Bond Dissociation Energies of CF_3-X Bonds (X = C, O, N, S, Br): Ab Initio Molecular Orbital Calculation and Application to Evaluation of Fire Suppression Ability

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The C−X (X = C, O, N, S, Br) bond dissociation enthalpies (BDEs) of perfluoroalkanes, perfluoroethers, perfluorotrimethylamine, perfluorodimethyl sulfide, and trifluoromethyl bromide were evaluated by the G2, G2MP2, and G2MS methods. Perfluoroethers had high BDEs of the C−O bond because of the strong negative hyperconjugation between the CF_3 group and lone pair orbitals of oxygen. The BDEs of CF_3−X bonds could be used as an index of the fire suppression ability.

Introduction

Halons are perfluorinated carbons containing one or two bromine atoms such as CF_3Br (Halon 1301), CF_2BrCl (Halon 1211), and CF_2BrCF_2Br (Halon 2402). They were ideal fire suppression agents with high efficiency, low toxicity, cleanliness, and low electrical conductivity until the appearance of the ozone depletion problem. Conventional fire fighting agents, such as water and carbon dioxide, suppress the fire only by a physical action, i.e., cooling and dilution. Chemical suppression by removing the free radicals from the combustion zone plays an important role in halon fire extinguishings.[1,2] Hydrogen atoms and hydroxyl radicals are considered to be the main active species in the combustion reaction. Bromine atoms from halons convert them to relatively unreactive H_2 or H_2O molecules by the following reactions:

$$Br^\bullet + H^\bullet + M \rightarrow HBr + M^*$$

$$HBr + H^\bullet \rightarrow H_2 + Br^\bullet$$

$$HBr + OH^\bullet \rightarrow H_2O + Br^\bullet$$

The high efficiency of halon fire extinguishers is well explained by this established suppression mechanism. Halons' use is, however, regulated because they are harmful to stratospheric ozone.

Bromine-containing compounds cannot be used as halon replacements in view of the ozone depletion problem, whereas non-bromine-containing compounds are not expected to have high fire suppression efficiency because of the lack of the chemical fire suppression played by bromine atoms. The dilemma caused by the dual bromine actions makes it difficult to develop a halon alternative. We found, however, that several perfluoroalkylamines having no bromine atom showed a good fire extinguishing ability.[3,4] We have proposed a new fire suppression mechanism for such non-bromine-containing perfluoroalkylamines in which the trifluoromethyl radical mimics the fire extinguishing role played by the bromine atom.[5] Because the $CF_3^\bullet$ has no potential to deplete ozone,[6] our proposed idea of using the $CF_3^\bullet$ instead of $Br^\bullet$ could be a new strategic guideline for the development of new halon replacements.

According to the $CF_3^\bullet$-mediated fire suppression mechanism, the compounds easily to release $CF_3^\bullet$ could be good candidates for halon replacements. We describe here the bond dissociation enthalpies of the CF_3−X bond (X = O, N, S) to estimate $CF_3^\bullet$-releasing abilities.

Computational Methods

Calculations were carried out by using the Gaussian 98 suite of programs.[7] All geometries were fully optimized at the MP2-(Full)/6-31G(d) levels. The zero-point energies and the thermal energy corrections were calculated at the HF/6-31G(d) level and scaled by 0.8929. The G2[8] and G2MP2[9] methods were used for the single-point energy calculations because they yield far better agreement with experimental values.[5b,c] The G2MS method[10] was also used because we could not calculate some species by the G2 or G2MP2 method because of the limitation of the computational resources. We included the high level correction (HLC) term of G2MS as defined in ref 10b.

Results and Discussion

The bond dissociation enthalpies (BDEs) of perfluoroalkanes, perfluoroethers, perfluorotrimethylamine, perfluorodimethyl sulfide, and trifluoromethyl bromide are listed in Table 1 with those of hydrocarbon analogues. The available experimental data are also included in the table.[11] The BDEs calculated by the G2 method showed good agreement with the experimental values almost within the experimental uncertainty. The results obtained by the G2MP2 method were similar to the ones obtained by the G2 method within 0.9 kcal/mol. Though the G2MS method was the least expensive among the methods we used, the BDEs calculated by the G2MS method were comparable to those by the G2 and G2MP2 methods.

Perfluorinations of ethers remarkably increased the BDEs; that is, the calculated BDEs of CF_3−OCF_3 and CF_3−OC_2F_5 were 24 and 23 kcal/mol higher than those of CH_3−OCH_3 and CH_3−OC_2H_5, respectively. These surprisingly high BDEs of these ether bonds could be explained by the negative hyperconjugation effect of the CF_3 group.[12] The CF_3 group acts as a

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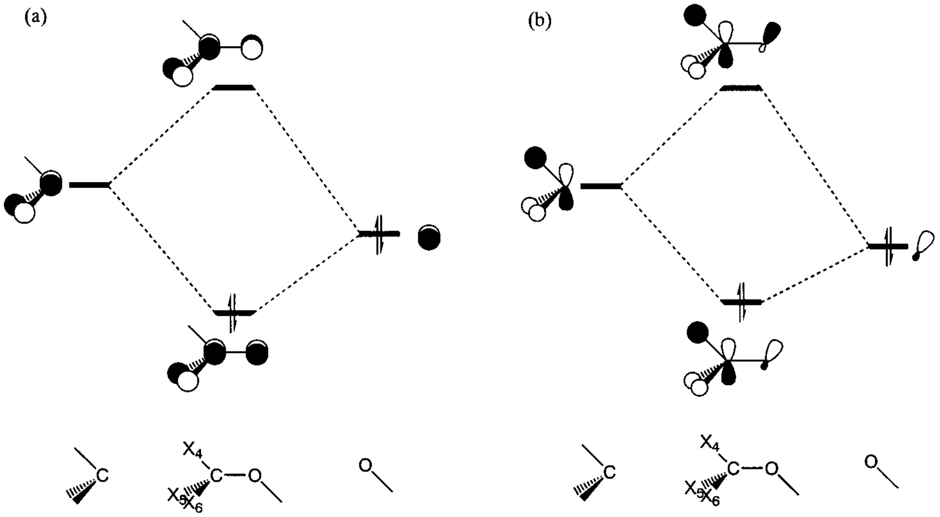


Figure 1. Orbital interactions between π^* of methyl group and lone pairs of oxygen.

TABLE 1: Bond Dissociation Enthalpies at 298.15 K (in kcal/mol)

bond	G2	G2MP2	G2MS	expl.
$CH_3-n\text{-}C_3H_7$	91.3	91.5	92.3	
$C_2H_5-C_2H_5$	90.3	90.6	91.2	
$CF_3-n\text{-}C_3F_7$	$-^a$	97.0	97.2	
$C_2F_5-C_2F_5$	$-^a$	94.4	94.7	
$CF_3-CHFCF_3$	$-^a$	97.8	98.0	
CH_3-OCH_3	85.9	86.8	86.4	83.1^c
$CH_3-OC_2H_5$	86.8	87.6	87.3	82.5^c
$CH_3O-C_2H_5$	88.7	89.6	89.3	84.2^c
CH_3-OCF_3	99.2	99.8	99.5	
CF_3-OCF_3	110.2	110.5	110.3	
CF_3-OCH_3	108.8	109.3	109.1	
$CF_3-OC_2F_5$	$-^a$	109.9	109.8	
$CF_3O-C_2F_5$	$-^a$	108.1	108.1	
$CH_3-N(CH_3)_2$	80.8	81.4	83.2	75.3^c
$CF_3-N(CF_3)_2$	$-^a$	$-^a$	99.8	
CH_3-SCH_3	73.2	74.1	74.7	73.6 ± 0.8^b
CF_3-SCF_3	$-^a$	$-^a$	78.4	
CH_3-Br	73.6	74.0	73.8	70.0 ± 1.2^b
CF_3-Br	74.8	75.1	74.8	70.6 ± 3.1^b

[a] Could not be calculated. [b] Reference 11. [c] Calculated from the heats of formation tabulated in ref 11.

π acceptor and stabilizes an adjacent bond by interacting with two sets of lone pairs of oxygen (Figure 1). One of the lone pairs, normal to the COC plane, is essentially pure p in character and can interact strongly with CF_3 (Figure 1a).[12d]

It is well-known that the negative hyperconjugation affects the geometry such as bond lengths.[13] When the orbital interaction like that in Figure 1a occurs, the out-of-plane $C-X_5$ and $C-X_6$ bonds lengthen. On the other hand, the orbital interaction like that in Figure 1b shorten the in-plane $C-X_4$ bond. Both interactions shorten the C−O bond.

Figure 2 shows the optimized geometry at MP2(Full)/6-31G(d). The gas-phase experimental values of the C−O and C−N bond lengths were also shown in square brackets.[14] In dimethyl ether, which has C_{2v} symmetry, the two out-of-plane C−H bonds, C(1)−H(5) and C(1)−H(6) in Figure 2a, were lengthened 0.009 Å compared to the in-plane C−H bond, C(1)−H(4). In the case of perfluorodimethyl ether, though the symmetry was broken because of the repulsion of F(6)−F(9) and F(5)−F(7), a similar trend appeared; that is, the C(1)−F(5) and C(1)−F(6) bonds were lengthened compared to the C(1)−F(4) bond, 0.011 and 0.009 Å, respectively. These geometry changes are consistent with those expected by the negative hyperconjugation effect.

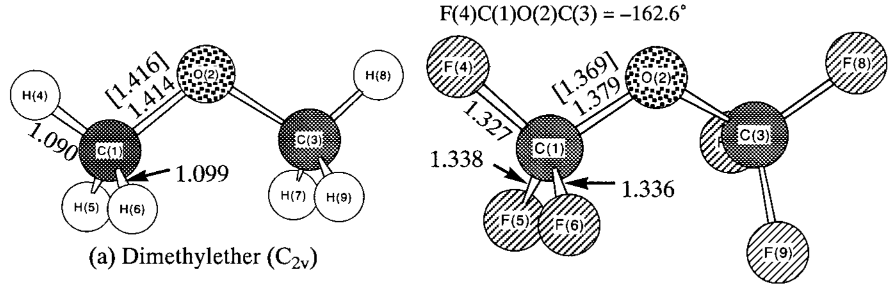
The most striking difference found in the geometry between dimethyl ether and perfluorodimethyl ether was on the C−O bond length, thus, that of the latter (1.379 Å) was 0.035 Å shorter than that of the former (1.414 Å). The remarkable bond shortening is quite consistent with the experiment; that is, the C−O bond of perfluorodimethyl ether in the gas-phase experiment (1.369 Å) was 0.047 Å shorter than that of dimethyl ether (1.416 Å).[14] The low-lying π^* orbital of the CF_3 group could more strongly interact with lone pair orbitals of oxygen compared with the case of the CH_3 group. This is the reason for the short C−O bond in perfluorodimethyl ether.

Trifluoromethyl methyl ether has two types of the C−O bonds. The BDE of CF_3-OCH_3 was almost the same as that of CF_3-OCF_3, 110 kcal/mol, whereas the CH_3-OCF_3 was strengthened 13 kcal/mol compared with the CH_3-OCH_3 bond. It is well-known that the CF_3 group has β stabilization influence.[12d,15] The CH_3-O bond strengthening in trifluoromethyl methyl ether could be caused by the β stabilization effect of the CF_3 group. The β stabilization effect, 13 kcal/mol, was smaller than the α one, 23 kcal/mol.

Perfluorination of trimethylamine increased the BDE about 17 kcal/mol, which was smaller than that for ethers, 23−24 kcal/mol. Trimethylamine has only one lone pair, and the lone pair is not pure p in character because trimethylamine has a pyramidal structure (Figure 3). Therefore, negative hyperconjugation of the CF_3 group is less effective in the bond stabilization of trimethylamine compared with that of ethers.

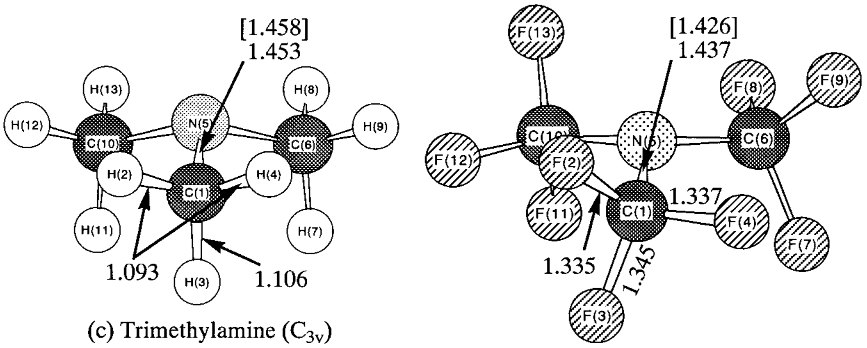
The effect of negative hyperconjugation on methyl C−H bond lengths was also found in trimethylamine. When the orbital interaction like that in Figure 3 occurs, lengthening of the $C-X_3$ and shortening of the C−N bond are expected. The C−H bond located at the trans position with respect to the lone pair of nitrogen, C(1)−H(3) in Figure 2c, was lengthened 0.013 Å compared to the other C−H bonds, C(1)−H(2) and C(1)−H(4). In the case of perfluorotrimethylamine, the symmetry was broken again, a similar trend appeared; that is, the C(1)−F(3) bond was lengthened compared to the C(1)−F(2) and C(1)−F(4) bonds, 0.010 and 0.008 Å, respectively. The C−N bond length of perfluorotrimethylamine was 0.016 Å shorter than that of trimethylamine because of the strong interaction between the lone pair of nitrogen and the CF_3 group compared with the CH_3 group.

The bond stabilizing effect on the fluorination of dimethyl sulfide and methyl bromide were very small: 4 and 1 kcal/mol, respectively. The negative hyperconjugation effect in these



(a) Dimethylether (C_{2v})

(b) Perfluorodimethylether (C_2)



(c) Trimethylamine (C_{3v})

(d) Perfluorotrimethylamine (C_3)

Figure 2. Optimized geometries at MP2(Full)/6-31G(d). The experimental values are shown in brackets.

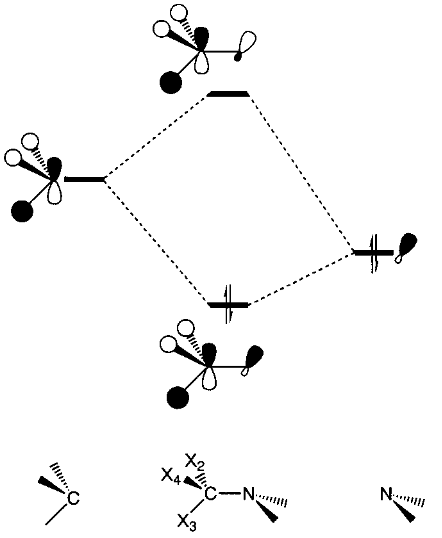


Figure 3. Orbital interactions between π^* of methyl group and a lone pair of nitrogen.

compounds could be small, because the interaction between the CF_3 group and the lone pair on the second- or third-row atom are weak compared with that on the first-row atom.[16]

We found that perfluoroethers exhibited a poor fire extinguishing ability compared with perfluoroalkylamines and perfluoroalkanes.[17] According to the $CF_3^{\bullet}$-mediated fire suppression mechanism,[5] the releasing capability of $CF_3^{\bullet}$ directly affects the fire extinguishing ability. The high bond dissociation enthalpies of the CF_3-O bonds of perfluoroethers, 105−110 kcal/mol, could be a reason for their poor extinguishing ability. Figure 4 shows the relationship between the experimental fire extinguishing concentration[17] and the BDE calculated by the G2MS method. The BDEs of CF_3-X bonds could be used as an index of the fire suppression ability, because they had a good linear relationship with the extinguishing concentration. From Figure 4, perfluorodimethyl sulfide, which has a BDE of 78 kcal/mol, is expected to have an extinguishing concentration of 3.8%. The

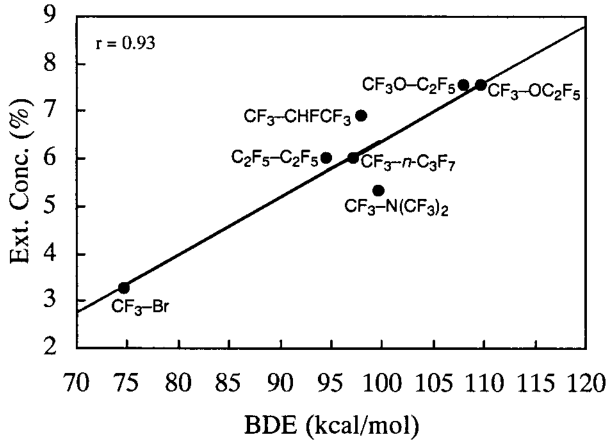


Figure 4. Relationship between the fire extinguishing concentration (%) and the bond dissociation enthalpy calculated by the G2MS method (kcal/mol). The extinguishing concentration were taken from ref 17.

extinguishing concentration of 3.8% is comparable to that of Halon 1301, which was the most widely used halon. Because perfluorodimethyl sulfide has no bromine atom harmful to stratospheric ozone, it could be one of the most promising candidate for a new halon replacement. Thus, the CF_3-X bond dissociation enthalpies could be used as an index of the fire extinguishing ability, and they are helpful in developing new halon replacements.

Conclusions

The G2MS method, which was less expensive than the G2 and G2MP2 methods, was reliable for predicting BDEs of the CH_3-X and CF_3-X bonds (X = O, N, S) as well as the G2 and G2MP2 methods. The C−O bond of perfluorodimethyl ether had a high BDE because of the strong negative hyperconjugation between the CF_3 group and lone pair orbitals of oxygen, and it could be a reason for the low fire extinguishing ability of perfluorodimethyl ether compared with those of perfluoroalkylamines and perfluoroalkanes. On the basis of the bond dissociation enthalpy, perfluorodimethyl sulfide should be a good candidate for a new halon replacement.

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References and Notes

(1) Rosser, W. A.; Wise, H.; Miller, J. *Symp. (Int.) Combust.*, [*Proc.*], *7th* **1959**, 175.

(2) Westbrook, C. K. *Symp. (Int.) Combust.*, [*Proc.*], *19th* **1982**, 127.

(3) Fukaya, H.; Hayashi, E.; Hayakawa, Y.; Baba, H.; Taoda, H.; Osaki, T.; Abe, T. *J. Environ. Chem.* **1993**, *3*, 271.

(4) (a) Takahashi, K.; Sekiuji, Y.; Inomata, T.; Abe, T.; Fukaya, H.; Hayashi, E.; Inoue, G. *Combust. Sci. Technol.* **1995**, *102*, 213. (b) Takahashi, K.; Inomata, T.; Abe, T.; Fukaya, H.; Hayashi, E.; Ono, T. *Combust. Sci. Technol.* **1998**, *131*, 187.

(5) (a) Fukaya, H.; Ono, T.; Abe, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1207. (b) Fukaya, H.; Ono, T.; Abe, T. *J. Comput. Chem.* **1998**, *19*, 277. (c) Fukaya, H.; Ono, T.; Abe, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 207.

(6) Ravishankara, A. R.; Turnipseed, A. A.; Jensen, N. R.; Barone, S.; Mills, M.; Howard, C. J.; Solomon, S. *Science*, **1994**, *263*, 71.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(9) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(10) (a) Froese, R. D. J.; Humbel, S.; Morokuma, K. *J. Phys. Chem. A* **1997**, *101*, 227. (b) Grandinetti, F.; Cecchi, P.; Vinciguerra, V. *Chem. Phys. Lett.* **1997**, *281*, 431.

(11) *CRC Handbook of Chemistry and Physics*, 74th ed; Lide, D. R., Ed.; CRC Press: Boca Raton, 1994.

(12) (a) Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221. (b) David, S.; Eisenstein, O.; Hehre, W. J.; Salem, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 3806. (c) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141. (d) Schneider, W. F.; Nance, B. I.; Wallington, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 478.

(13) Pross, A.; Radom, L.; Riggs, N. V. *J. Am. Chem. Soc.* **1980**, *102*, 2253.

(14) Oberhammer, H. *J. Fluorine Chem.* **1983**, *23*, 147.

(15) (a) Descamps, B.; Forst, W. *J. Phys. Chem.* **1976**, *80*, 933. (b) McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Schneider, W. F.; Wallington, T. J. *J. Phys. Chem.* **1993**, *97*, 12783.

(16) Magnusson, E. *J. Am. Chem. Soc.* **1986**, *108*, 11.

(17) Fukaya, H.; Hayashi, E.; Abe, T. *J. Fluorine Chem.* **2000**, *106*, 143.