $CX_xY_{3-x}O+NO_2$ radical pair reactant and decomposition species have been refined by employing G2MP2, G3//B3LYP and single-point CCSD(T)//B3LYP calculations [38]. It is worth mentioning at this point the very different zero point energy values for the nitrogen oxides NO_x calculated at each optimization method, MP2 and B3LYP. Differences of $2.2 \text{ kcal mol}^{-1}$ for NO and $1.2 \text{ kcal mol}^{-1}$ for NO_2 have been obtained. Thus, it was thought desirable to calculate two series of reaction energies based on the single-point CCSD(T)//B3LYP results, taking into account both MP2 and B3LYP based zero-point energy (ZPE) corrections. For the nitrates the ZPE differences in MP2 and B3LYP do not exceed $0.5 \text{ kcal mol}^{-1}$. Finally, the heat of formation values, ΔH_f , for all species studied were determined using G2MP2, G3//B3LYP and CBS-QB3 computational thermochemistry protocol [39] by following the procedure based on atomization energies, as outlined by Curtiss et al. [40].

All calculations have been carried out with the use of the Gaussian 03 series of programs [41].

Structural and frequency results

The calculated structural results are summarized in Table 1 while the optimized geometries are depicted in Figure 1. The comparison to the corresponding theoretical data for CH_3ONO_2 [32] demonstrates the significant geometrical changes caused upon substitution of the methylic hydrogens by chlorine and fluorine atoms. Comparison is also made with recent experimental and theoretical findings for CF_3ONO_2 [33], which shows a good overall agreement between the present theoretical results and the literature data for the perfluorinated methyl nitrate.

As already said, the comparison of the optimized geometries of the halogenated nitrates to the equilibrium geometry of the plain methyl nitrate shows interesting structural changes that arise from the halogen electron withdrawing effect and which have been suggested to assist among other factors, in the enhancement of the reactivity of the halogenated alkylperoxy radicals towards NO relative to the $\text{CH}_3\text{O}_2+\text{NO}$ system [14]. Indeed, the strong polarization of the X-C bond (X=Cl, F) opposite to H-C, causes the severe tightening of the C-O bond and the large expansion of the O-N bond with parallel implications for the other neighboring bonds. Specifically, a severe reduction is observed in the C-O equilibrium length which decreases from 1.432 Å (1.440 Å) in CH_3ONO_2 to 1.368 Å (1.376 Å) in the perchlorinated species, CCl_3ONO_2 , at the MP2 (B3LYP) level, and similarly in the other halogenated compounds. For CF_3ONO_2 for instance, C-O reduces to 1.367 Å in good agreement with the literature data [33]. On the other hand, the O-N bond distance expands significantly from 1.412 Å (1.422 Å) in CH_3ONO_2 to 1.630 Å (1.563 Å) in CCl_3ONO_2 and such an expansion has been supposed to facilitate the kinetics of the $\text{CCl}_3\text{O}_2+\text{NO}\rightarrow\text{CCl}_3\text{O}+\text{NO}_2$ reaction [14]. Also the bond distances between nitrogen and terminal oxygen atoms decrease substantially, particularly at the MP2 theory level. Thus, the N-O1 and N-O2 bond lengths reduce from 1.206 Å (1.198 Å) and 1.212 Å (1.208 Å) in CH_3ONO_2 to 1.182 Å (1.183 Å) and 1.184 Å (1.187 Å) in CCl_3ONO_2 respectively, and similarly in the other halogenated species.

The angular parameter variations are less pronounced and are mainly due the corresponding bond length differentiations. The only notable changes relate to the O1NO2 bond angle which increases from 130.2° (130.0°) in CH_3ONO_2 to 137.1° (134.0°) in CCl_3ONO_2 and to the NOC angle that changes from 112.8° (113.8°) to 117.5° (120.3°) in the perchlorinated species at the MP2 (B3LYP) level of theory and similarly for the other halogenated nitrates.

Tables 2 and 3 contain the vibrational frequencies of the nitrates under consideration. Again the good agreement with the experimental findings for CH_3ONO_2 [42] and CF_3ONO_2 [33] shows the reliability of our calculations.

Energy results

Table 4 summarizes the reaction energies with respect to dissociation to either RO_2+NO or $\text{RO}+\text{NO}_2$. To the best of our knowledge, there are no other computational studies dealing with the reaction energy of the dissociation process of halogenated methyl nitrates to either RO_2+NO or $\text{RO}+\text{NO}_2$ radicals with the exception of the $\text{CF}_3\text{O}+\text{NO}_2$ system [22].

The comparison of the results among the various methods employed in Table 4, shows that the G2MP2 and the G3//B3LYP calculations give close relative energy values with differences equal or less than 2 kcal mol^{-1} in all cases. The only exception is CH_3ONO_2 where the difference between G2(MP2) and G3//B3LYP becomes $2.9 \text{ kcal mol}^{-1}$. The single-point coupled-cluster CCSD(T) calculations on the other hand, performed at the B3LYP optimized geometries and incorporating either MP2 or B3LYP zero-point energy corrections, present significant deviations in the calculated dissociation energies of the order of $6\text{--}8 \text{ kcal mol}^{-1}$ from the results of G2MP2, G3 methods. We have no clear explanation for these discrepancies. It is true though that relatively large deviations between CCSD(T) and G2, G3 results have been reported in the literature for other systems too. For example, the computational investigation of the HOOCIO adduct at the G2M theory level has located this minimum at $-5.8 \text{ kcal mol}^{-1}$ below the reactants HO_2+ClO [44], while the calculation at the CCSD(T)/6-311+G(3df,3pd) level has produced a negligible dissociation energy of $0.02 \text{ kcal mol}^{-1}$ [45]. It is worth noting that the CCSD(T) reaction energies for CF_3ONO_2 dissociation to $\text{CF}_3\text{O}+\text{NO}_2$ are in better

agreement than the G2MP2, G3 values, with the only other existing theoretical result reported by Caralp et al. [22] computed using the BAC-MP4 method (Table 4).

Regardless of the deviations in the computed relative stabilities among the various methods employed, a clear picture emerges. In all methods the dissociation energies to RO_2+NO or to $\text{RO}+\text{NO}_2$ radicals follow the same tendencies compared to the corresponding CH_3ONO_2 relative energy values, also included in Table 4 for comparison. Specifically, all halogenated nitrate species present more or less similar relative stability values with respect to RO_2+NO , similar to that of methyl nitrate. We can conclude that all nitrates are located at a similar well depth in the potential energy surface of the reaction between methylperoxy radicals and NO, independent of the halogenation. Examination of the dissociation energies to $\text{RO}+\text{NO}_2$ on the other hand, shows that a systematic decrease of the relative stability of the chlorinated nitrates is obtained with respect to $\text{RO}+\text{NO}_2$ radical pair formation, compared to CH_3ONO_2 system in all methods. With the exception of CF_3ONO_2 , the chlorine containing nitrates are less stable than methyl nitrate with respect to the alkoxy radical and nitrogen dioxide, $\text{RO}+\text{NO}_2$. The lower stability parallels the expansion of the O-N bond distance and may be taken to be one the factors that enhance the reactivity of the halogenated peroxy species. The relative energy reduction does not appear as prominent in the CCSD(T) calculations but it is still evident for the chlorinated species. The perfluorinated nitrate presents a similar decomposition energy as the methyl nitrate in both CCSD(T) and G2(MP2), G3 methods, and thus, the higher reactivity in this case must be attributed rather to the critical energy lowering in the $\text{CF}_3\text{O}_2+\text{NO}$ system. The larger dissociation energy of CF_3ONO_2 compared to the chlorinated analogs is consistent with the high stability of this molecule, as can be seen in the heat of formation values.

We may summarize that the halogen electron-withdrawing effect appears to have no influence on the reaction energy of channel (1b). However, the reaction energy for the decomposition process



is affected upon chlorination and may facilitate the kinetics of relevant halogenated systems, leading this way to higher rate constant values for the chlorinated peroxy radical reactions (1), in agreement with the experimental measurements, as we shall see below. Since the perfluorinated species shows similar dissociation energies as the methyl analog and the enhanced kinetics in the case of the $\text{CF}_3\text{O}_2 + \text{NO}$ reaction compared to $\text{CH}_3\text{O}_2 + \text{NO}$ must be obviously attributed to other factors such as the lowering of the critical energies involved. From this point of view, the detailed computational examination of the reaction $\text{CF}_3\text{O}_2 + \text{NO}$ in comparison to the plain methylperoxy+NO reaction may present particular interest.

A realistic idea about the thermodynamic stability of the halogenated methyl nitrates may be obtained from Table 5 which summarizes the calculated heat of formation values and compares with the available literature data. The comparison shows good agreement with the present computational results. Chlorination clearly raises the thermodynamic stability. The striking stabilization however, is observed for the fluorine containing nitrates as it has been observed for other fluorinated species of atmospheric significance.

Summary

The structural, spectroscopic and stability features of the halogenated methyl nitrates are examined using quantum mechanical and density functional methods. Comparison with the plain methyl nitrate characteristics shows the significant effect of the halogen electron withdrawing effect on both the structural and energy data. The most striking result is the considerable reduction of the C-O bond and the parallel expansion of the O-N bond with

immediate consequences for the stability of the chlorinated nitrates with respect to $RO+NO_2$ dissociation. With the exception of CF_3ONO_2 , the halogenation reduces significantly the dissociation energy to CX_3O+NO_2 , $CX_xY_{3-x}O+NO_2$ radical pair formation, compared to the corresponding energy of the plain methyl nitrate and it is suggested to be one of the factors that enhances the reactivity of halogenated methylperoxy radicals towards NO. The dissociation energy to CX_3O_2+NO , $CX_xY_{3-x}O_2+NO$ appears to be constant for all methyl nitrates independent of halogenation.

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Table 1. Equilibrium geometries of halogenated methyl nitrates (Å, degrees)

	CH ₃ ONO ₂	CCl ₃ ONO ₂	CF ₃ ONO ₂	CClF ₂ ONO ₂	CFCl ₂ ONO ₂
R(N-O1) ^a	1.206 1.198	1.182 1.183	1.184 1.181, 1.183 ^b	1.182 1.180	1.182 1.180
R(N-O2)	1.212 1.208	1.184 1.187	1.188 1.187, 1.187 ^b	1.185 1.184	1.184 1.184
R(N-O)	1.412 1.422	1.630 1.563	1.576 1.532, 1.493 ^b	1.619 1.560	1.629 1.562
R(C-O)	1.432 1.440	1.368 1.376	1.367 1.381, 1.397 ^b	1.360 1.374	1.361 1.374
R(C-X1)	1.089 1.089	1.769 1.795	1.327 1.332, 1.321 ^b	1.752 1.779	1.356 1.349
R(C-X2)	1.091 1.090	1.784 1.798	1.335 1.337	1.346 1.344	1.760 1.787
R(C-X3)	1.091 1.090	1.784 1.798	1.335 1.337	1.346 1.344	1.777 1.795
(O1NO2)	130.2 130.0	137.1 134.0	136.0 134.1, 137.2 ^b	136.9 134.5	137.1 134.6
(O2NO)	117.2 117.3	116.1 117.4	116.0 116.8, 115.0 ^b	115.9 116.8	115.9 117.0
(NOC)	112.8 113.8	117.5 120.3	115.0 116.7, 117.0 ^b	114.8 116.6	115.9 117.9
(O-C-X1) ^c	103.2 103.1	103.4 102.8	106.3 105.5	106.7 106.0	105.2 104.3
(O-C-X2)	111.1 111.0	112.3 112.5	112.5 112.4	112.0 112.0	113.5 113.6
(O-C-X3)	111.1 111.0	112.3 112.5	112.5 112.4	112.0 113.0	111.1 111.3
(ONO1O2)	180.0 180.0	180.0 180.0	-180.0 180.0	-180.0 -179.1	-179.3 -179.6
(CONO1)	-180.0 -180.0	-180.0 -180.0	-180.0 -180.0	-179.9 -179.5	-178.3 -179.6
(X1CON)	-180.0 -180.0	-180.0 -180.0	-180.0 -180.0	-180.0 -174.0	-175.7 -174.5
(X2CON)	61.4 61.6	61.8 62.2	60.9 61.4	59.8 54.1	63.1 65.0
(X3CON)	-61.6 -61.6	-61.8 -62.3	-61.0 -61.4	-59.8 -66.4	-58.1 -57.3

^a The first line at each entry gives the MP2 result and the second the B3LYP result,

^b Experimental values from ref. [33], ^c X1 represents the methylic atom located on the CON plane (X1CON~180.0°), while X2, X3 represent the methylic atoms located about 60° on each side of the X1CON plane

Table 2 : B3LYP vibrational frequencies (cm⁻¹) of CX₃ONO₂

Mode Assignment	CH ₃ ONO ₂		CCl ₃ ONO ₂		CF ₃ ONO ₂	
	Harm-Anharm	Exp ^a	Harm-Anharm		Harm-Anharm	Exp ^b
CX ₃ as str	3156-3005	3008	833-814		1224-1197	1265
XCX as str	3136-2991	3008	763-742		1190-1162	1243
CX ₃ s str	3053-2956	2941	409-401		1135-1113	1152
ONO as str	1715-1674	1678	1837-1790		1828-1785	1744
XCX bend	1498-1458	1468	563-552		506-498	518
CX ₃ bend	1458-1425	1430	632-621		737-725	732
CX ₃ twist	1470-1424	1455	388-384		602-593	610
ONO s str	1325-1295	1287	1364-1330		1382-1353	1332
CX ₃ rock	1188-1161	1176	317-313		680-668	693
XCX twist	1164-1142	1136	277-273		423-418	430*
CO str	1014-981	1017	1015-993		918-897	923
ONO bend	863-845	854	767-754		789-777	788
NO ₃ rock	768-754	758	719-706		740-726	747
Molecule bend	661-643	657	247-244		414-407	418
CONO rock	569-555	578	219-216		309-303	332*
Molecule rock ip	336-327	340	145-139		184-176	204*
Molecule rock op	198-161		110-103		107-101	134*
Molecule twist	131-133		55-53		54-52	

^a Ref. [42], ^b Gas phase IR frequencies from Table 1 of Ref. [33] with the * denoted values being Raman results

Table 3 : B3LYP vibrational frequencies (cm^{-1}) of $\text{CX}_x\text{Y}_{3-x}\text{ONO}_2$

Mode Assignment	$\text{CF}_2\text{ClONO}_2$ Harm-Anharm	Mode Assignment	$\text{CFCl}_2\text{ONO}_2$ Harm-Anharm
ONO as str	1836-1792	ONO as str	1837-1791
ONO s str	1378-1345	ONO s str	1369-1339
FCF as str	1130-1102	C-F str	1082-1058
CO str	1117-1090	C-O str	1014-994
CF str	1016-995	CCl str	884-864
CON bend	870-856	CON bend	732-723
ONO bend	777-765	ONO bend	784-688
NO_3 rock	729-716	NO_3 rock	719-705
FCCl as str	606-597	ClCCl a str	503-496
FCF bend	573-561	CF_2Cl twist	569-555
FCCl twist	542-537	FCCl twist	431-442
FCCl bend	422-415	FCCl bend	379-373
Molecule bend	402-399	Molecule bend	346-341
CF_2Cl twist	339-330	CFCl_2 twist	274-270
CONO rock	242-237	CONO rock	228-224
Molecule rock ip	159-154	Molecule rock ip	154-150
Molecule rock op	103-98	Molecule rock op	106-102
Molecule twist	52-48	Molecule twist	52-50

Table 4. Reaction energies, ΔE_r (kcal mol⁻¹), at various levels of theory including ZPE corrections

ΔE_r relative to RO ₂ +NO						
	MP2	B3LYP	CCSD(T)// MP2 ^a	CCSD(T)// B3LYP ^a	G2MP2	G3// B3LYP
CH ₃ ONO ₂	-64.8	-47.7	-47.5	-45.2	-54.9	-53.8
CF ₃ ONO ₂	-66.1	-47.5	-46.8	-44.3	-52.8	-52.7
CCl ₃ ONO ₂	-66.0	-45.6	-45.5	-43.0	-51.5	-51.1
CF ₂ ClONO ₂	-66.8	-47.8	-46.9	-46.4	-52.8	-52.7
CFCl ₂ ONO ₂	-66.8	-46.9	-46.7	-44.2	-52.1	-52.1

ΔE_r relative to RO+ NO ₂							
	MP2	B3LYP	CCSD(T)// MP2 ^a	CCSD(T)// B3LYP ^a	G2MP2	G3// B3LYP	Lit. ^b
CH ₃ ONO ₂	-42.8	-32.0	-35.8	-34.2	-44.3	-41.4	
CF ₃ ONO ₂	-42.9	-30.9	-34.9	-33.1	-41.7	-43.7	-36.5
CCl ₃ ONO ₂	-41.5	-20.5	-30.4	-28.6	-36.6	-34.2	
CF ₂ ClONO ₂	-41.2	-24.3	-32.2	-31.7	-37.7	-36.0	
CFCl ₂ ONO ₂	-40.1	-21.5	-29.9	-28.4	-35.9	-34.1	

^a CCSD(T)//B3LYP energies with ZPE corrections based on the MP2 and B3LYP optimizations, respectively, ^b Ref. [22]

Table 5 . Heat of formation values , ΔH_f^0 (kcal mol⁻¹)

Species	$\Delta H_{f,0}^0$				$\Delta H_{f,298}^0$			
	G2MP2	G3// B3LYP	CBS-QB3	lit.	G2MP2	G3// B3LYP	CBS-QB3	lit.
CH ₃ ONO ₂	-30.7	-26.9	-29.3		-31.5	-27.6	-28.5	-29.2 ^a -28.6 ^b
CF ₃ ONO ₂	-189.9	-181.8	-186.0	-177.7 ^c	-189.4	-181.1	-184.0	-180.5 ^c
CCl ₃ ONO ₂	-41.6	-33.4	-40.0		-40.2	-31.7	-38.9	
CF ₂ ClONO ₂	-138.6	-130.4	-135.4		-137.9	-129.4	-133.0	
CFCl ₂ ONO ₂	-88.8	-80.6	-86.5		-87.8	-79.5	-83.7	

^a Ref. [43], ^b Ref. [5], ^c Ref. [22]

Figure 1

Optimized structures of perhalogenated methyl nitrates at the MP2(B3LYP) levels of theory.

