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Theoretical study of ozone depletion by Halon -1211.

Abbas A-Ali Drea*, and Roaa A-Hussien

Babylon University College of Science Chemistry Department, Hilla – Iraq.

ABSTRACT

Theoretical study has been carried out to investigate the mechanism of Ozone depletion by Halon -1211 (1-bromo 1-chloro 1,1-diflouromethane) that's performed through different calculation methods like semi-empirical method, Ab-initio, and density functional theory. Mean features such as Geometry optimization and single point calculation have been done to understand the configuration interaction singly excited state for all chemical species of the suggested reactions andtheir transition states. Examination of Halon-1211 bonds reactivity have been determined to estimate the responsible bond of initiation cleavage step. They found bond of C-Br is the responsible bond of first initiation cleavage step of photolysis reaction that's produced bromine radicals and other radicals by energy barrier value of 46.954,70.767 kCal/mol . Different radical species (*Br, *Cl, and *F) are librated through the photolysis reaction to deplete ozone species by free radical seriously reactions . The transition state examination of these reaction, indicated that bromine radicals are the most probable species than other radicals to depleted ozone by Halon-1211. The depletion reaction is spontaneous and exothermic with enthalpy change of reaction equal to -353.536kCal mol^{-1}

Keywords: Ozone depletion, Halon-1211, theoretical calculation, transition state, DFT, Ab- intio, and semiemperial.

Corresponding author

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INTRODUCTION

Our live is provided with energy by Sunlight as a main source but some kind of this energy(UV-radiation) is harmful. Ozone layer protect our atmospheric field from harmful radiations that's been reached the troposphere layer, since stratospheric ozone species produced byphotolysis of oxygen molecules at ultraviolet wavelengths below than 242 nm at last with sequence rapid reaction to form ozone species. The usualthickness of the ozone layer in a column of air is $2.687*10^{16}$ ozone molecules per square centimeter . Ozone species are found in two structural forms, the first is bent form and the second is cyclic form, both of them are transform to each other at equilibrium ratio within the time [1].

Due rapid development of industrial technologies formodern Human's requirements, air pollution increased dramatically. Different chemical agents reached higher layers of atmosphere such as Halons that's chemical compounds provided with halogens are necessary of different industrial life purpose. These compounds are anthropogenic and natural in origin result from industries and used as refrigerants and propellants in deodorizers, drug delivery pumps, etc [2, 3].

Halon -1211 compound is a color less gas with density equal to 1.799g/cm^3 ,melting point of -159.5C°, and Boiling Point of -3.7C°. The chemical structure contain bromine atoms and chlorine atoms which is anthropogenic in origin. This Halon don't react with hydroxyl radicals in the troposphere and a large fraction of released amount reaches the stratosphere also due to it is long troposphere lifetime which equal to 16year.It is diffuse into the stratospheric layer ,where under intense UV-radiation they release Bromine radicals and Chlorine radicals which then participates to ozone depletion through the BrO moiety and ClO moiety catalytic cycle, so it is production regulated in developed countries in accordance with the Montreal protocol [4-6]. It was ideal fire suppression agent with high efficiency also continue to be used by military organizations where alternative are not technically or economically practical these uses include the portable extinguishers, accessory power units, flammable liquid, and storage rooms [7, 8].

The application of theoretical and computational principles are practical to study the complexes systems that's out of control for the reaction conditions to be studied experimentally. Calculations of quantum methods helps in investigation and study the reaction mechanism. Quantum chemical calculations can be use to estimate the optimized structure of chemical species such as reactants and products, that result from the photolysis of chemical air pollutants [9].

To suggested reaction mechanism of ozone depletion through photolysis of Halon-1211 in vacuum, interesting with different methods of quantum calculations at present work to investigate the geometry optimization structures of chemical species that's responsible on ozone depletion mechanisms. Different controlling parameters such as Zero point energy, bonds stability examination, characterization of molecular orbital with their energetic gaps, vibration modes, and electrical charges distribution. semiempirical (PM3)method, DFT/B3LYB correlation method and ab-initio with moller –pleset second order perturbation theory respective to different basis sets will be usesfor all resultant species in photolysis reactions.

Computational Details:-

Ab-initio molecular orbital calculation on Halon -1211 where performed at the Hartree fock method (restricted Hartree fouck (RHF)and the method including electron correlation such as the moller-plesset second order (MP2)perturbation theory and the density functional method (DFT)with B3LYB correlation method. These two method performed with small 3-21G(d) and minimal STO-3G basis's set ,geometry optimization was run to find the stationary points at each of these methods [10]. Frequencies of Halon-1211have been calculated by semi-empirical method PM3 for characterization the nature of stationary point and energy values calculations of these compound [11].Highest occupied molecular orbital (HOMO)and lowest unoccupied molecular orbital (LUMO),energy gap(E_g), bond length, charge of atoms are performed with these method. Semi-empirical calculation PM3 method have been used to estimate the bond stability calculation with configuration interaction CI(3*3) singly exited to calculate thermodynamic parameters($\Delta H,\Delta G,\Delta S$)[12] . All calculations are performed with hyperchem version 8.09 program [13].

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RESULTS AND DISCUSSION

Halon-1211 is a synthetic chemical compound that's consisted from two fluorine atoms, chlorine atom, and bromine atom attached to central carbon atom. Figure 1 shown the geometry optimization of Halon-1211 has been calculated to estimate the reactivity and charge distribution around the molecule.

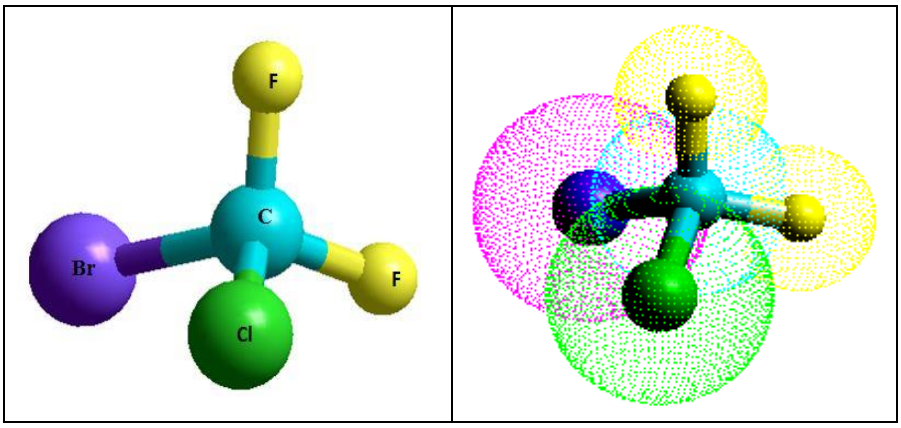

Figure 1: Geometry optimized structure of Halon-1211calculated by DFT3-21G (d)full MP2 level of theory.

Different calculation methods have been used to estimate the chemical structures as represented in table 1.They found positive charge on carbon and bromine atoms and negative charge on fluorine computed by all the method as show in figure 2,also dipole moment calculation for Halon -1211 give lowest value measured by MP2/3-21G(d) which equal to 0.2766 D. Full MP2 method give high value for energy gab calculation than other method equal to 375.4 and 346.23 by STO-3G ,3-21G(d) respectively. The zero point energy values that's calculated by semi-empirical and ab-initio methods give in the range 8.4 and 8.9kCal/mol respectively also all calculation methods give a positive imaginary frequency for the structure of Halon-1211 due its stability at normal conditions(without photolysis conditions).

Table 1: Geometrical properties of Halon-1211 calculated by different calculation methods levels of theory, energetic units calculated by kCal mole^{-1}.

type of calculation	Semiempirical		Ab- initio/MP2		DFT/B3LYB	
	AM1	PM3	STO-3G	3-21G(d)	STO-3G	3-21G(d)
Total energy	-4209.28	-3851.21	-202856.77	-2041338.8	-203073.2	-204333.76
Dipole moment D	0.6238	0.8095	1.3214	0.2766	1.877	0.89
ZPE	8.447	8.68233	8.935	8.925	7.999	7.66
HOMO	-7.71	-6.171	-225.69	-269.79	-132.589	-194.1
LUMO	54.86	47.065	149.71	76.436	25.659	25.666
Energy gap	62.571	53.236	375.4	346.23	158.247	219.766
Imaginary frequency	+	+	+	+	+	+

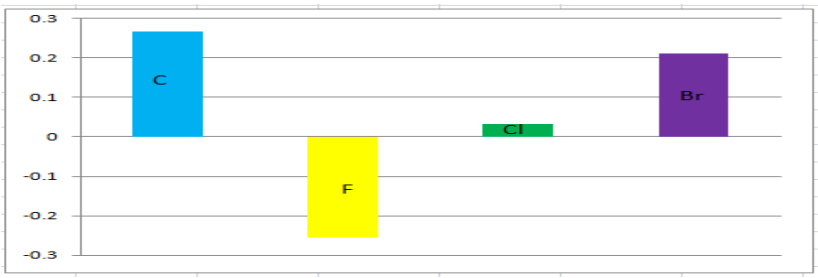

Figure 2: atomic Mullikan charge calculated by DFT/3-21G(d).

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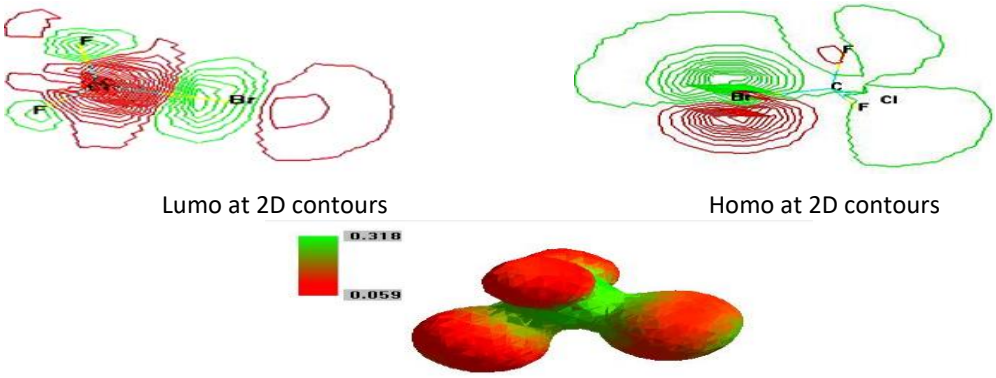
The HOMO (highest occupied molecular orbital) is the orbital that acts as an electron donor (Lewis base) and lumo (lowest unoccupied molecular orbital's is the orbital that acts as the electron acceptor (Lewis acid) [14] , also negative charge densities are noticed by red color and distribute on the fluorine atoms due to the high value of electronegativity and the positive charge densities are remarked by the green color and distribute on the carbon atoms [15] these physical properties shown in figure 3.



Lumo at 2D contours Homo at 2D contours

Electrostatic potential at 3Dmapped isosurface

Figure 3: physical properties of Halon -1211 calculated by DFT /STO-3G.

Vibrational analysis has been calculated at different levels of basis set as shown in table 2. Some of these frequencies have intensity less than 15 km/mol and we are mainly interested in the frequencies with value of intensity higher than 15km/mol units, with highly accuracy value that estimate the real significant values.

Table 2: Vibration frequencies of Halon -1211 calculated by semi-empirical PM3 method, frequencies in cm^{-1} units and intensities in km/mol unit.

Vibration frequencies		intensity	Experimental [16]	Description
V_1	166.72	0.21279	214.5	C-Cl-Br scissor bending
V_2	302.8	0.00064	307	CF_2 twist bending
V_3	398.74	4.0157	408.4	CF_2 rock bending
V_4	409.3	2.511	337.7	CF_2Br differential bending
V_5	430.89	0.7596	443.3	CF_2 scissor bending
V_6	629.58	16.5346	645.1	C-Br symmetric stretching
V_7	748.29	135.235	871.6	C-Cl symmetric stretching
V_8	1419.6	115.1879	1100.2	CF_2 symmetric stretching
V_9	1560.26	68.4263	1151.5	CF_2 anti symmetric stretching

Halon-1211 have four type of bond angle F-C-Br, Cl-C-Br, Cl-C-F, F-C-F which give a value equal to 109.237°,111.812°,108.824°,108.85° measured by MP2/3-21G(d) respectively. The calculated values of bond length (Å) and bond angle are shown in table 3 . The bond length of C-F bond computed by different method give a value equal to 1.3523Å which represent the mean of all value and the DFT/STO-3G method give a value equal to 1.38Å which is reached to the experimental value 1.39 Å ,and the C-Cl bond length give a value equal to 1.85 Å by MP2/STO-3G which is equal to experimental value ,also the PM3 method give a value equal to 1.95 Å for C-Br bond length which is the same value as experimental value [14].

Table 3: Geometrical of bond stability of Halon-1211 calculated by different calculation methods levels of theory

Method of calculation		Semi-empirical		Ab-initio/MP2		DFT/B3LYB	
		AM1	PM3	STO-3G	3-21G(d)	STO-3G	3-21G(d)
	C-F	1.371	1.3375	1.3613	1.304	1.3767	1.3631

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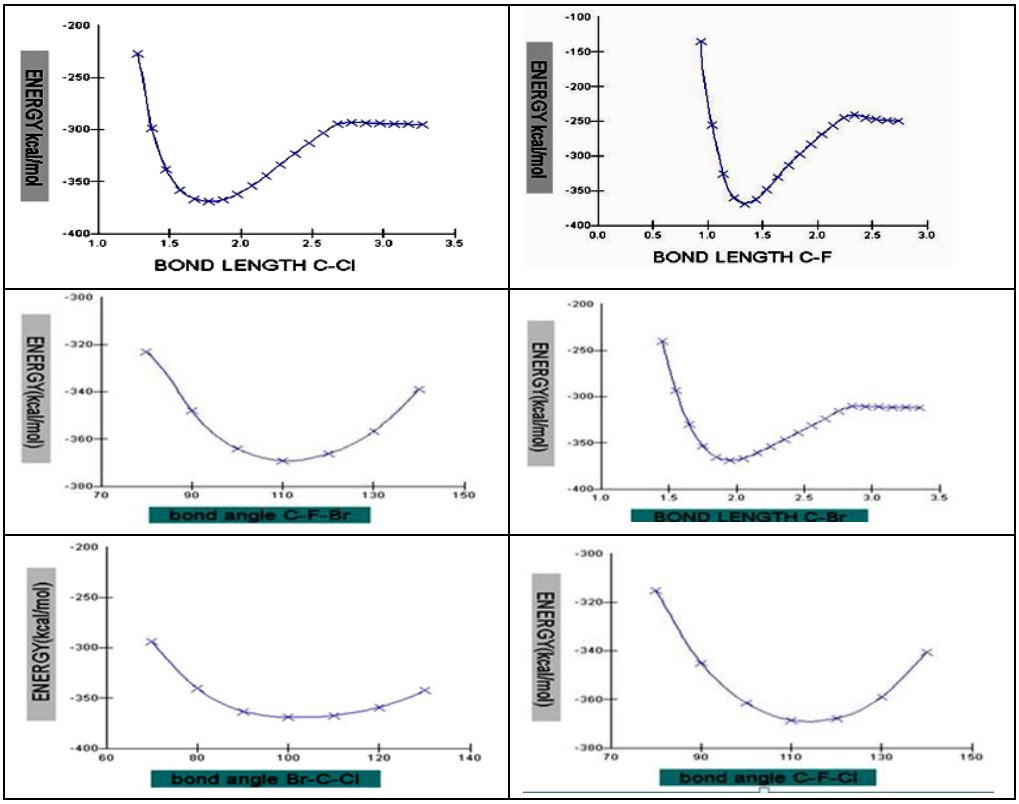
Bond length Å	C-Cl	1.8065	1.776	1.852	1.7402	1.9296	1.821
	C-Br	2.0242	1.9518	1.939	1.9221	1.9957	1.8756
Bondangle degree	F-C-Br	113.30	101.88	110.79	109.237	111.63	110.776
	Cl-C-Br	105.31	110.68	111.08	111.812	109.875	112.104
	Cl-C-F	111.64	114.02	107.88	108.824	107.464	107.492
	F-C-F	101.87	105.66	108.28	108.858	109.588	107.454

The bond stability have been computed by using potential energy measurement [13] of three bonds C-F,C-Br, and C-Cl, they found C-Br bond is more active toward photolysis reaction. Bond length and dissociation energy values 1.952Å and 58.0284kCal mol^{-1} of C-Br bondare comparable with other bonds like C-Cl bond and C-F bond that's are broken down at 76.254 and 112.99 kCal mol^{-1} respectively . The calculated energetic values are matched to the experimental values [17], as shown in table 4 & figure 4.Previous investigation refers that C-Br bond is more favorable toward the photolysis reaction than other bonds due to the C-Br bond have lowest value of dissociation energy.

Table 4: potential energy stability of Halon-1211 bonds, computed by PM3/Cl(3*3).

BondType	Equilibrium energy	Length Å	Breaking energy *	Dissociation energy *
C-F	-359.9899	1.394	-246.9984	112.99
C-Cl	-369.2163	1.776	-292.9623	76.254
C-Br	-369.216	1.952	-311.1875	58.0284

* energetic values in kCal mol^{-1} unit.



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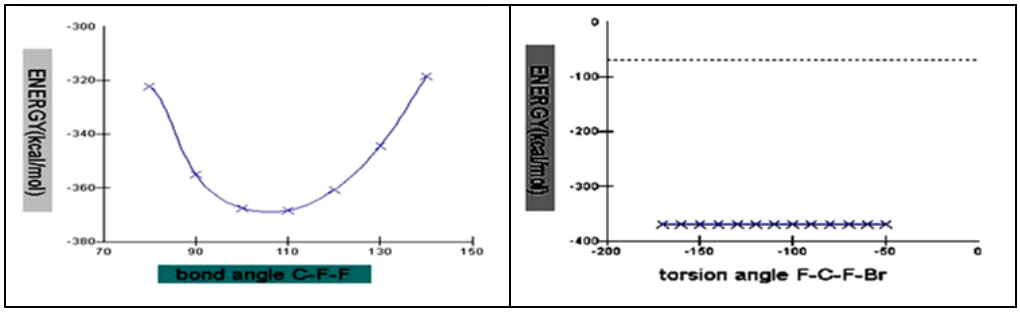

Figure 4: potential energy search of bonds stability of Halon-1211 computed by PM3/Cl(3*3).

According to the potential energy calculation of the bonds, the photo dissociation of Halon-1211 by UV-radiation in stratospheric layer occurs in three pathway The first pathway involves the C-F bond dissociation, the second pathway is the C-Br bond dissociation and the last third pathway is C-Cl bond dissociation. Figure 5, Show these three pathways that's calculated at different method to investigate the most probable pathway in photolysis reaction according to transition state search calculations.

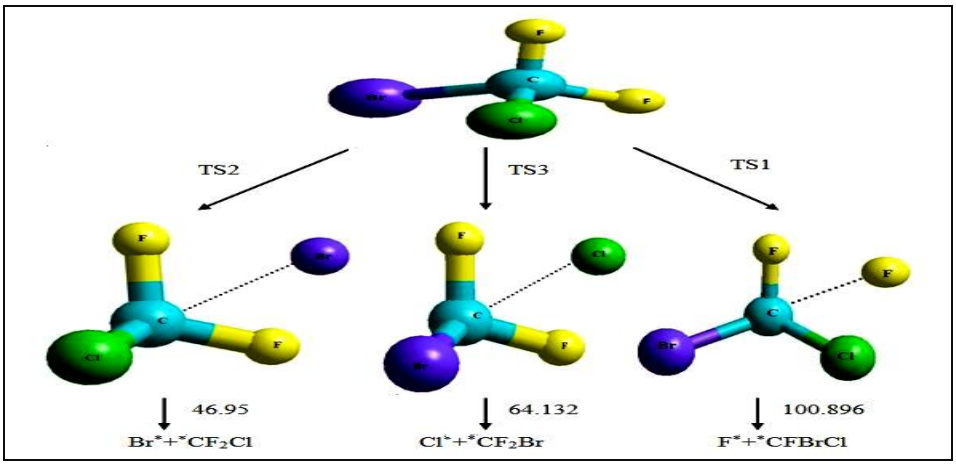

Figure 5: The most probable pathway of photolysis reaction according to transition state search of Halon-1211.

Table 5, represented that the transition state two(TS2) is the real transition state due to lowest value of energy barrier of reaction 46.954,70.767kCal mol^{-1} through the examining methods of semiempirical/PM3,and DFT/STO-3Grespectively. Also lowest value of heat of formation and total energy by the same both methods. The C-Br bond is more favorable toward the photolysis reaction than other bonds due to the C-Br bond has the lowest value of the dissociation energy so the initiation steps of photodissociation reaction of Halon-1211 occurs through the fission of weakest bond C-Br with a quantum yield equal to ≥ 0.78 , This reaction occurs in competition with the fission of the stronger C-Cl bond [18, 19].

Table 5: Transition state search of photodissocation of Halon- 1211 computed at different method.

Type of calculation	Semiempirical/PM3			DFT/STO-3G		
	TS1	TS2	TS3	TS1	TS2	TS3
Total energy *	-38411.19	-38465.133	-38447.96	-2030596.1	-2030650.97	-2030613.9
Binding energy*	-268.319	-322.262	-305.0842	-	-	-
Heat of formation*	-3.91997	-57.8622	-40.6842	-	-	-
Energy Barrier*	100.8964	46.954	64.132	125.617	70.767	107.756
Enthalpy reaction change*	101.134	49.749	69.449	-	-	-

*Energetic values in kCal mol^{-1}.

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Chemical species that's involved in the photodissocation reaction have been optimized as shown in table 6. To get on the most probable reaction pathway than other probabilities. The resulting free radical from Halon-1211 photolysis reaction bromine, which is the most probable radical in competition with chlorine and the other free radical contributing to ozone depletion, These radical participate in three principal reaction cycles that destroy ozone. The importance of bromine and its chemistry in the atmosphere is receiving renewed interest based on the ability of bromine is almost 100 times more destructive to stratospheric ozone than chlorine atoms[1].Bromine radical reacts with ozone through the BrO cycle ,table 7 shows the energetic and thermodynamic values for bromine radical with ozone molecule . The results show that the reaction is exothermic and spontaneous due to $\Delta E_r<0$, $\Delta H_r< 0$, $\Delta G_r< 0$ and $\Delta S_r> 0$ that mean the reaction to the products is possible , according to thermodynamic aspect [10, 20]. From the literature , they found the change in heat of formation for reaction $Br^{\cdot} + O_3 \rightarrow BrO + O_2$ equal to ΔHr = -32.2 kCal mol^{-1} at 298.15 K [21],and the value measured in this study equal to -38.122 which is reached the experimental value.

Table 6. Geometry optimization of chemical species result in photolysis of Halon -1211calculated at DFT /B3LYP 6-311G(d) & PM3 method .

Chemical species#	Total energy	Binding energy	Heat of formation	Homo*	Lumo*	E_g*	symmetry	ZPE
F·	-54717.693	-0.003897	18.886	-	-	-	-	-
Cl·	-288717.694	0.00119	28.991	-	-	-	-	-
Br·	-1615181.171	0.002375	26.7423	-	-	-	-	-
CF_2Br·	-1764360.297	-299.768	-64.358	-7.07	-0.894	6.18	CS	5.63
CF_2Cl·	-437906.773	-319.4693	-81.809	-14.18	-3.207	10.97	C_1	6.05
CFBrCl·	-1990461.079	-268.078	-22.5679	-10.11	-3.1	7.01	C_1	4.77

#Energy values in kCal mol^{-1},*The values in ev unit.

Table 7: Thermodynamic functions of the reaction $Br^{\cdot}+O_3$ computed at PM3/Cl(3*3).

Thermodynamic# change	Br	O_3	BrO	O_2	$_{REACTION}\Delta$
Total energy*	-1607520.151	-140600.7	-1654423.96	-93781.122	-84.231
Heat of formation	26.7424	31.4	15.6	4.6	-38
Free energy	-14655	-20157	-83	-134703	-38.557
entropy	0.0385	0.05688	0.0527	0.0466	0.00392

#Energy values in kCal mol^{-1} unit.*E_{Total} computed by DFT/B3LYP /3-21G(d).

Chlorine radical is reacted with ozone through the ClO cycle, table 8 show the energetic values that's related with ozone depletion by Chlorine radicals. The reaction is exothermic and spontaneous as the reaction of bromine radicals, since it give up a negative value for ΔE,ΔG, and ΔH. The experimental activation energy for this reaction is ranged from 0.34 into 0.83kcalmol^{-1} [22].It was also found that $\cdot CF_2$(di- floro methyl radical) was formed under photolysis conditions by Halon-1211, was attributed to secondary photolysis of the $\cdot CF_2Br$,$\cdot CF_2Cl$ radicals because it possess sufficient internal energy to overcome through a respective activation barrier to give the product [19] , or its result from the primary photodissociation of Halon-1211 with $\Phi \approx 0.013$.Table 9 show the energetic properties of CF_2whith O_3 reaction. They found the reaction is exothermic with large value of heat formation compared with the bromine &chlorine reaction with ozone, also is the same phenomena of negative value for entropy &free energy .

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Table 8: Thermodynamic functions of ozone depletion reaction through chlorine radicals computed by PM3/Cl (3*3) method.

Thermodynamic change#	Cl	O_3	ClO	O_2	$\Delta_{reaction}$
Total energy *	-287368.313	-140600.7	-334275.93	-93781.122	-88.039
Heat of formation	28.9912	31.4	12.453	4.6	-43.338
Free energy	-7280.32	-20157	-14034	-134703	-44.778
entropy	0.04289	0.05688	0.058	0.0466	0.00483

#Energy values in kCal mol^{-1} unit.*E_{Total} computed by DFT/B3LYP /3-21G(d).

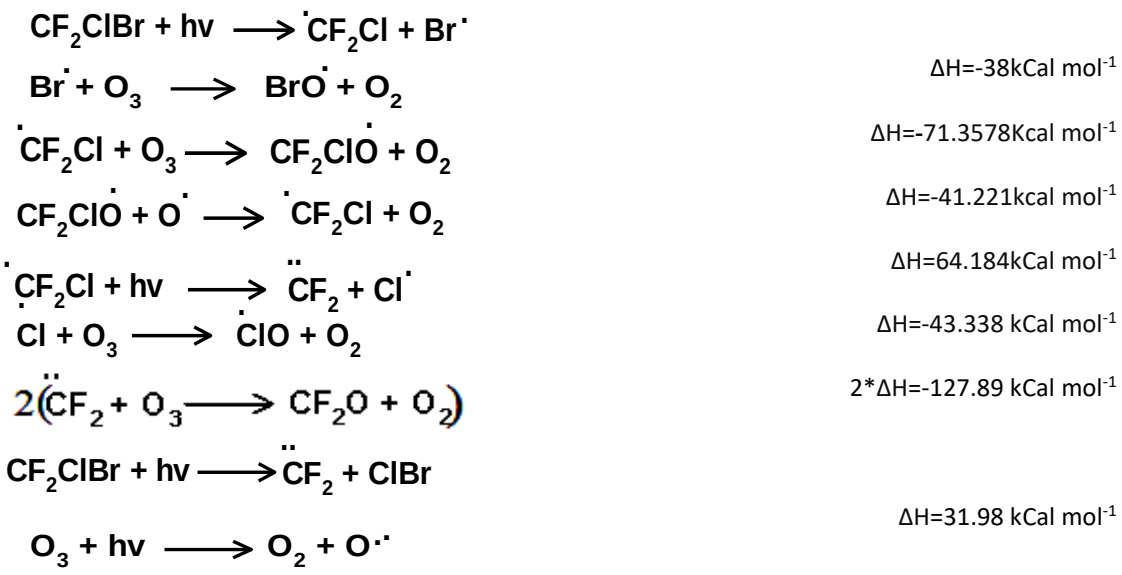
Table 9: Thermodynamic function for the reaction CF_2+O_3 computed by PM3/Cl (4*4) method.

Thermodynamic change#	CF_2	O_3	CF_2O	O_2	**$\Delta_{reaction}$**
Total energy*	-148337.03	-140600.7	-195349.983	-93781.122	**-193.375**
Heat of formation	-49.1193	31.4	-150.21	4.6	**127.89-**
Free energy	-23012	-20157	-29834	-134703	**-126.667**
entropy	0.0575	0.05688	0.0637	0.0466	**-0.0041**

#Energy values in kCal mol^{-1} unit.*E_{Total} computed by DFT/B3LYP /3-21G(d).

The photolysis of Halon-1211 under atmospheric conditions will form $\cdot CF_2Cl$ (di-floro chloro methyl radical) and $Br\cdot$ radicals. The CF_2Cl radical undergoes secondary decomposition depends upon the energy light of photolysis to give up CF_2 and Cl radical. The reaction mechanism of ozone depletion began with these radical, where CF_2Cl radical react with ozone to form CF_2ClO with enthalpy of reaction change equal to -71.3578, ΔG=-69.6, and ΔS=-0.00588kCalmol^{-1} with high value of the rate constant $1.081*10^{40}$ s^{-1}.At last CF_2ClO react with atomic oxygen atom that available in the media of reaction to give CF_2Cl radical again with ΔH=-41.22,ΔG=-53.8476, and ΔS=0.04235 kCal mol^{-1}.

The CF_2Cl radical undergo secondary decomposition to give Cl and CF_2 radical ,these radicals contribute to ozone depletion through ClO &CF_2O cycle. The net heat formation of photolysis reaction of Halon-1211 equal to -353.536 kCal mol^{-1}. Schem 1. Show the mechanism of ozone depletion by Halon-1211.



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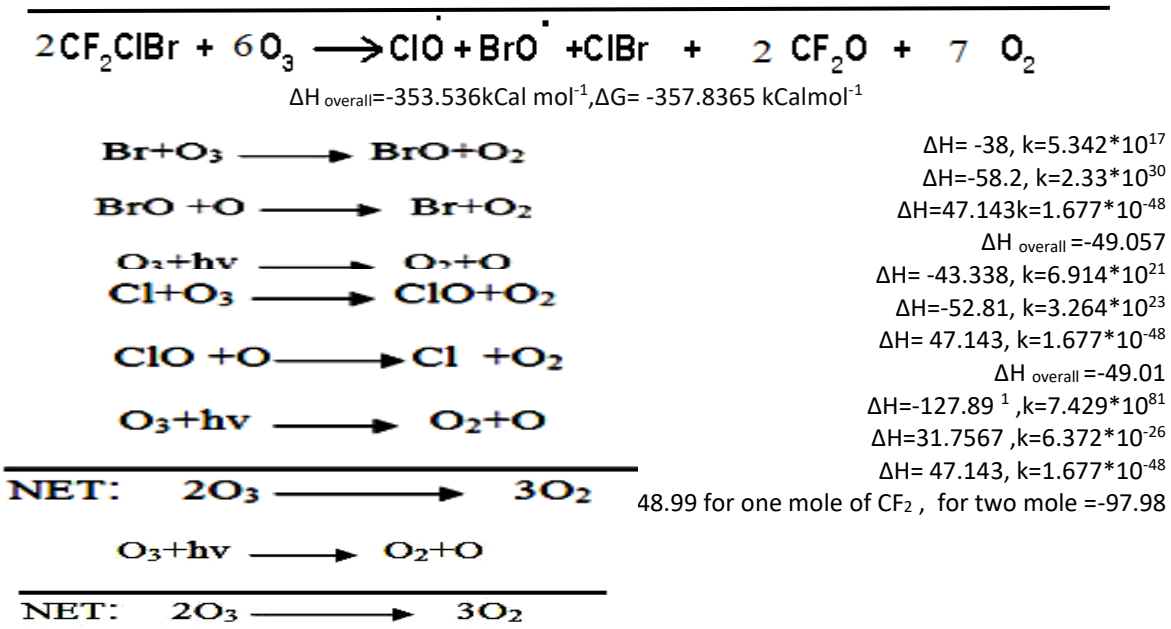

Scheme 1: Mechanism of ozon deepletion through photolysis of Halon-1211, computed by PM3 method, enthalpy change in kCal mol^{-1},rate constant in s^{-1} unit.

CONCLUSION

- Depletion of ozone in the stratospheric layer occurs in the presence of Halon-1211 through photolysis of C-Br bond byenergy barrier equal to 46.954 kcalmol^{-1} in competition with C-Cl bond by energy barrier equal to64.132 kcalmol^{-1} .
- The reaction of bromine radical with ozone is spontaneous and exothermic with ΔH=-38.122,ΔG=-38.557kCalmol^{-1}, the same thing for Chlorine radical with ΔH=-43.338,ΔG=-44.778 kCal mol^{-1}.
- The reaction of CF_2 radical with ozone is spontaneous and exothermic has ΔH=-127.89,ΔG=-126.667kCal mol^{-1} and negative value of ΔS=-0.0041kCal mol^{-1} .
- Halon-1211 is photolysis in stratospheric layer to give up radicals as in following equation :- $2CF_2ClBr+6O_3+ hv \rightarrow BrO +ClO+ 2CF_2O+ ClBr +7O_2$with ΔH value equal to -353.536kCal mol^{-1}.

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