J. Phys. Chem. A **2000,** *104,* 10713−10720

O−O Bond Dissociation Enthalpy in Di(trifluoromethyl) Peroxide (CF_3OOCF_3) as Determined by Very Low Pressure Pyrolysis. Density Functional Theory Computations on O−O and O−H Bonds in (Fluorinated) Derivatives

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Received: December 17, 1999; In Final Form: July 31, 2000

The thermal decomposition of di(trifluoromethyl) peroxide (between 575 and 900 K) and di-*tert*-butyl peroxide (between 425 and 650 K) has been investigated by means of a very low pressure pyrolysis method. The Arrhenius equations for homolytic oxygen−oxygen bond rupture obey $\log(k_1/\mathrm{s}^{-1}) = 15.30 - 45.0$ kcal mol^{-1}/2.303RT for $CF_3O{-}OCF_3$ and $\log(k_2/\mathrm{s}^{-1}) = 15.30 - 37.4$ kcal mol^{-1}/2.303RT for $Me_3CO{-}OCMe_3$. The oxygen−oxygen bond dissociation enthalpies, BDE(O−O), at 298 K for the peroxides are derived to be 47.5 ± 0.5 ($CF_3O{-}OCF_3$) and 38.9 ± 0.5 kcal mol^{-1} ($Me_3CO{-}OCMe_3$). Various density functional theory calculations have been utilized to compute the BDEs for XO−H, XO−OH, and XO−OX, with X = H, CF_3, and Me_3C. Expansion of the basis set and the application of the restricted open-shell (RO) formalism for the radical species affords better agreement with experimental values. Using isodesmic reactions, a convergence is obtained for the BDE(O−H) in trifluoromethanol ($CF_3O{-}H$) toward 118.8 ± 0.5 kcal mol^{-1}. Reevaluation of literature thermokinetic data leads to BDE($F{-}CF_2O^\bullet$) of 27 ± 1, and BDE($CF_3O{-}F$) of 48 ± 1 kcal mol^{-1}.

Introduction

The development of replacements for chlorofluorocarbons utilized as cooling fluids or propellant agents has sparked new areas of research. The major objective encompasses the introduction of compounds that can be easily degraded within the troposphere to avoid further transport into the stratosphere and to prevent the depletion of the protective ozone layer at higher altitudes. The replacements, such as hydrofluorocarbons (e.g., CF_3CFH_2), contain labile hydrogen atoms, making the photochemical oxidation by hydroxyl radicals possible, and limiting their atmospheric lifetime.[1]

Upon tropospheric degradation, the trifluoromethoxyl ($CF_3O^\bullet$) radical is formed. To understand the fate of this species, the thermochemistry of the processes in which it may participate needs to be determined and explained. Various theoretical[2] and experimental[3] studies have produced values for the oxygen−hydrogen bond dissociation enthalpy, BDE(O−H), in trifluoromethanol ($CF_3O{-}H$) ranging from 110 to 124 kcal mol^{-1}. Now, if one accepts that the BDE is comparable to that in water, that is, the BDE(O−H) in $CF_3O{-}H$ is about 119 kcal mol^{-1}, then on the basis of a reaction enthalpy assessment a similar reactivity for $CF_3O^\bullet$ relative to $HO^\bullet$ may be anticipated in hydrogen atom abstraction reactions. However, kinetic studies have shown that the (upper limit) rate constant for hydrogen atom abstraction from water by $CF_3O^\bullet$ is lower relative to that for the hydroxyl radical.[4] This implies that next to enthalpic considerations, other factors are playing a decisive role in the kinetic behavior of $CF_3O^\bullet$.

Following the enthalpic analogy, it can be expected that the BDE(O−O) in $CF_3O{-}OCF_3$ is higher compared with nonfluorinated analogues, and should be close to the BDE(O−O) in hydrogen peroxide of 51 kcal mol^{-1}. To date, the BDE(O−O) in CF_3OOCF_3 depends on an experimental value of about 46 kcal mol^{-1}, established some 25 years ago using static gas-phase thermolytic methods with nickel or aluminum reactors.[5] In contrast, a recent density functional theory (DFT) calculation predicts a BDE(O−O) of 39.3 kcal mol^{-1}.[2h]

To provide more experimental evidence, we have conducted thermolytic experiments with CF_3OOCF_3 under very low pressure pyrolysis (VLPP) conditions to derive kinetic and enthalpic data for the O−O bond homolysis (eq 1):

$$CF_3OOCF_3 \rightarrow 2\, CF_3O^\bullet \qquad (1)$$

In the past, we have demonstrated that the VLPP method[6a,b] is quite useful in establishing thermokinetic properties for covalent bonds.[6c−e] To verify the feasibility for peroxides, the BDE(O−O) in di-*tert*-butyl peroxide has been determined as well. Next, DFT calculations have been performed with various basis sets and methodologies on the O−O, O−H, and O−F bonds in the (fluorinated) peroxides and related compounds to allow an assessment of the reliability of the applied quantum chemical methodology for such types of chemical bonds.

Experimental Section

The VLPP instrument and the experimental procedures have been described before.[6] In short, the reagents were introduced to a Knudsen quartz reaction chamber of 28.1 mL via a glass

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10.1021/jp994434w CCC: $19.00

capillary. The $Me_3COOCMe_3$ was introduced from a vessel placed in melting ice and CF_3OOCF_3 was obtained from a gas container. The pressure inside the reaction vessel was regulated by adjusting the flow rate of the reagent with a regulating valve (Nupro), and measured with a Baratron pressure transducer (MKS). Typically, the inlet flux was about 2×10^{13} molecules s^{-1}. The reactor was heated with a tube furnace (Carbolite) with an internal diameter of 25 mm. The temperature was measured with a chromel−alumel thermocouple placed inside the reactor via a quartz insert. The vacuum was maintained by an oil diffusion pump (Edwards). The pressure inside the reaction vessel was about 5×10^{-5} Torr. After escape through a single aperture (diameter 1.2 mm) the molecular beam was sampled continuously by a HP 5970 mass selective detector (Hewlett-Packard). The mass spectra between $m/z = 15-200$ were recorded using an ionization energy of 20 eV to avoid a large degree of fragmentation of the reagent and products. After temperature equilibration, 500 scans were averaged to improve the signal/noise ratio. Intensities were corrected for amounts that arose from the fragmentation of the starting compound as recorded during blank runs at 423 K for $Me_3COOCMe_3$ and at 570 K for CF_3OOCF_3, respectively. From the decrease of the molecular ion abundance (I) relative to I_0 (recorded before and after each set of temperatures), the rate constants for unimolecular decay, k_{uni}, were calculated at each temperature according to $k_{uni} = k_e(I_0 - I)/I$, with k_e as the escape rate constant: $k_e = 1.47\ (T/M)^{1/2}$ (M = molar mass of the reactant, and 1.47 an instrument constant containing the collision number for the applied reactor of 9200). Typically, between 10 and 80% decomposition of peroxide, the error in the k-values is around 2%. The decomposition followed a first-order behavior for both compounds since the rate of disappearance did not change by varying the initial reagent concentration from 5×10^{-6} to 6×10^{-5} Torr. The Arrhenius expression at the high-pressure limit was obtained by application of the Stein−Rabinovitch Rice−Ramsperger−Kassel−Marcus (RRKM) algorithm (which uses a purely vibrational model without taking into account the presence of internal rotors)[6b] and using either experimental or scaled DFT frequencies.

Chemicals. $Me_3COOCMe_3$ (Aldrich, purity 98%) was passed twice over alumina before use to remove the hydroperoxide. CF_3OOCF_3 (Prof. Willner, Universität Hannover, Germany, purity >99%) was used as received.

Method of Calculation. This has been described elsewhere.[7,8] In short, the high-level methodology of DiLabio et al. for obtaining X−H bond energetics was used to calculate the O−H bond strengths in HO−H, CF_3O−H, and Me_3CO−H.[7] This method calls for geometry optimizations and vibrational frequency calculations using the B3LYP functional and the 6-311+G(2d,2p) basis set. Zero point energies (ZPE) were scaled by 0.9806, and the vibrational enthalpy corrections (H_{vib}) were scaled by 0.9989.[9] A restricted open-shell (RO) Hartree−Fock guess was used and the electronic energy of the hydrogen atom was set to its exact value of −0.5 au. All other BDEs (O−O, O−F, and C−F) in this series were determined by an approach that is identical to the procedure described above, but uses the B3P86 functional and the 6-311G(d,p) basis set in the calculation.[8] BDEs calculated using these two models are hereafter referred to as DFT(I) results. For comparison, B3LYP calculations in combination with the 6-311+G(2d,2p), 6-31G(d,p), and 6-31G(d) basis sets were performed, with both the RO and unrestricted (U) Hartree−Fock formalism for the radicals [DFT(II) − DFT(V)]. This is more representative of what is commonly used in the literature.[10] The DFT(I) calculations for both peroxides studied experimentally were also performed at elevated temperatures (573 K for $Me_3CO-OCMe_3$, 723 K for CF_3O-OCF_3) to obtain high-temperature corrections for the experimental data. From the DFT-computed electronic energies (E_e), the enthalpies of the species (H_T) were obtained from $H_T = E_e + \mathrm{ZPE} + H_{vib} + 4RT$ to include the scaled ZPE, the scaled H_{vib}, translational (3/2 RT) and rotational (3/2 RT) contributions, and an RT term for converting energy into enthalpy.[8] BDE at 298 K for, for example, $ROOR \rightarrow 2RO^\bullet$ are given by $\mathrm{BDE(O-O)} = 2H_{298}(RO^\bullet) - H_{298}(ROOR)$.

Results

Di-*tert*-butylperoxide: Products. At 20 eV and zero conversion (at 423 K) the fragmentation pattern for di-*tert*-butylperoxide consists of m/z (percentage of the total abundance): 57 (Me_3C, 60) , 73 (Me_3CO, 4), and 146 ($Me_3COOCMe_3$, 11). VLPP between 475 and 650 K revealed a strongly increased presence of m/z = 58, 43, and 15 in the effluent stream, corresponding to the formation of acetone and methyl radicals according to eqs 2 and 3:

$$Me_3COOCMe_3 \rightarrow 2\ Me_3CO^\bullet \tag{2}$$

$$Me_3CO^\bullet \rightarrow Me_2CO + {}^\bullet CH_3 \tag{3}$$

Di-*tert*-butyl Peroxide: Kinetics. The decay of I_{57} was used to derive the rate constant, k_2. Under the VLPP conditions, the bond fission reaction is in the falloff or pressure-dependent region of unimolecular reactions. The RRKM theory provides a method to derive high-pressure rate constants. However, the VLPP data cannot simultaneously yield the enthalpy of activation and the preexponential factor. In the RRKM analysis we have adopted a preexponential factor of $\log(A/s^{-1}) = 15.30$, on the basis of studies dealing with similar reactions.[6b−e] A thermodynamic rationale is provided in the section detailing the di(trifluoromethyl) peroxide homolysis. Applying the scaled (by 0.9558[9]) DFT(I) frequencies,[11] the RRKM fitting yields the high-pressure Arrhenius expression of $\log(k_2/s^{-1}) = 15.30-37.4$ kcal $mol^{-1}/2.303RT$ (see Figure 1). For this particular reaction a large body of experimental data exists. In fact, gas-phase kinetic studies on the homolytic bond cleavage for $Me_3COOCMe_3$ have been performed over a period of the last 50 years using a variety of experimental methods.[12] A summary linear correlation yields $\log(k_2/s^{-1}) = 15.6-37.3$ kcal $mol^{-1}/2.303RT$, in excellent agreement with the results obtained in this study.

The enthalpy change for eq 2 at 298 K can be derived by means of $\mathrm{BDE(O-O)} = \Delta_2H_{298} = E_a + RT_m - \Delta_2Cp(T_m - 298)$ with T_m the medium temperature of the experiment (573 K) and Δ_2C_p (−1.4 cal $mol^{-1}\ K^{-1}$) the average change in heat capacity of the species involved as computed by DFT(I). This results in a BDE(O−O) at 298 K for $Me_3CO-OCMe_3$ of 38.9 ± 0.5 kcal mol^{-1}. Hence, $\Delta_fH_{298}(Me_3CO-OCMe_3) = -81.6$[13a] and $\Delta_fH_{298}(Me_3COH) = -74.7$[13b,c] yields a $\Delta_fH_{298}(Me_3CO^\bullet)$ of −21.3, and a BDE(O−H) in Me_3CO−H of 105.5 kcal mol^{-1} is obtained, in excellent agreement with the accepted literature value[13c] of 105.2 kcal mol^{-1}. The findings underscore the accuracy of the applied VLPP method, and that the used preexponential factor in the RRKM analysis provides accurate thermodynamic values.

Di(trifluoromethyl) Peroxide: Products. At 20 eV and zero conversion (at 570 K) the fragmentation pattern in the mass spectrometry (MS) analyzer for di(trifluoromethyl) peroxide consists of m/z (percentage of the total abundance): 69 (CF_3, 90) and 170 (CF_3OOCF_3, 3). In contrast with di-*tert*-butyl

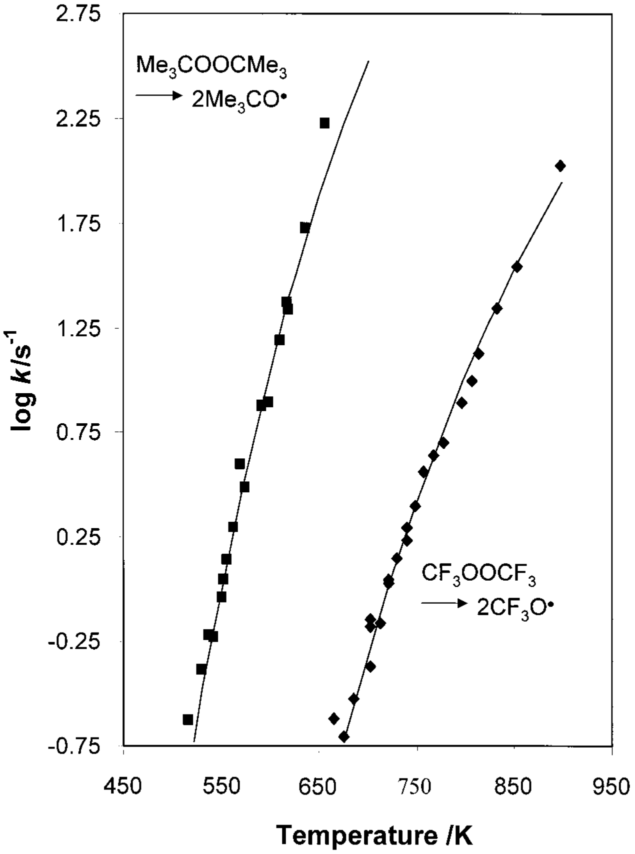

Figure 1. VLPP data for unimolecular decomposition of $Me_3COOCMe_3$ and CF_3OOCF_3 and the RRKM curve fittings (solid lines). High-pressure rate parameters: $\log(k_1/s^{-1}) = 15.30 - 45.0$ kcal mol^{-1}/2.303RT (CF_3OOCF_3), $\log(k_2/s^{-1}) = 15.30 - 37.4$ kcal mol^{-1}/2.303RT ($Me_3COOCMe_3$).

peroxide, CF_3O (m/z = 85) is not a part of the fragmentation pattern. At 70 eV the distribution changes only slightly: m/z (%): 69 (CF_3, 80), 85 (CF_3O, 0.5), and 170 (CF_3OOCF_3, 1.1). Upon raising the reaction temperature from 570 to 900 K, the ratio I_{69}/I_{170} in the effluent stream remained fairly constant, to indicate that they stem from the starting material only. At high degree of conversion, due to noise level, only the change in I_{69} could be reproducibly monitored. The sole detectable product could be identified as CF_2O with m/z (%): 66 (CF_2O, 95) and 47 (CFO, 5), emerging from the decomposition of the $CF_3O^{\bullet}$ radical inside the quartz reaction vessel (eq 4):

$$CF_3O^{\bullet} \rightarrow CF_2O + F^{\bullet} \qquad (4)$$

At high degree of conversion, minute amounts of C_2F_4 (m/z = 100) were observed as well. Fluorine atoms could not be detected by the MS analyzer probably because of their high ionization potential compared with the low operational ionization potential.

The rate constant for eq 4 has been derived from a complex kinetic scheme.[5a] At high pressures and at 750 K, k_4 is 3×10^5 s^{-1}, whereas bond homolysis is considerably slower (k_1 is 1.5×10^2 s^{-1}, see below). Hence, the stable end product in the effluent stream of the thermal cleavage of di(trifluoromethyl) peroxide will be CF_2O. Indeed, the decay of the peroxide (I_{69}) as a function of the reaction temperature nicely corresponds with the increase of CF_2O (I_{66}), as is displayed in Figure 2.

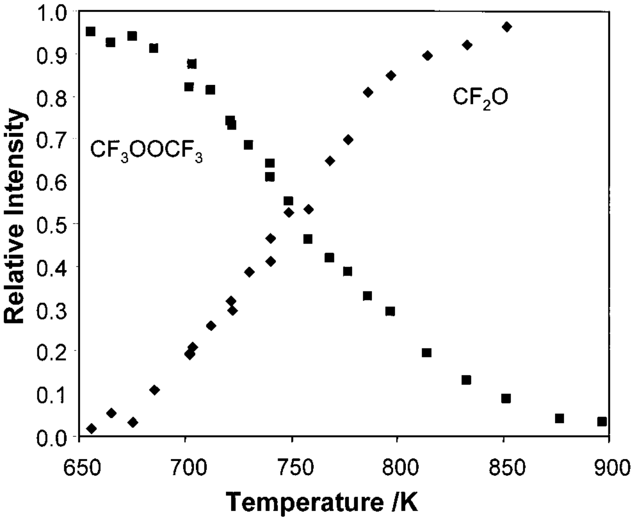

Figure 2. Thermal profile for the unimolecular decomposition of CF_3OOCF_3. Intensities of m/z 69 (CF_3OOCF_3) and m/z (66 + 47) (CF_2O) relative to I_{69} at zero conversion.

In view of the low operational pressure (concentrations), interaction of two $CF_3O^{\bullet}$ radicals to recombine yielding the starting material or to disproportionate affording CF_2O and CF_3OF is highly unlikely. These reactions have been encountered in CF_3OOCF_3 pyrolysis at subatmospheric pressure.[5]

Di(trifluoromethyl) Peroxide: Kinetics. The decay of the most abundant fragment (I_{69}, CF_3) as a function of reaction temperature was used to derive the rate constants, k_1, at low pressure. For the RRKM fitting, experimental vibrational frequencies[14] for CF_3OOCF_3 have been used. As was the case with di-*tert*-butylperoxide, the preexponential factor needs to be fixed to obtain the rate expression at the high-pressure limit. The standard entropy change for bond homolysis has been estimated using group additivity rules: Δ_1S_{298} = 35.6 cal mol^{-1} K^{-1} for CF_3OOCF_3,[15] and Δ_2S_{298} = 34.7 cal mol^{-1} K^{-1} for $Me_3COOCMe_3$.[13c,15b] On the basis of microscopic reversibility and assuming that the recombination rate constants for both radical species are similar, the preexponential factors for reactions 1 and 2 will be the same: $\log(A/s^{-1}) = 15.30$. The Arrhenius expression at the high-pressure limit becomes $\log(k_1/s^{-1}) = 15.30 - 45.0$ kcal mol^{-1}/2.303RT (see Figure 1).

The enthalpy change for eq 1 at 298 K can be derived with the use of the medium temperature of the experiment (750 K) and Δ_1C_p (−2.1 cal mol^{-1} K^{-1}), the average change in heat capacity of the species involved as computed by DFT(I). This results in a BDE(O−O) for CF_3OOCF_3 at 298 K of 47.5 ± 0.5 kcal mol^{-1}.

At first sight, this experimental value seems to be at the upper limit when compared with an evaluated BDE(O−O) of 46.8 ± 0.5 kcal mol^{-1} on the basis of three separate studies.[15a] Inspection of the original reports reveals that high-pressure activation enthalpies are found to be 46.2,[5a] 46.2,[5b] and 46.35[5c] kcal mol^{-1}, respectively, but a larger variance exists in the preexponential factors $\log(A/s^{-1})$: 15.2, 15.9, and 16.1.[16] Transformation to BDE(O−O) as outlined above and using the reported activation enthalpies yields an average of 47.6 ± 0.5 kcal mol^{-1}. This means that all studies are in excellent agreement.

At this point it would be desirable to determine the heat of formation of the trifluoromethoxyl radical ($CF_3O^{\bullet}$) in a similar way as was carried out with data obtained for di-*tert*-butyl peroxide. The heat of formation for di(trifluoromethyl) peroxide has been derived from the equilibrium constant for eq 5:

$$CF_3OOCF_3 \rightleftharpoons CF_3OF + CF_2O \qquad (5)$$

TABLE 1: DFT-Computed and Experimental BDEs (kcal mol^{-1}) at 298 K

compound	density functional theory[a] (I)	(II)	(III)	(IV)	(V)	exp.	ref
HO−H	118.3	117.0	113.9	113.1	109.5	119.2	13b,c
CF_3O−H	117.5	116.1	113.6	112.6	109.1	124.7, 117.5	3a, 3b
Me_3CO−H	104.2	102.6	100.9	99.9	96.6	105.5	this work
HO−OH	53.2	48.0	51.5	49.7	49.8	51.1	13b,c
HO−F	51.0	48.0	51.8	50.2	50.1	51.7[b]	13b,c
CF_3O−OH	51.1	46.4	49.4	47.6	47.5	49.4	note *c*
CF_3O−F	45.0	42.9	47.0	45.4	45.4	44.0	15a
F−$CF_2O^•$	27.3	22.6	30.3	30.6	30.6	21.0	note *d*
CF_3O−OCF_3	43.6[e]	40.1	42.9	41.0[f]	41.1	47.5	this work
Me_3CO−OH	45.8	39.7	43.6	41.8	41.6	44.1[g]	this work
Me_3CO−$OCMe_3$	35.9[h]	29.4	33.8	31.9	31.8	38.9	this work
Me−$CMe_2O^•$	3.3	-1.0	3.6	3.6	3.9	4.2	13b,c
eq 5[i]	25.9	19.8	26.3	26.3	26.3	24.5	17
MAD[j]	1.7	4.3	2.4	3.3	3.9		

[a] Computational methods: DFT(I) = (RO)B3P86/6-311G(d,p)// (RO)B3P86/6-311G(d,p); for the O−H bonds the same procedure as DFT(II) is applied but uses the exact electronic energy for the hydrogen atom: $E_e(H) = -0.5$ au[7]; DFT(II) = (RO)B3LYP/ 6-311+G(2d,2p)//(RO)B3LYP/ 6-311+G(2d,2p); DFT(III) = (RO)B3LYP/ 6-31G(d,p)//(RO)B3LYP/6-31G(d,p); DFT(IV) = (U)B3LYP/ 6-31G(d,p)//(U)B3LYP/6-31G(d,p), DFT(V) = (U)B3LYP/ 6-31G(d)//(U)B3LYP/6-31G(d). DFT(II) to DFT(V) uses the DFT-computed $E_e(H)$. [b] Recently the $\Delta_f H_{298}$(FOH) of −23.5 kcal mol^{-1} has been questioned; with $\Delta_f H_{298}$(FOH) = −20.6 the BDE(O−F) becomes 48.8 kcal mol^{-1}.[20] [c] By means of interpolation between HO−OH and CF_3O−OCF_3. [d] BDE(F−$CF_2O^•$) = −BDE(CF_3O−OCF_3) + $\Delta_5 H$ + BDE(CF_3O−F) (see text). [e] At 723 K: 42.8 kcal mol^{-1}. [f] At 763 K: 41.9 kcal mol^{-1}. [g] With $\Delta_f H_{298}(Me_3COOH) = -56.1$ kcal mol^{-1}.[13b,c] [h] At 573 K: 35.5 kcal mol^{-1}. [i] Enthalpy change for $CF_3OOCF_3 \rightarrow CF_3OF + CF_2O$ (eq 5). [j] MAD: Mean absolute deviation from the listed experimental values excluding CF_3O−H and F−$CF_2O^•$ ($n = 11$).

From a gas-phase experiment a $\Delta_5 H$ of 24.5 kcal mol^{-1} is obtained.[17] Combined with the independently determined $\Delta_f H_{298}(CF_2O) = -152.7$[13b] and $\Delta_f H_{298}(CF_3OF) = -182.8$[13b] is the $\Delta_f H_{298}(CF_3OOCF_3)$ of −360.0[17] kcal mol^{-1}. However, the quality of the thermodynamic data has been frequently questioned. In this area numerous efforts have been made to furnish the required quantitative thermodynamic information. By group increments a $\Delta_f H_{298}(CF_2O)$ of -148 ± 1[18] is found, whereas by computational methods −145.3[2e] and − 143.6[19a] have been obtained; a previous experimental study[19b] has provided −149.1 kcal mol^{-1}. They are all at variance (up to 9 kcal mol^{-1}) with the original reported experimental value. A similar deviation can be found for the $\Delta_f H_{298}(CF_3OF)$, with −173[2e], −180.4[2c], and −176.9[3b] kcal mol^{-1}. Hence, given these uncertainties, the $\Delta_f H_{298}(CF_3OOCF_3)$ ranges between −341 and −360 kcal mol^{-1} and thus, according to eq 1, $\Delta_f H_{298}(CF_3O^•)$ varies from −146.7 to −156.2 kcal mol^{-1}.

Alternatively, the $\Delta_f H_{298}(CF_3O^•)$ can be derived from the corresponding alcohol, CF_3OH, provided that the $\Delta_f H_{298}(CF_3OH)$ and the BDE(O−H) are known. The $\Delta_f H_{298}(CF_3OH)$ cannot be determined by conventional calorimetric methods (upon liquefaction this compound decomposes readily into CF_2O and HF), but quite recently by means of a gas-phase photoionization study, $\Delta_f H_{298}(CF_3OH)$ has been established as −217.2 kcal mol^{-1}.[3b] This value nicely agrees with the values derived by the group additivity method (-215 ± 1)[2b] and by quantum chemical calculations (−217.7)[2a] at the MP4/6-311+G(d,p)// MP2/6-31G(d,p) level and applying isodesmic reactions to combine computed reaction enthalpies and experimental heats of formation of the species involved. Because the BDE(O−H) in trifluoromethanol has not been firmly established, we have applied DFT calculations to try to resolve this matter.

Computations. The absolute O−H, O−O, and O−F BDEs in various related fluorinated and nonfluorinated compounds have been computed using several DFT methods. The results are summarized in Table 1. The first procedure, DFT(I), was adopted since it has been shown that the X−H[7] and X−X[8] BDEs for several benchmark molecules could be calculated within 2 kcal mol^{-1} relative to the experimental data. Subsequently, two basis sets [6-311++G(2d,2p) and 6-31G(d,p)] were used in combination with the (RO)B3LYP formalism [DFT(II) and DFT(III)], and finally, calculations were performed using the (U)B3LYP with the 6-31G(d,p) and the 6-31G(d) basis sets [DFT(IV) and DFT(V)].

Inspection of Table 1 reveals several trends. For the BDE(O−H) in HO−H, CF_3O−H, and Me_3CO−H, the extension of the basis set provides a better agreement with the experiment. For example, in the case of Me_3COH, the BDE(O−H) increases from 96.6 [DFT(V)] to 104.2 [DFT(I)]; the latter approaches the experimental value of 105.5 kcal mol^{-1}. The (U)B3LYP method with the 6-31G(d,p) basis set [DFT(IV)] underestimates the oxygen−hydrogen BDEs by about 6 kcal mol^{-1}, whereas the deviation for carbon−hydrogen BDEs is only 0−2 kcal mol^{-1}.[10] Application of the RO formalism [DFT(III)] provides some improvement for oxygen−hydrogen bonds, whereas in this case for carbon−hydrogen BDEs an almost perfect match is obtained.[10] Of particular interest is the BDE(O−H) in CF_3OH. Our result with the DFT(I) procedure of 117.5 kcal mol^{-1} compares well with other computational studies using MP2: 119.4,[2a] MP2: 118.3,[2f] B3PW91: 115.2,[2h] G2: 120.4,[2h] or G2-MP2: 121.4,[2h] all of which are substantially lower than Huey et al.'s experimental value[3a] of 124.7 kcal mol^{-1}.

The oxygen−oxygen BDEs in the hydroperoxides HO−OH, CF_3O−OH, and Me_3CO−OH increase from DFT(V) to DFT(I). However, in this case DFT(I) overestimates the BDEs up to ca. 2 kcal mol^{-1}. Only with (RO)B3LYP/6-31G(d,p) [DFT(III)] is a satisfying agreement with the experimental data found.

None of the computational methods is able to predict the BDE(O−O) in CF_3OOCF_3 and Me_3CO−$OCMe_3$ with an accuracy of better than 3 kcal mol^{-1}, DFT(I) being closest to the experimental values, differing by 3.0 (Me_3CO−$OCMe_3$) and 3.9 kcal mol^{-1} (CF_3OOCF_3). The extension of the basis sets or the change in functionals only marginally improves the agreement with experimental values. Using a very large basis set even results in an increased underestimation (albeit using a different, less widely accepted functional): a B3PW91/6-311++G(3df, 3pd) calculation of the BDE(O−O) for CF_3OOCF_3 has been reported as 39.3 kcal mol^{-1}, which is too low by 8 kcal mol^{-1}.[2h] For this particular example we have analyzed the effect of a (possible) basis set superposition error (BSSE) on the BDE(O−O) when using the B3LYP functionals. The counterpoise correction on the B3LYP/6-31G(d,p)//B3LYP/6-

TABLE 2: DFT Bond Lengths (Å) and Torsion Angles (°)[a]

	DFT(I)	DFT(III)	exp.[b]		DFT(I)	DFT(III)	exp.[b]
r(HO−H)	0.9609	0.9652	0.9578	r(Me_3CO−OH)	1.4377	1.4576	n.a.
r(CF_3O−H)	0.9645	0.9683	n.a.	r(Me_3C−OOH)	1.4424	1.4503	n.a.
r(CF_3−OH)	1.3451	1.3502	n.a.	<(C−O−O−H)	109.7	110.8	n.a.
r(Me_3CO−H)	0.9620	0.9670	1.016	r(CF_3O−OCF_3)	1.4324	1.4514	1.419
r(Me_3C−OH)	1.4430	1.4379	1.446	r(CF_3−OOCF_3)	1.3833	1.3925	1.399
r(HO−OH)	1.4368	1.4554	1.475	<(C−O−O−C)	124.7	120.4	123.3
<(H−O−O−H)	118.4	118.3	120.1	r(Me_3CO−OCMe_3)	1.4522	1.4729	1.480
r(CF_3O−OH)	1.4297	1.4479	1.447	r(Me_3C−OOCMe_3)	1.4356	1.4427	1.460
r(CF_3−OOH)	1.3680	1.3778	1.376	<(C−O−O−C)	157.8	160.9	165.8
<(C−O−O−H)	102.5	98.5	95				

[a] For computational details see Table 1. [b] Experimental data from ref 21; n.a.: not available.

31G(d,p) level, DFT(III), gives a downward correction of 3 kcal mol^{-1}, whereas at the B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p) level, DFT(II), the correction term is only 0.6 kcal mol^{-1}. When incorporating the BSSE, the BDE(O−O) for CF_3OOCF_3 now becomes 39.5 and 39.9 kcal mol^{-1} for DFT(II) and DFT(III), respectively. With two different basis sets the same result is obtained, but the BDE(O−O) is 8 kcal mol^{-1} below the experimental value. Thus, the underestimation of the BDE(O−O) by DFT cannot be attributed to the BSSE, but rather to the inadequate treatment of the electron correlation.

For the oxygen−fluorine BDEs in HO−F and CF_3O−F, the variations between DFT(I) and DFT(V) are rather small, and the absolute values are close to the (assumed) experimental data [see the Discussion section on BDE(CF_3O−F)]. Once again with DFT(II), using the most extended basis set, the results are less satisfying.

The computed enthalpy change described thus far refers to cleavage of a molecule into two radical species. For the decomposition of a radical into a molecule and another radical, the decomposition of $Me_3CO^\bullet$ (and presumably $CF_3O^\bullet$, see below) DFT handles enthalpy change quite well, with a clear exception for DFT(II).

The overall performance of DFT(I) for the compounds investigated appears to be the most satisfying, with a mean absolute deviation (MAD) for O−O and O−F BDEs of 1.7 kcal mol $^{-1}$. This is followed by DFT(III), DFT(V), DFT(IV), and DFT(II) at 2.4, 3.3, 3.9, and 4.3 kcal mol^{-1}.

DFT-Optimized Geometries. Table 2 summarizes some key features of the optimized geometries as obtained by DFT(I) and DFT(III). Both methods predict a C_2 symmetry for the peroxides (CF_3OOCF_3, $Me_3COOCMe_3$) and a C_s symmetry for the corresponding alkoxyl radicals. It is interesting to note that on average DFT(III) affords bond lengths and torsion angles in better agreement with the available experimental data than the other method.[21] The relation between bond length and BDE is not straightforward but B3P86 [DFT(I)] consistently predicts the O−O bond to be ca. 0.02 Å shorter than B3LYP. This translates to an elevation of the BDE(O−O) by 0.7 to 2.2 kcal mol^{-1}, which in three of the five cases (the hydroperoxides) results in an overestimation of the BDE(O−O) by DFT(I) and good agreement for B3LYP. For the two compounds that are in poor agreement (the dialkyl peroxides), this is not true. Whereas the O−O bond length in CF_3OOCF_3 is actually predicted as *longer* than experiment suggests, resulting in a predicted BDE(O−O) that is too low by 3.9 and 4.6 kcal mol^{-1}, the O−O bond length in $Me_3COOCMe_3$ is predicted to be *shorter* than the experimental value, but the BDEs are still underestimated by 3.0 and 5.6 kcal/mol. This suggests that both DFT methods underestimate the effects of the bulky *tert*-butyl groups on the geometry, but overestimate their effects on the BDE, whereas the opposite is true for CF_3OOCF_3.

The calculated torsion angles in hydrogen peroxide of 118.4° [DFT(I)] and 118.3° [DFT(III)] are in good agreement with the experimental value of 120°. The agreement remains acceptable for the other (hydro)peroxides for both methods.

The torsion angles in the different peroxides are easily rationalized when both hyperconjugation and oxygen−oxygen lone pair or substituent−oxygen lone pair repulsions are considered.[21e] In hydrogen peroxide, the mixing of the σ^*_{OH} with a lone pair on the adjacent oxygen dictates the lowest energy conformation with a torsion angle of 120°. In di-*tert*-butyl peroxide, the repulsions of the bulky *tert*-butyl groups are dominant over the weaker hyperconjugation. Consequently, the torsion angle is closer to the trans orientation. In *tert*-butyl hydroperoxide, the torsion angle is slightly smaller than the optimal 120° because of repulsion between two adjacent lone pairs and the *tert*-butyl group and a neighboring lone pair. To explain the trends seen in the trifluoromethyl derivatives, one should consider that the anitbonding σ^*_{O-CF3} orbital is substantially lower in energy compared with an alkyl analogue. An anomeric-type stabilization is maximized when this orbital is lined up with a lone pair on the adjacent oxygen, to result in a torsion angle of 60°. In trifluoromethyl hydroperoxide, the σ^*_{OH}−lone pair interaction dominates over the σ^*_{O-CF3}−lone pair interaction, resulting in a compromise of 95° (closer to 120° than to 60°). In di(trifloromethyl) peroxide, the σ^*_{O-CF3}−lone pair interactions prefer a 60° torsion angle, but the steric interaction of the CF_3 groups, which would be minimized at 180°, forces the molecule to adopt an intermediate conformation with torsion angle of 123°.

Experimental and DFT-Computed Frequencies. For the CF_3OOCF_3 molecule, the vibrational frequencies have been determined experimentally.[14a] Comparison with the 24 DFT-calculated frequencies reveals that for B3P86 a scaling factor 0.958 ± 0.092 and for B3LYP 0.999 ± 0.054, respectively, needs to be applied.[14b] This is in good agreement with the recommended average frequency scaling factors at this level of theory (0.9558 for B3P86 and 0.9614 for B3LYP).[9] In the original report,[14a] the assignment of the O−O stretching frequency at 890 cm^{-1} is in error; after inspection of the vibrational model this band belongs to a symmetric C−O stretching mode, whereas the 975 cm^{-1} band is the symmetric O−O stretching frequency.

Discussion

BDE(O−O) in CF_3OOCF_3. A combination of the experimental and computational data has provided a list of recommended values for the heats of formation of many fluorinated species of interest.[2e] From this list it can be inferred that, as a consequence of data averaging, the BDE(O−O) in di(trifluoromethyl) peroxide is reduced to 44.4 kcal mol^{-1}, a value that is too low by 3 kcal mol^{-1}as determined in this study. The

TABLE 3: BDEs Derived from Isodesmic Reactions (kcal mol^{-1}) at 298 K.

	density functional theory[a]					
compound	I	II	III	IV	V	exp.
CF_3O-H[b]	118.4	118.3	118.9	118.7	118.8	124.7, 117.5
CF_3O-H[c]	118.8	118.2	119.3	119.1	119.4	124.7, 117.5
Me_3CO-H[b]	105.1	104.8	106.2	106.0	106.3	105.5
Me_3CO-H[c]	105.5	106.1	107.1	106.9	107.5	105.5
CF_3O-OH[d]	49.0	49.5	49.0	49.0	48.8	49.4
Me_3CO-OH[e]	43.7	42.8	43.2	43.2	42.9	44.1
$HO-F$[e]	48.9	51.2	51.4	51.7	51.4	51.7
CF_3O-F[f]	45.7	46.6	46.9	46.9	47.0	44.0

[a] For computational details see Table 1. [b] With the isodesmic eq 7 and experimental BDE(HO−H). [c] With the isodesmic eq 8 and the experimental BDE(HO−H), BDE(CF_3O-OH)/(MeO−OH)/(Me_3CO-OH) and BDE(HO−OH). [d] With the isodesmic eq 9: $XOOH + {}^\bullet OH \rightarrow XO^\bullet + H_2O_2$ with $X = CF_3$, CMe_3, and the experimental BDE(HO−OH). [e] With the isodesmic eq 9: $FOH + {}^\bullet OH \rightarrow F^\bullet + H_2O_2$ and the experimental BDE(HO−OH). [f] With the isodesmic eq 9: $CF_3OF + {}^\bullet OH \rightarrow CF_3O^\bullet + FOH$ and the experimental BDE(F−OH).

oxygen−oxygen bond is still weaker relative to the one in hydrogen peroxide. The interaction between the oxygen lone pair and the CF_3 group weakens the oxygen−oxygen bond. On the other hand, the experimental O−O bond length in CF_3O-OCF_3 is substantially shorter relative to HO−OH (difference of 0.06 Å, see Table 2), which does suggest that other factors than mere repulsion are dominant.

BDE(O−H) in CF_3OH. Many attempts have been made to determine the BDE(O−H) in trifluoromethanol. We have used the DFT values from Table 1 to compute the scaled BDE(O−H)s for CF_3OH by applying two isodesmic reactions:

$$XOH + {}^\bullet OH \rightarrow XO^\bullet + H_2O \quad (7)$$

$$XOH + H_2O_2 \rightarrow XOOH + H_2O \quad (8)$$

In this way any erroneous handling of radical species by DFT should be reduced. The results are summarized in Table 3. Comparison with Table 1 shows that the BDE(O−H) are now almost invariant with the applied computational methodology and range from 118.2 to 119.4 kcal mol^{-1} (average of 118.8 ± 0.6 kcal mol^{-1}), in good agreement with other related computational studies. Thus, the BDE(O−H) in trifluoromethanol is, within the error margins, identical to that in water. Combination of $\Delta_f H_{298}(CF_3OH) = -217.2$[3b] and a BDE(O−H) of 118.8 now leads to $\Delta_f H_{298}(CF_3O^\bullet)$ of −150.5 kcal mol^{-1}. Consequently, with the BDE(O−O) of 47.5 for di(trifluoromethyl) peroxide, as obtained in this study, a $\Delta_f H_{298}(CF_3OOCF_3)$ of −348.5 kcal mol^{-1} is found, which is about 12 kcal mol^{-1} higher than the only available experimental number of −360 kcal mol^{-1}, as determined by eq 5.[17]

With the same type of isodesmic reactions, a somewhat larger range is manifested for the BDE(O−H) in *tert*-butyl alcohol (106.3 ± 1.5 kcal mol^{-1}), and the average is above the experimental value of 105.5 kcal mol^{-1} (see Table 3).

The BDEs for oxygen−oxygen bonds in hydroperoxides, the oxygen−fluorine bonds in hypofluorous acid (HOF), and the oxygen−fluorine bond in trifluormethylhypofluorite (CF_3OF) have been also calculated applying the general isodesmic eq 9:

$$XOY + {}^\bullet OH \rightarrow XO^\bullet + YOH \quad (9)$$

As with the alcoholic compounds, the computed BDEs are almost independent of the computational method, and the averages, on the basis of isodesmic eq 9, are quite compatible with the experimental data, as can be inferred from Table 3.

Hence, quantitative enthalpic information in the absence of sufficient experimental data can be best provided by isodesmic reactions using a combination of calculated DFT BDEs and known experimental data. The type of functionals and the extension of the basis set appear to play only a minor role for the overall reliability.

BDEs in $F-CF_2O^\bullet$ and CF_3O-F. Since we have now established reliable values for the $\Delta_f H_{298}$ and the BDE(O−O) for CF_3OOCF_3, it is of interest to analyze the implication for eq 5, which consists of three elementary reactions: O−O bond cleavage of the peroxide (eq 1), decomposition of $CF_3O^\bullet$ (eq 4), and O−F bond formation (reverse of eq 10) in such a way that $\Delta_5 H = \Delta_1 H + \Delta_4 H - \Delta_{10} H = 24.5$ kcal mol^{-1}.[17]

$$CF_3OF \rightarrow CF_3O^\bullet + F^\bullet \quad (10)$$

The BDE(C−F) ($\Delta_4 H$) for the $CF_3O^\bullet$ radical can be derived by summation of the experimental enthalpic data (see Table 1) to provide a BDE(C−F) of 21 kcal mol^{-1}. The kinetic expression for unimolecular fragmentation of $CF_3O^\bullet$ into CF_2O and $F^\bullet$ obeys: $k_4/s^{-1} = 3.2 \times 10^{14} \exp(-31 \text{ kcal mol}^{-1}/RT)$.[5a] Combination with $\Delta_4 H$ yields an appreciable enthalpy of activation, E_{-4}, of 10 kcal mol^{-1} for the reverse reaction: the addition of a fluorine atom to CF_2O. For comparison, the rate of decomposition of the methoxyl radical into formaldehyde and a hydrogen atom, eq 11, obeys $k_{11}/s^{-1} = 1.6 \times 10^{14} \exp(-25 \text{ kcal mol}^{-1}/RT)$.[12]

$$CH_3O^\bullet \rightarrow CH_2O + H^\bullet \quad (11)$$

In this case, with a well-established reaction enthalpy viz. the BDE(C−H) in $CH_3O^\bullet$) of 22 kcal mol^{-1}, the enthalpy of activation for the reverse reaction, the addition of a hydrogen atom to the carbon of formaldehyde, is about 3 kcal mol^{-1}.[13b,c] The C−F bonds in closed-shell molecules are definitively stronger than the C−H bonds, and it seems quite reasonable to assume that this is also the case for $CF_3O^\bullet$ relative to $CH_3O^\bullet$. The activation enthalpy for atom/radical addition commonly reflects to some degree the reaction enthalpy for comparable reactions.[22] Supposing that the E_{-4} and E_{-11} are similar (halogens atoms are usually more reactive in addition to double bonds than hydrogen atoms), then the BDE(C−F) in $CF_3O^\bullet$ would increase from 21 to 28 kcal mol^{-1}. Inspection of the Table 1 also reveals that the DFT-calculated BDE(C−F) for the $CF_3O^\bullet$ radical deviates substantially from the original experimental value by about 6−9 kcal mol^{-1}. Such a large deviation is clearly outside the inaccuracy range of the DFT methods used in this study, with a possible exception for DFT(II). Combination of thermokinetic arguments and our DFT results strongly suggest that a more reasonable value for the BDE(C−F) in $CF_3O^\bullet$ is 27± 1 kcal mol^{-1}.

Consequently, with the revised value for $\Delta_4 H$, the BDE(CF_3O-F) increases to 50 kcal mol^{-1}, in considerable contrast with the often-cited experimental value[15a] of 44.0 kcal mol^{-1}, which stems from two kinetic studies on the homolysis of the oxygen−fluorine bond in CF_3OF.[23] The reported preexponential factors are surprisingly low (2×10^{14} and 8×10^{14} s^{-1}); if one takes a more reasonable A_{10} factor of 2×10^{15} s^{-1} and recalculates the rate constants in the usual manner, a BDE(CF_3O-F) of 47 kcal mol^{-1} is obtained at 298 K (without ΔC_p correction). Group additivity treatments reveal similar values. The oxygen−fluorine bond in HOF is as strong as the oxygen−oxygen bond in HOOH; thus the BDE(CF_3O-F) can be

TABLE 4: Recommended BDEs for Fluorinated Species (kcal mol^{-1}) at 298 K

compound	BDE[a]
$CF_3O{-}H$	118.8
$F{-}CF_2O^\bullet$	27
$CF_3O{-}F$	48
$CF_3O{-}OCF_3$	47.5

[a] Error margin ±1 kcal mol^{-1}.

estimated to be identical to BDE($CF_3O{-}OH$) and becomes 49 kcal mol^{-1} (see Table 1). Recently, the BDE(O−Cl) in CF_3OCl has been determined as 53 kcal mol^{-1}.[3b] If the same bond-weakening effect is manifested as between the BDE(HO−F) of 51.7 and the BDE(HO−Cl) of 56.1 kcal mol^{-1},[13b,c] a BDE($CF_3O{-}F$) of 48.5 kcal mol^{-1} is obtained. Hence, kinetic and group additivity arguments lead to a BDE($CF_3O{-}F$) of 48 ± 1 kcal mol^{-1}. According to our DFT results and applying an isodesmic reaction (see Table 3) an average of 47 kcal mol^{-1} is found.

Obviously, more experimental work needs to be performed to establish the BDEs for $F{-}CF_2O^\bullet$ and $CF_3O{-}F$ with high precision.

Our recommended BDEs for fluorinated species obtained here are summarized in Table 4.

Reactivity of $CF_3O^\bullet$ versus $OH^\bullet$. In view of the similarity between the BDE(O−H) of CF_3OH and H_2O, the reactivity for the two radicals in hydrogen atom abstraction may be quite comparable on the basis of a reaction enthalpy consideration. Recently, the activation enthalpy has been established for the hydrogen atom abstraction by the hydroxyl radical from water (eq 12) at low temperatures: a thermoneutral reaction with an $E_{a,12}$ of 4.2 kcal mol^{-1} and with a rate constant at 298 K of 1.2 × 10^5 $M^{-1}s^{-1}$.[25] Hydrogen atom abstraction from methane requires an E_a of 3.5 kcal mol^{-1}, although the reaction is already 14 kcal mol^{-1} exothermic, with a kinetic isotope effect for CH_4/CD_4 of 7.2.[26] For other hydrocarbons the E_a decreases steadily with the increasing exothermicity according to the Evans−Polanyi relation. The behavior of $CF_3O^\bullet$ is somewhat different. For the hydrogen atom abstraction from water, eq 13, the upper-limit rate constant is around a factor of 10 lower (1 × 10^4 M^{-1} s^{-1}) relative to hydroxyl.[4] On the other hand, the reactivity toward methane (and other hydrocarbons) is somewhat higher, and the kinetic isotope effect for CH_4/CD_4 is 3.75.[4b]

$$HO^\bullet + H_2O \rightarrow H_2O + {}^\bullet OH \tag{12}$$

$$CF_3O^\bullet + H_2O \rightarrow CF_3OH + {}^\bullet OH \tag{13}$$

Clearly, the transition states for eqs 12 and 13 are not identical. Additional DFT calculations on the transition states show that because of a somewhat higher degree of the charge separation for HO··H··OH a relatively more stabilized (polar) entity emerges, and hence a lower enthalpy of activation.[27] Computational studies have demonstrated that hydrogen-bonded precursor complexes exist for OH/H_2O[28a] and $CF_3O^\bullet/H_2O$,[28b] to be more stable relative to the reactants by 2.1 and 2.5 kcal mol^{-1}, respectively. Thus, the overall thermochemisty for $^\bullet OH$ and $CF_3O^\bullet$ reacting with water may be the same, which does not necessarily imply a comparable dynamic behavior, as is also not the case for hydrogen atom abstraction by H or by Cl despite the fact that the BDE(H−H) and BDE(H−Cl) are almost identical.

Acknowledgment. We thank Gino DiLabio, Edwin Dorrestijn, and Martine de Heer for stimulating discussions, Jan Reedijk for supporting this work, AKZO Nobel Chemicals B.V (H. Jaspers) and the AFEAS for the assistance to obtain di(trifluoromethyl) peroxide, and the Hochschulrechenzentrum Essen for the generous allotment of computer resources. D.A.P. thanks NRC Canada and NSERC Canada for their support.

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(23) Two kinetic expressions have been reported for eq 10: k_{10}/ s^{-1} = 2×10^{14}exp (−43.5 kcal mol^{-1}/RT)[24] between 490 and 510 K and k_{10}/ s^{-1} = 8×10^{14}exp(−45 kcal mol^{-1}/RT)[5a] between 480 and 560 K.

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