A Reassessment of the Bond Dissociation Energies of Peroxides. An *ab Initio* Study

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Abstract: The strength of the O−O bond is of fundamental importance in a variety of chemical processes. Traditionally, a value of 34 kcal/mol has been ascribed to a generic O−O bond dissociation energy. The present, high-level *ab initio* calculations indicate that the average O−O bond energy is significantly higher, *ca.* 45 kcal/mol, and that the bond energy is sensitive to the bonding environment. Calculations at the G2 level of theory give bond dissociation enthalpies at 298 K of 50 kcal/mol for HOOH, 45 kcal/mol for CH_3OOH, 39 kcal/mol for CH_3OOCH_3, and 48 kcal/mol for HC(O)OOH and $CH_3C(O)OOH$. The G2(MP2) results are similar and, additionally, give bond dissociation enthalpies of 38 kcal/mol for diacetyl peroxide, 49 kcal/mol for trifluoroperoxyacetic acid, 23 kcal/mol for isopropenyl hydroperoxide, and 22 kcal/mol for peroxynitrous acid.

Introduction

An understanding of the basic chemical principles and energetics of the oxygen−oxygen bond is fundamental to oxygen atom transfer from an oxygen donor under industrial, laboratory, biochemical, combustion, or atmospheric conditions. The electronic features of molecules possessing an O−O bond constitute an active area of research that has provided considerable insight into the reactivity trends exhibited by this class of highly reactive molecules.[1] Average bond energies (kcal/mol) of oxygen atoms bound to carbon (C−O = 84), nitrogen (N−O = 53), and fluorine (F−O = 44) are all presumed to be substantially greater than that of oxygen bound to itself, possibly reflecting a greater ionic character of an X−O single bond.[1a] A relatively low bond energy (O−O = 34 kcal/mol) has typically been ascribed to a generic peroxide.[1b] The average X−X bond energy in the absence of lone pairs of electrons is, however, also typically greater than that of an O−O bond (e.g., C−C = 84 kcal/mol), and this effect has been ascribed to the role of lone pair repulsion in lowering the bond strength of the peroxo group. The unusual reactivity of peroxides is generally attributed to weakness of the O−O bond linkage and hence the ease with which it is homolytically cleaved.

Experimental heats of formation of a series of peroxides have been used to derive individual group contributions which form the basis of a group additivity method for estimating unmeasured heats of formation. Benson and Shaw[2a] have derived the

Table 1. Generally Accepted Activation Parameters for Peroxide Bond Homolysis[a]

peroxide	$\Delta H^\ddagger$ (kcal/ mol)	$\Delta S^\ddagger$ [cal/ (mol K)]	peroxide	$\Delta H^\ddagger$ (kcal/ mol)	$\Delta S^\ddagger$ [cal/ (mol K)]
HO−OH	47	11	PhCO−O−*t*−Bu	35	8
t−BuO−OH	41	12	RCOO−OCOR	30	6
RO−OR	~36	~14	ROCO−OCOR	29	5

[a] For the source of the estimated $\Delta H^\ddagger$ see refs 1b and 3a.

[O−(O)(C)] group value of −4.5 kcal/mol by subtracting the known hydrocarbon heats of formation from the measured heats of formation of dialkyl peroxides. The [O−(O)(H)] group value of −16.3 kcal/mol is obtained directly from the heat of formation of HO−OH. The kinetics of the thermal decomposition of a number of peroxides have been studied, and these bond dissociation enthalpies (BDE) have been used to derive O−O bond strengths. From these data it was concluded that the strength of the O−O bond in dialkyl peroxides is about 37 ± 1 kcal/mol and is independent of the alkyl group. The BDE of the O−O bond in diacyl peroxides was estimated by this method to be only 30 ± 1 kcal/mol.[1b]

Established estimates of the amount of energy required to cleave homolytically a generic peroxide ZO−OY varies from 47 for hydrogen peroxide down to about 29 kcal/mol for dialkyl peroxodicarbonates (Table 1).[1b,3] A more accurate value has recently been determined for H_2O_2, $D_0 = 48.75 \pm 0.005$ kcal/ mol[8b] which corresponds to 50.5 kcal/mol for the BDE at 298 K ($\Delta(H^\circ_{298} - H^\circ_0) = 1.79$ kcal/mol).[8c] It has been assumed by most workers in this field that the enthalpy for homolysis of related peroxides such as ZO−OY can be derived from the mean BDE for ZO−OZ and YO−OY. For example, the enthalpy for O−O dissociation in peroxyacetic acid ($\Delta H^\ddagger_{298} = 38.5$ kcal/ mol) has been derived[3a] from the enthalpies of HO−OH (47 kcal/mol) and $CH_3COO−OCOCH_3$ (30 kcal/mol). A rate constant of 6×10^{-12} s^{-1} can be estimated for O−O bond rupture at 25 °C (eq 1) that is consistent with a very low rate

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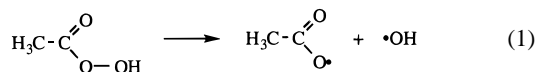
$$H_3C-C{\overset{O}{\underset{O-OH}{}}} \longrightarrow H_3C-C{\overset{O}{\underset{O\bullet}{}}} + \bullet OH \qquad (1)$$

of bond dissociation in the gas phase or in the absence of a catalytic influence. Because of difficulties in preparing and purifying peroxy acids, the estimates for bond dissociation energies in this class of oxidant has remained obscure. Heterolytic bond cleavage leading to $CH_3CO_2^-$ and HO^+ is disfavored over a homolytic process in the gas phase by nearly 222 kcal/mol on the basis of the ionization potential of OH and the electron affinity of CH_3CO_2.[23]

Another important thermodynamic issue that remains unresolved is the relationship between bond dissociation energies and rates of oxygen atom transfer. This problem is further complicated by the fact that a great many oxidative reactions are believed to proceed by a heterolytic process involving an S_N2 displacement on the O−O bond (eq 2).[3,4] The oxidizing

$$:NUC \quad {\overset{Z}{\underset{Y}{\diagdown}}}O-O \longrightarrow ZO-\overset{+}{N}UC + YO^- \qquad (2)$$
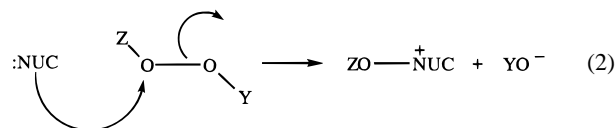
power of RO−OH shows an inverse relationship with the pK_a of the leaving group RO$^-$. Thus, H_2O_2 is much less reactive than CH_3CO_3H, and CF_3CO_3H is an extremely effective oxygen donor.[5] In general electron-withdrawing groups on the −CO$_3$H moiety markedly increase the rate of oxygen atom transfer. This phenomenon has generally been attributed to the increase in the thermodynamic stability of the leaving group (RCO_2^-). Rates of oxidation can also be influenced by protic solvents.[6] Alkene epoxidation with peroxyacids is dramatically slowed in alcohol solvents due to ground state solvation and possibly to disruption of intramolecular hydrogen bonding; oxidation reactions with alkyl hydroperoxides, however, enjoy a rate enhancement in protic solvents as a consequence of acid catalysis or proton transfer to the departing RO$^-$ leaving group.[7a]

The bond dissociation energy of hydrogen peroxide has been accurately predicted by high-level *ab initio* theory,[7−10] and we have found that adequate relative energetics can be calculated

at the MP2/6-31G* level for a variety of oxygen atom transfer processes.[9] Although the predicted O−O bond energy in peroxyformic acid is only 1.0 kcal/mol by Hartree−Fock theory, at the MP4//MP2/6-31G* level D_e values for HO−OH and HCO_2−OH are predicted to be 49.2 and 50.7 kcal/mol, respectively.[9b] The fact that these two BDEs are significantly higher than the accepted average bond energy of 34 kcal/mol and that our predicted O−O bond energy for HCO_3H was significantly higher than the estimated 38.5 kcal/mol for peroxyacetic acid[3] prompted us to initiate a systematic and reliable theoretical study of O−O bond energies.

We suggest that the source of discrepancy between the accepted experimental O−O bond energies and our theoretical values lies in the fact that the experimental O−O bond energies for diacyl peroxides are in error. The bond dissociation enthalpies used to derive the O−O bond energies were predicted on the basis of the assumption that a unimolecular one-step O−O bond dissociation was involved. We now present theoretical arguments that the mechanism of O−O bond cleavage in diacyl peroxides is more complex than had been assumed initially. In the present study, a variety of bond dissociation enthalpies at 298 K have been calculated at the G2(MP2), CBS-Q, and G2 levels of theory.

Methodology

There are several general theoretical procedures available to obtain thermodynamical data within chemical accuracy (ca. 2 kcal/mol). One such method, the Gaussian-2 (G2) theory introduced by Pople and co-workers,[10a] was shown to have a mean absolute deviation over a set of 125 experimental energies of 1.21 kcal/mol and constitutes the state-of-the-art calculation for molecules with four to six heavy atoms. The limited applicability computationally of the G2 theory comes with the use of fourth-order Møller−Plesset calculations along with various large basis sets up to 6-311G(2df,p). Later, the G2(MP2) procedure, which limits basis set corrections to second-order Møller−Plesset perturbation theory, was developed to allow the treatment of larger systems and to circumvent this drawback.[10b] The G2(MP2) procedure replicates the set of 125 experimental energies[13] with a mean absolute deviation of 1.58 kcal/mol. Both methods are based upon geometries optimized at the MP2/6-31G* level. At 0 K the G2 and G2(MP2) enthalpies are obtained by addition of the following components:

$$\begin{aligned} E(G2) = {} & QCISD(T)/6\text{-}311G^{**} + MP4/6\text{-}11{+}G^{**} + \\ & MP4/6\text{-}311G(2df,p) - 2^*MP4/6\text{-}311G^{**} + \\ & MP2/6\text{-}311{+}G(3df,2p) - MP2/6\text{-}311G(2df,p) - \\ & MP2/6\text{-}311{+}G^{**} + MP2/6\text{-}311G^{**} + ZPE + HLC \quad (3) \end{aligned}$$

$$\begin{aligned} E(G2(MP2)) = {} & QCISD(T)/6\text{-}311G^{**} + MP2/6\text{-}311{+}G(3df,2p) - \\ & MP2/6\text{-}311G^{**} + ZPE + HLC \quad (4) \end{aligned}$$

In the above equation, ZPE is the zero point vibrational energy and HLC is a high-level correction that provides the G2 energies with the best fit to the set of experimental data. The ZPE and the thermal corrections to the enthalpies are routinely obtained by the scaling of HF/6-31G* frequencies by 0.8929 or MP2/6-31G* frequencies by 0.95, whereas the HLC contribution is given by HLC = $(-4.81n_\beta - 0.19n_\alpha)$ $\times 10^{-3}$ au, where n_β and n_α are the number of β and α valence electrons.

More recently, Petersson, Tensfeldt, and Montgomery developed a series of procedures based upon the complete basis set (CBS) extrapolation.[11] Among these procedures are the CBS-Q, CBS-q, and CBS-4. This methodology performs remarkably well over the test set

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Table 2. O−O Bond Dissociation Enthalpy (kcal/mol) for the Studied Peroxides

	D_0			BDE[a]			bond strength from the lit.
	G2MP2	G2	CBSQ	G2MP2	G2	CBSQ	
1, HO−HO	49.87	48.92	49.20	51.40	50.45	50.72	50.5[b]
2, CH₃O−OH	44.86	43.78	43.49	46.04	44.96	44.68	44.6[c]
3, CH₃O−OCH₃	39.98	38.72	37.77	40.68	39.43	38.52	37.8[c]
4, HC(O)O−OH	47.68	46.94	46.48	49.16	48.41	47.95	
5, N(O)O−OH	21.15	20.28	18.75	22.83	21.96	20.44	
6, CH₃C(O)O−OH	46.41	45.63	45.20	48.32	47.55	47.12	
6′, CH₃C(O)O−OH, anti	42.03			43.36			
7, CF₃C(O)O−OH	47.01			48.90			
8, CH₃C(CH₂)O−OH	21.35			22.73			
9, (CH₃C(O)O)₂	37.28			37.89			30[d]

[a] Bond dissociation enthalpy at 298 K. [b] BDE from ref 8b,c. [c] BDE from ref 2b. [d] Activation energy from ref 17.
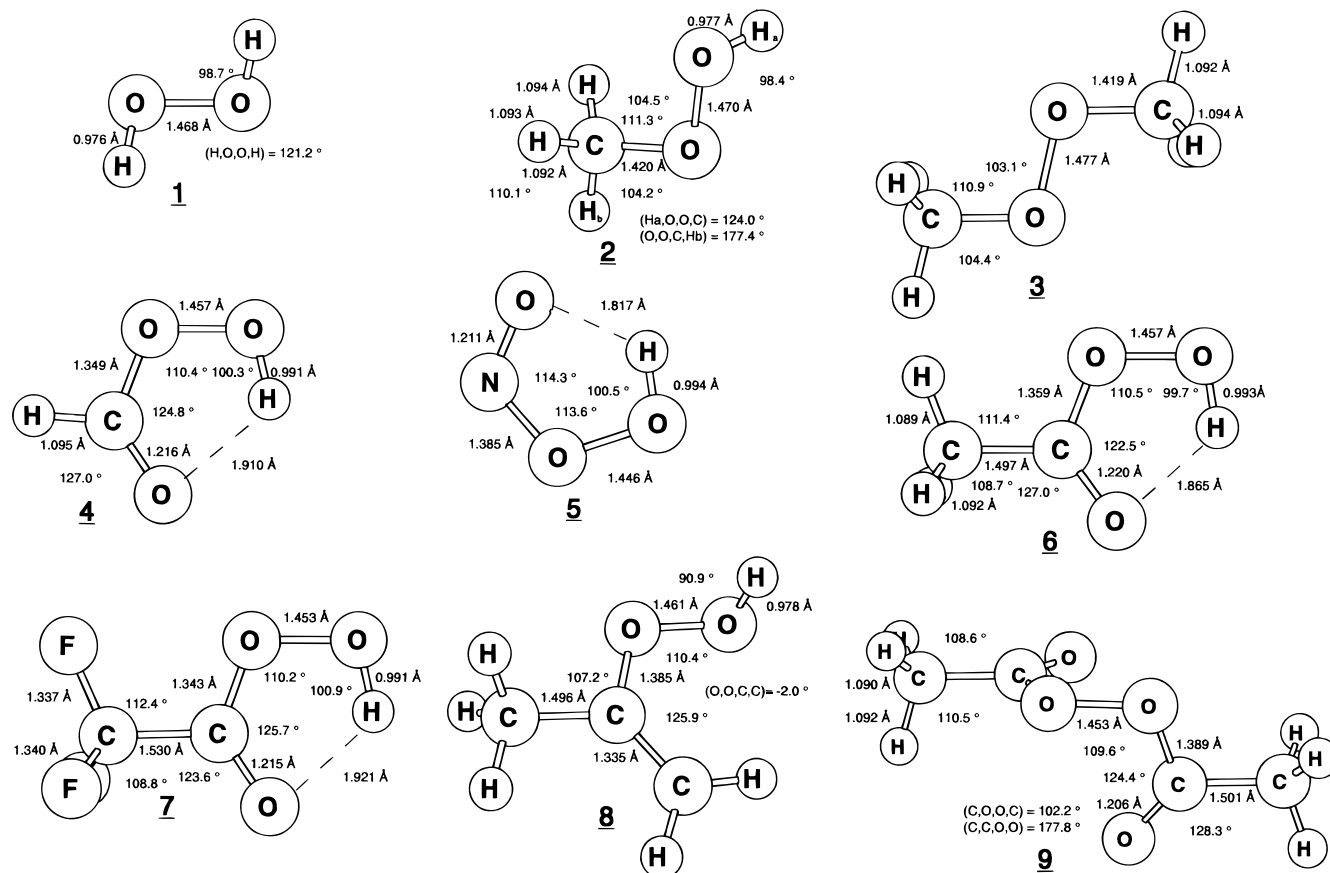
Figure 1. Structures of peroxides, peroxy acids, and diacetyl peroxide optimized at the MP2(full)/6-31G* level of theory.

of experimental data (mean absolute deviation of 1.0, 1.7, and 2.0 kcal/mol, respectively) at a lesser computational cost than G2. These energies are comprised of seven components as described elsewhere.[10,11] The CBS-4 and CBS-q are based upon structures optimized at the HF/3-21G* level whereas CBS-Q utilizes MP2/6-31G† optimization. In brief, the CBS-Q protocol involves the UHF/6-311+G(df,2p), MP2/CBS2, MP4(SDQ)/6-31+G(d(f),d,p), and QCISD(T)/6-31+G† energies at the optimized MP2/6-31G† geometry as well as a HF/6-31G† ZPE and thermal corrections and an empirical correction based upon the 2-electron overlap integrals, the intraorbital interference factors, and the amount of spin contamination.

Molecular orbital calculations were carried out using the Gaussian 94 program system[12b] utilizing gradient geometry optimization.[12c] All geometries for the G2(MP2) and G2 series were optimized without geometry constraints with the 6-31G* basis set using second-order Møller−Plesset perturbation theory (MP2/6-31G*). The thermody-

namical analysis at 298 K was carried out using the rigid rotor and harmonic oscillator approximations.[12d] The D_0 and bond dissociation enthalpy for the O−O bond computed at the G2(MP2), G2, and CBS-Q levels of theory are listed in Table 2. The structures of the nine peroxides described in this study are given in Figure 1. Total energies for individual species are provided in the Supporting Information.

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Results and Discussion

Hydrogen Peroxide. Hydrogen peroxide (**1**) has been studied quite extensively theoretically[1a] because of its relatively small size and perhaps because it is the only peroxide for which accurate enthalpy, entropy, and heat capacity data exist.[2,8] One of our objectives in this study is to establish a level of theory that will give adequate bond dissociation energies for an entire series of peroxides. Consequently, we will provide a comparison among G2, G2(MP2), and CBS methods. One of the more useful criteria to employ is the atomization energies at the various levels of theory. The atomization energies obtained by the G2, G2(MP2), and CBS-Q methods (252.08, 253.49, and 252.51 kcal/mol) are in good agreement with the experimental value of 251.4 kcal/mol using the $D_0(HO-OH)$ obtained by Rizzo et al.[8b] (CBS-4 and CBS-q underestimate the stability of H_2O_2 by 2−3 kcal/mol primarily because of a problem with the HO−OH dihedral angle at the UHF/3-21G* level[11d]). The calculated bond dissociation energies also parallel these trends, and we find that energies built upon MP2/6-31G* or MP2/6-31G† structures (G2, G2(MP2), and CBS-Q) are in excellent agreement with experiment. The experimental D_0 for HO−OH is reported[8b] to be 48.75 kcal/mol, compared to $D_0 = 48.9$ kcal/mol at the G2 level of theory, and the O−O bond dissociation enthalpy is estimated at 50.5 kcal/mol,[8b,c] compared to 50.5 kcal/mol at the G2 level of theory.

In order to assess the effect of an alkyl group upon the O−O bond energy, we also examined methyl hydroperoxide (**2**). There are two competitive electronic states for the methoxy radical (CH_3O). The $^2A'$ and $^2A''$ states are essentially degenerate at the G2 level, with the latter state being 0.73 kcal/mol lower in energy. The predicted BDE for CH_3O-OH is 46.09 kcal/mol at G2(MP2), 45.0 kcal/mol at G2, and 44.7 kcal/mol at CBS-Q. These data are in good agreement with the BDE of 44.6 kcal/mol reported by Benson.[2c] Despite the obvious inductive effect of halogen substituents, the O−O bond in trifluoro- and trichloromethyl hydroperoxide is calculated to be stronger than in methyl hydroperoxide.[26]

Dimethyl Peroxide. The atomization energy of dimethyl peroxide (**3**) at the G2 level (794.7 kcal/mol) lies between that predicted by the G2(MP2) and CBS-Q methods (795.6 and 792.9 kcal/mol), and there is a consistent estimate of the bond energies that range from $D_0 = 40.0$ to $D_0 = 37.8$ kcal/mol for G2(MP2) and CBS-Q. The G2 O−O bond energy of $D_0 = 38.7$ kcal/mol and a bond dissociation enthalpy of 39.4 kcal/mol compare very favorably with the Arrhenius activation energy of $E_a = 37.1 \pm 1.0$ kcal/mol reported by Benson[2b] for the dissociation of dimethyl peroxide. Benson, later, reported[2c] a BDE of 37.8 ± 1.0 kcal/mol.

The pronounced decrease in the O−O bond energy of CH_3O-OCH_3 relative to HO−OH obviously reflects the greater stability of the methoxy radical as compared to HO. The substituent effects on the O−O bond enthalpy appear to be nearly additive since the G2 mean O−O bond enthalpy for dimethyl peroxide and hydrogen peroxide yields a BDE of 45.0 kcal/mol, equal to the G2 value for methyl hydroperoxide.

Peroxyformic Acid and Peroxynitrous Acid. We have used peroxyformic acid (**4**) quite extensively in our mechanistic studies of oxidation of alkenes and related nucleophiles.[9] A potential energy scan of O−O bond elongation in HCO_2-OH suggested that the energetics of oxidation reactions can be treated adequately at the MP4/6-31G*//MP2/6-31G* level of theory since it is consistent with the QCISD(T)/6-31G*//QCISD/6-31G* energy profile out to 2.5 Å. We predicted an O−O bond dissociation energy of $D_e = 50.0$ kcal/mol at the QCISD(T)//QCISD/6-31G* level. The facts that the bond
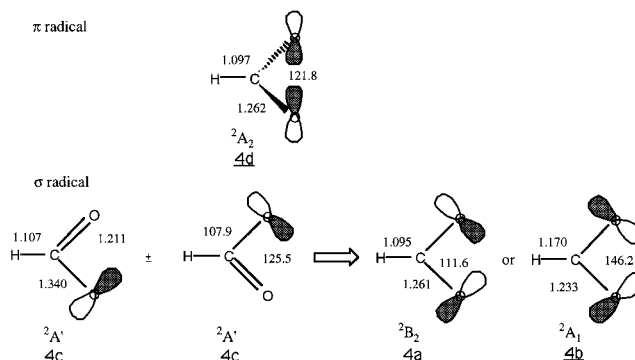

Figure 2. Lowest π state ($^2A_2$) and the two lowest σ states ($^2B_2$ and $^2A_1$) of the formyloxyl radical (MP2/6-31G* geometries). The delocalized σ states can be described by two localized configuration resonance.

energy for HCO_2-OH is comparable to that of HO−OH and is much greater than the widely accepted estimate of 34 kcal/mol for a generic peroxide[1b] or the 38.5 kcal/mol estimated for peroxyacetic acid[3] prompted this systematic study of peroxide bond energies. The O−O bond dissociation enthalpy of the peroxynitrous acid (**5**), which is isoelectronic with peroxyformic acid, is also reported here.

Calculating the O−O bond dissociation energy in peroxy acids is not without difficulties. Alkyloxyl radicals (RCO_2) and NO_2 have a σ ground state, and both σ and π types of radicals share problems of symmetry breaking.[15] The symmetry-breaking problem is best understood in terms of resonance structures, as shown in Figure 2, where the odd electron can be either localized on one of the two oxygen atoms or delocalized over the symmetrical OCO framework. In the case of the formyloxyl radical, this leads to C_s (localized) or C_{2v} (delocalized) wave functions that are not treated equally well by a single determinant *ab initio* method. Indeed, the energy does not change smoothly as the geometry changes from a C_{2v} structure with a symmetry-constrained wave function to a C_s structure with a symmetry-broken wave function. The instability persists even with the use of the Bruckner doubles (BD) model[14] and BD(T). This type of system is of course best treated by multireference calculations. The instability of the C_{2v} σ HCO_2 radical is so acute that only very careful MRCI calculations[15a] managed to yield a proper description of the ground state surface. The $^2B_2$ state is the minimum, lying 2.3 kcal/mol below the $^2A_1$ σ state. Rauk et al.[15b] found that symmetry-constrained single-reference MPn calculations give the same order of states as CASPT2 calculations, which is consistent with the observation that the dominant configuration in the CASSCF and CASPT2 calculations has a coefficient of 0.95. They also found that their QCISD(T) and MRCI calculations gave nearly the same energy separations for the $^2B_2$ and $^2A_1$ σ states and for the $^2B_2$ and $^2A_2$ π states. These facts suggest that the electronic energies for alkyloxyl radicals should be estimated reliably by G2 calculations on the symmetry-constrained wave functions. Furthermore, the present calculations indicate that the basis set additivity assumption in the G2 procedure, eq 3, introduces an error of only 1.04 kcal/mol compared to the QCISD(T)/6-311+G(3df,2p) energy of the $^2B_2$ HCO_2 radical. Negligible change in the energetics is also expected for the use of Bauschlicher's G2(B3LYP/MP2/CC)[10d] method over the traditional G2(MP2) method since the estimate of the O−O bond

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dissociation energy for peroxyformic acid at the CCSD(T)/6-311G*//B3LYP/6-31G* level of theory is within 0.7 kcal/mol of the bond dissociation energy computed at QCISD(T)/6-311G*//MP2/6-31G*.

Experimental data on alkyloxyl radicals are scarce, and the quality of the G2 thermodynamics is difficult to assess. However, reliable experimental data exist on the NO_2 radical, which is isoelectronic with HCO_2. The photodetachment experiment of Ervin et al.[21] gives an electron affinity for NO_2 of 2.273 ± 0.005 eV compared to 2.334 eV at the G2 level of theory, and Armentrout et al.[22] determine the ionization energy of NO_2 to be 9.60 ± 0.03 eV, compared to 9.587 eV at the G2 level of theory; the O—H BDE of nitrous acid (HONO) is 78.8 kcal/mol[8c], compared to 79.7 kcal/mol at the G2 level of theory. We predict a G2 O—O BDE of 22.0 kcal/mol for peroxynitrous acid, N(O)O—OH, in agreement with Hamilton et al. who estimate a BDE of 23.2 kcal/mol.[23b] Considering the traditional success of the G2 level of theory on closed shell molecules and the above agreement for reactions involving NO_2, the symmetry-breaking problem appears to contribute less than 1 kcal/mol error to the energy of NO_2 relative to NO_2^+, NO_2^-, and HONO. Similar behavior can be expected for the isoelectronic HCO_2 and related species.

Calculation of the zero point energies for σ alkoxyl radicals requires some care. Because of the symmetry-breaking problem, the asymmetric vibrations of R—CO_2 are greatly perturbed at the HF or MP2 level of theory. This problem, however, does not occur at the B3LYP level of theory. The zero point energy for the $^2B_2$ σ state is estimated at 12.4 kcal/mol at the B3LYP/6-31G* level of theory,[10c] compared to 12.3 kcal/mol as reported by Rauk et al.[15b] at the CASPT2 level of theory. Bauschlicher et al.[10d] reported that in general zero point energies calculated at the B3LYP/6-31G* level of theory compare very well with experimental data, and they suggest that the frequencies be scaled by 0.98. The B3LYP/6-31G* level of theory was therefore used in the calculation of the zero point energy and thermodynamical properties for the O—O bond dissociation in the peroxy acids and diacyl peroxide.[10e]

As mentioned before, accurate experimental data on akyloxyl radicals are scarce, and comparison with similar thermodynamic cycles as the ones used for NO_2 is not possible. The electron affinity of HCO_2 estimated at the G2 level of theory is EA = 84.2 kcal/mol, compared to 74.5 ± 4.8 kcal/mol[23a] observed experimentally; for CH_3CO_2 the electron affinity estimated at the G2(MP2) level of theory is 78.2 kcal/mol, compared to 77.48 ± 1.2 kcal/mol[23a] observed experimentally. Holmes et al.[24] have determined the heats of formations of HCO_2 and CH_3CO_2 by measuring the appearance potential of R^+ from HCO_2R and CH_3CO_2R. They report ΔH_f° for HCO_2 and CH_3CO_2 of -37.7 ± 3.0 and -51.7 ± 3.0 kcal/mol, respectively, leading to O—H BDEs of 104.7 and 103.8 kcal/mol for HCO_2H and CH_3CO_2H. The calculated O—H BDEs are 114.1 and 113.9 kcal/mol at the G2(MP2) and G2 levels of theory for HCO_2H and 111.3 at the G2(MP2) level of theory for CH_3CO_2H. The disagreement between calculated and experimental results is well outside the typical errors for these calculations and is much greater than for HONO, which is isoelectronic with HCO_2H. Furthermore, a heat of formation of -51.7 kcal/mol for the acetoxyl radical would correspond to a O—O BDE of 25.6 kcal/mol for diacyl peroxide, which is ca. 5 kcal/mol lower than the activation energy in the pyrolysis experiment of Szwarc.[17] These data, along with calculations, suggest that the appearance energy measurements may have overestimated the stability of HCO_2 and CH_3CO_2 by ca. 2–3 kcal/mol.
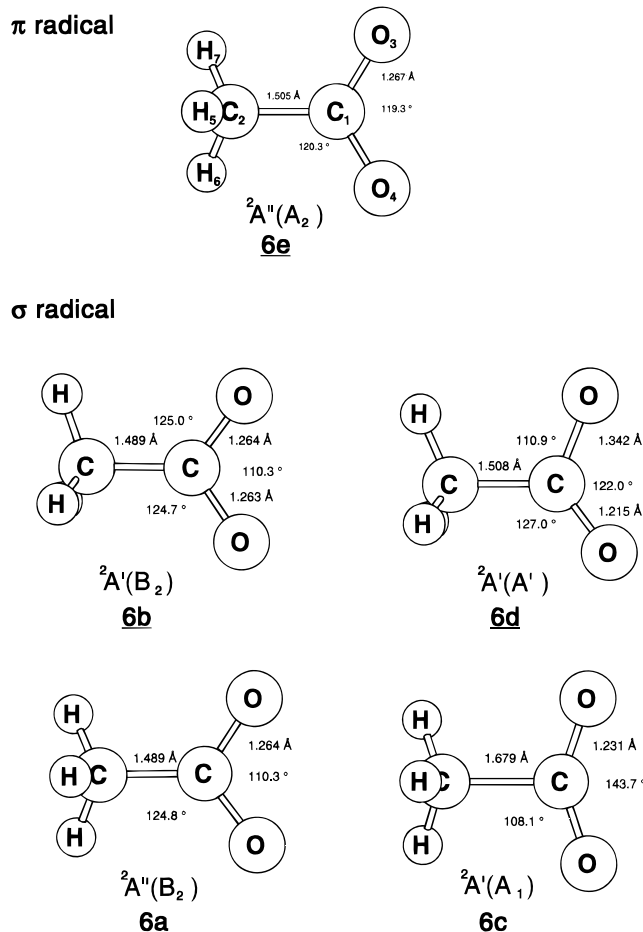

Figure 3. Structures for the acetyloxy radical optimized at the MP2(full)/6-31G* level of theory.

Peroxyacetic and Trifluoroperoxyacetic Acids. Methyl substitution of the formyloxy radical offers a greater number of σ and π radicals due to methyl group rotation in peroxyacetic acid (**6**). To emphasize the analogy with the formyloxy radical, the various radicals found are labeled according to the overall symmetry of the wave function and that of the unpaired electron orbital. The analogs of the $^2B_2$ HCO_2 radical are then identified as $^2A'(B_2)$ and $^2A''(B_2)$, depending on the orientation of the methyl group in the acetoxyl radical (Figure 3). At the G2(MP2) level of theory, the ground state for the acetoxyl radical is found to be the analog of the $^2B_2$ σ state of the formyloxy radical and the methyl group orientation has no effect on the stability of the radical (the energy difference between the $^2A'(B_2)$ and $^2A''(B_2)$ radicals is 0.04 kcal/mol). In the acetyloxy radical, the analog of the $^2A_1$ σ state lies consistently higher than the $^2B_2$ state and the calculated $\sigma-\pi$ ($^2B_2-^2A_2$) energy gap goes from 10.9 kcal/mol for HCO_2 to 14.5 kcal/mol for CH_3CO_2.

The number of basis functions involved with the trifluoroperoxyacetic acid (**7**) precluded our calculating the O—O bond dissociation energy at the G2 level, but we have observed a fairly consistent deviation between the G2 and G2(MP2) bond energies. For the five peroxides computed at both levels we see that the G2(MP2) values are on average 1.0 kcal/mol higher. We therefore predict a G2 bond dissociation enthalpy of 47.6 kcal/mol for peroxyacetic acid and estimate a G2 BDE of 47.9 kcal/mol for trifluoroperoxyacetic acid. On the basis of the energy difference for rotation from the hydrogen-bonded syn conformation to the anti conformation of peroxyacetic acid, the strength of the hydrogen bond for these peroxy acids is evaluated at $\Delta H_{298} = 5.0$ kcal/mol at the G2(MP2) level of theory.

Scheme 1
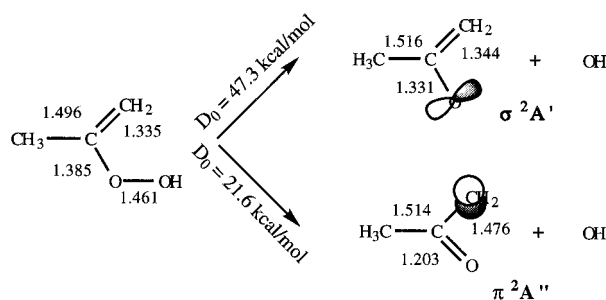
The calculated O−O bond dissociation enthalpy at 298 K in simple peroxy acids, 48.4 kcal/mol for HCO_3H, 47.6 kcal/mol for CH_3CO_3H, and 47.9 kcal/mol for CF_3CO_3H, is virtually unaffected by either methyl or trifluoromethyl substitution of peroxyformic acid. This is a significant observation because trifluoroperoxyacetic acid is clearly one of the most reactive peroxy acids in the arsenal of the synthetic chemist.[16] For example, it is used to oxidize aromatic rings and is often employed successfully in situations where essentially "no reaction" is observed with peroxyacetic acid. Since the O−O bond dissociation energy is virtually unaffected by electron-withdrawing substituents, the origin of its increased reactivity must now be attributed solely to the increased stability of the developing $CF_3CO_2^-$ anion resulting from heterolytic O−O bond cleavage. This concept is consistent with transition structures that we have located for alkene epoxidation and oxidation of a series of nucleophiles bearing heteroatoms.[9]

Isopropenyl Hydroperoxide. To illustrate the importance of orbital interactions with O−O bond dissociation, we include isopropenyl hydroperoxide (**8**) in this study. It is well known that carbon free radicals are generally more stable than open shell oxygen-containing species. Indeed, the predicted O−O bond energy in isopropenyl hydroperoxide is consistent with this suggestion. This problem is, however, further complicated by the fact that the ground state for the isopropenoxyl radical is the π state with the majority of the spin residing on the carbon (Scheme 1). We predict a homolytic O−O bond cleavage endothermicity of only $D_0 = 21.6$ kcal/mol relative to the π state of the radical. The O−O bond energy relative to the higher lying σ state is predicted to be $D_0 = 47.3$ kcal/mol.

The homolytic O−O bond cleavage process in **8** correlates with the π state of the radical whenever the C−O−O−H torsion angle is allowed to open. Thus, one would predict that isopropenyl hydroperoxide would react by a homolytic process and would be a very labile oxygen donor. By contrast, a peroxy acid exists as an intramolecular hydrogen bond structure, and the intramolecular 1,4 proton shift associated with alkene epoxidation affords a neutral carboxylic acid leaving group, resulting in greatly diminished obligatory charge separation during heterolytic O−O bond breaking. In the transition state the peroxy acid moiety remains planar, and any homolytic character would correlate with the lower lying ground state σ radical. On the basis of the exceptionally low O−O bond dissociation energy, it is not surprising that vinyl and phenyl hydroperoxides are not commonplace synthetic reagents. These data also point out that, in order to predict the bond dissociation energy of an O−O bond that is adjacent to a multiple bond, it is essential that consideration be given to orbital interaction effects associated with O−O bond cleavage and the relative stability of the σ and π electronic states of the resulting delocalized oxygen free radical.

Diacetyl Peroxide. The internal consistency between the peroxides treated thus far and the excellent agreement between theory and experiment for hydrogen peroxide strongly suggested to us that the estimated O−O bond strength for diacyl peroxides of 30 ± 1 kcal/mol was simply too low.[1b] Indeed, we predict an O−O bond dissociation enthalpy of 37.9 kcal/mol for diacetyl peroxide (**9**) at the G2(MP2) level. Applying the same correction as for trifluoroperoxyacetic acid (1.0 kcal/mol), the G2 bond dissociation enthalpy at 298 K is 36.9 kcal/mol. The near additivity of substituent effects still holds. Taking the mean of this bond strength and that predicted for hydrogen peroxide would give an estimated BDE of 43.7 kcal/mol for peroxyacetic acid, without a hydrogen bond, identical to the 43.4 kcal/mol computed at G2(MP2) for *anti*-peroxyacetic acid. Adding ΔH_{298} = 5.0 kcal/mol for hydrogen bonding gives a BDE of 48.7 kcal/mol, compared to 47.6 kcal/mol at G2 for hydrogen-bonded *syn*-peroxyacetic acid. From these data, it should be concluded that the concept of using the mean value of ZO−OZ and YO−OY to estimate the ZO−OY bond energy is valid to within 1 kcal/mol, provided that contributing effects such as hydrogen bonding are taken into account.

Although the G2 and CBS methods have performed remarkably well for predicting bond dissociation energies, the discrepancy of ∼7 kcal/mol between experiment[17] and theory for diacetyl peroxide remains a concern. It should also be noted that the G2(MP2) and Szwarc's experimental estimates of the atomization energy of diacetyl peroxide differ by 13.2 kcal/mol whereas G2(MP2) and Benson's group additivity estimates differ by only 3.2 kcal/mol. This great difference between Szwarc's and Benson's estimates for the stability of **9** is even more surprising since an agreement is found for dipropionyl and dibutyryl peroxides. The lack of experimental data on alkyloxyl radicals and diacyl peroxides makes it impossible to accurately assess the G2(MP2) estimate.

The value of 30 ± 1 kcal/mol for the bond dissociation of diacetyl peroxide reported by Szwarc[17] was based upon the assumption that this thermal decomposition can be represented by eq 5, with the first stage being the rate-limiting factor. The

$$(CH_3CO_2)_2 \rightarrow 2CH_3CO_2 \rightarrow 2CH_3 + 2CO_2 \qquad (5)$$
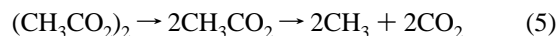
experimental decomposition of diacetyl peroxide was thus viewed as a unimolecular decomposition. He concluded that the observed activation energy of $E_a = 29.5$ kcal/mol represented the O−O bond dissociation energy. Szwarc never observed any product other than ethane, CO_2, and methane, and the reaction kinetics was demonstrated to be of first order. The presence of methane was attributed to reaction of methyl radicals with the carrier gas (toluene). The loss of diacyl peroxide by any other reaction pathway was thus ruled out, and the only possible remaining source for the discrepancy in the bond dissociation energy is to be found in the dissociation mechanism itself. Later studies focusing on substituent effects showed that both the rate and mode of decomposition of diacyl peroxides are influenced by the nature of the R group;[1c,d] i.e., either one-bond fission (eq 5) or simultaneous fission of the O−O bond and one or both of the R−C bonds could be involved. Also, the facile ^{18}O scrambling observed in diacyl peroxides hints of a complicated bond dissociation process. Although Shine[18] observed complete ^{18}O scrambling in diacetyl peroxide, he also concluded that its decomposition proceeded by one-bond fission. This conclusion was also supported by hydrogen secondary kinetic isotope effect studies.[1d] The decomposition process is

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(17) (a) Jaffe, L.; Prosen, E. J.; Szwarc, M. *J. Chem. Phys.* **1957**, *27*, 416. (b) Rembaum, A.; Szwarc, M. *J. Am. Chem. Soc.* **1954**, *76*, 5975.
(18) Shine, H. J.; Hoffman, D. M. *J. Am. Chem. Soc.* **1961**, *83*, 2782.

Scheme 2

[3,3]

[1,3]
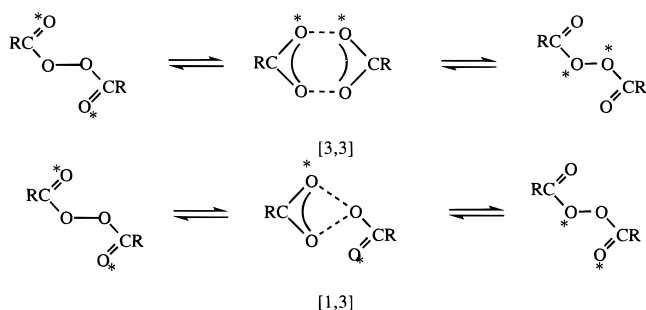
further complicated by the suggestion of Goldstein[19] that there are two pathways for ^{18}O scrambling, i.e., via [3,3] or [1,3] rearrangements (Scheme 2). Both [3,3]-sigmatropic and [1,3]-sigmatropic pathways have been proposed for oxygen scrambling in dialkyl peroxides. Goldstein[19] also reported that the dissociation of the peroxide, the [3,3] rearrangement, and the [1,3] rearrangement have essentially the same enthalpy of activation of ca. 30 kcal/mol ($\Delta H^{\ddagger} = 30.0 \pm 0.8$ kcal/mol for the dissociation, $\Delta H^{\ddagger} = 29.7 \pm 0.5$ kcal/mol for the [3,3] rearrangement, and $\Delta H^{\ddagger} = 29.4 \pm 0.2$ kcal/mol for the [1,3] rearrangement), the difference in rates being due to the frequency factor ($\Delta S^{\ddagger} = 7.0 \pm 2.5$ cal/(mol K), $\Delta S^{\ddagger} = 3.3 \pm 1.5$ cal/(mol K) and $\Delta S^{\ddagger} = 1.2 \pm 0.7$ cal/(mol K), respectively). Another point of interest in Goldstein's study[19] is the fact that the activation entropies are positive in contrast to the analogous Cope reaction which typically exhibits a negative entropy. From these data and the fact that RCO_2 radicals could not be trapped (thus ruling out gas phase recombination), it can be inferred that these reactions go through a very loose transition state consistent with the minimization of lone pair−lone pair repulsion. Collectively, these data suggest that the dissociation process is far more complex than a simple homolytic cleavage of the O−O bond. Even if multiple-bond fission processes seem unlikely for a simple diacyl peroxide such as diacetyl peroxide, a mechanism similar to the one represented by eq 6 could

(6)
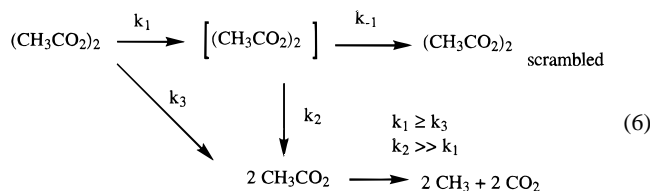
explain the low activation energy found experimentally along with the evidence of scrambling. The rate-limiting process in that case would not be the simple fission of the O−O bond (k_3) but could invoke the formation of an intermediate or transition state (k_1) that can either afford scrambling of the ^{18}O label (k_{-1}) or partition into two CH_3CO_2 radicals (k_2).

In an effort to illustrate this point, we explored several areas of the potential energy surface of $(HCO_2)_2$ and $(CH_3CO_2)_2$. Regions of high symmetry were chosen to reduce computational cost and to contain problems due to symmetry breaking. The various saddle points[20] (SP) found are represented in Figure 4. We first examined the overall reaction pathway for the dioxa-Cope rearrangement of diacetyl peroxide (**SP-1**, Figure 4). Since this type of [3,3]-sigmatropic rearrangement by necessity

involves two higher lying π-type radicals, we anticipated a relatively high activation barrier (the O−O bond fission of diacetyl peroxide yielding two π CH_3CO_2 radicals is endothermic by $D_e = 100.6$ kcal/mol and $D_e = 74.1$ kcal/mol at the MP2/6-31G* and G2(MP2) levels, respectively). MP2/6-31G* optimization of the Cope-type structure features a O−O bond length of 2.05 Å and shows no C−C or C−H elongation compared to the $^2A_2$ radical. **SP-1** lies 47.3 kcal/mol above diacetyl peroxide and 2.4 kcal/mol above isolated products, two $^2A''(B_2)$ CH_3CO_2, at the MP2/6-31G* level of theory. Likewise, the corresponding transition state for diformyl peroxide lies 2.7 kcal/mol above the isolated products at the MP2/6-31G* level. At the G2(MP2) level, **SP-1** is found 11.0 kcal/mol above the energy of two isolated formyloxyl radicals (HCO_2). Since σ alkyloxyl radicals are more stable than π, a more facile way to achieve ^{18}O scrambling via a [3,3] rearrangement is via **SP-2**. The O−O bonds (2.09 Å) in this σ-type structure are slightly longer than those in **SP-1**, the C−C bonds are longer, and the O−C−O angle is wider. However, these structures are greatly affected by the symmetry-breaking problems found in σ alkyloxyl radicals, and the MP2/6-31G* calculations vastly overestimate the stabilities for **SP-2** (49.3 and 38.3 kcal/mol more stable than the isolated radicals, respectively). However, this seems to affect the optimized geometry only moderately, and similar structures are found at the MP2/6-31G* and QCISD/6-31G* levels of theory. At the MP2/6-31G* level of theory, **SP-2** for diformyl peroxide features C−H bonds 0.028 Å smaller, O−O bonds 0.0038 Å smaller, O−C−O angles 0.91° larger, and C−O bonds 0.015 Å larger than at the QCISD/6-31G* level of theory. These slight differences in optimized geometry translate into an enthalpy difference for **SP-2** of 1.1 kcal/mol between the G2(MP2) energies computed using the MP2/6-31G* and QCISD/6-31G* optimized structures. At the G2(MP2) level **SP-2** for diformyl peroxide and diacetyl peroxide are found to be 12.9 and 0.8 kcal/mol, respectively, more stable than two radicals. The enthalpy difference at 298 K between **SP-2** and the isolated σ acyloxyl radicals is estimated at 13.3 and 0.53 kcal/mol, respectively, using vibrational frequencies calculated at the B3LYP/6-31G* level of theory.

The ^{18}O scrambling via a [1,3] rearrangement can potentially also be achieved via a structure such as **SP-3**. **SP-3** features a high degree of symmetry and has the two OCO planes at 90° to each other. **SP-3** could also be involved in the [3,3] rearrangement mechanism since it correlates with **SP-2** by rotation along the R−C···C−R axis. **SP-3** is found to be 7.3 kcal/mol less stable than **SP-2** ($\Delta H_{298} = 6.9$ kcal/mol using B3LYP/6-31G* frequencies) or 5.6 kcal/mol more stable than two formyloxyl radicals at the G2(MP2) level of theory.

Both **SP-2** and **SP-3** are accompanied on the MP2/6-31G* surface by structures **SP-4** and **SP-5** that closely resemble two very loosely bonded $^2A_1$ radicals. The presence of these structures makes the study of the rearrangement of diacyl peroxides very similar to the study of the Cope rearrangement of 1,5-hexadiene.[25] If the analogy with the [3,3] rearrangement of 1,5-hexadiene is carried further, the presence of the pair of structures **SP-2/SP-4** and **SP-3/SP-5** is likely to be an artifact of the method, the true saddle point lying in between.[25b]

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(20) Frequencies calculated at a higher level of theory than B3LYP/6-31G* would be needed to characterize these structures accurately.

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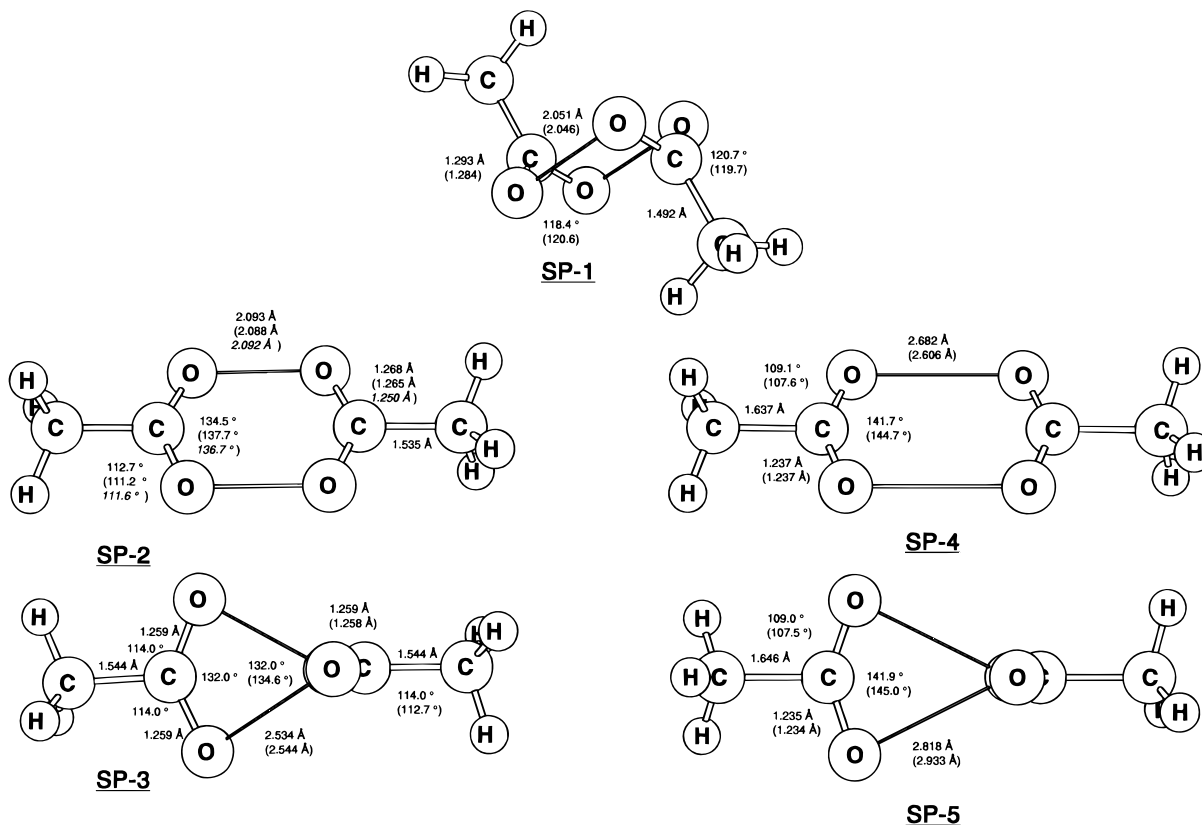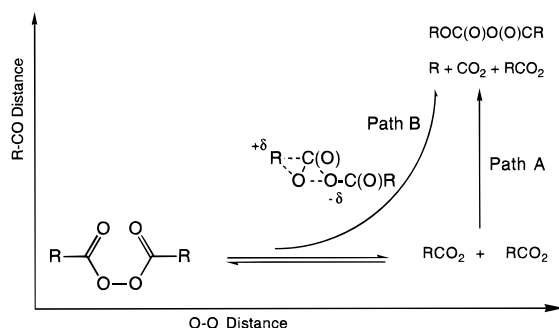
Figure 4. Saddle points for oxygen scrambling in diacetyl peroxide optimized at the MP2(full)/6-31G* level of theory. Values for diformyl peroxide $(HC(O)O)_2$ are given in parentheses (QCISD/6-31G* optimized structure for **SP-2** given in italics).

Scheme 3

Another point of interest in the [1,3] rearrangement of diacyl peroxides is the possible involvement of a structure such as the one represented in Scheme 2 with the OCO planes perpendicular to each other but with the migrating oxygen atom lying in the RCO_2 plane. This structure is very attractive since it is likely to be close to the least motion path for the homolytic cleavage of the O–O bond in diacyl peroxide considering that the O–O bond lies very close to the RCO_2 plane (cf. Figure 1). However, no stationary point could be found on this part of the C_s surface which is dissociative, leading to R + CO_2 + RCO_2. Thus, this suggests that passage from the C_1 to the C_s surface would involve a branching point because of symmetry. The importance of such a structure was recently suggested by Fujimori et al.[1f] in a study of the relative reaction rates for scrambling and dissociation in cycloalkylformyl peroxides; depending upon the nature of the R group, the decomposition of the peroxide is presumed to go through either path A or path B (Scheme 3).

The size of the molecule and the acuteness of the instability problems prevent us from more accurately studying these structures at this moment, but they remain the subject of further study. Nevertheless, their presence supports the possibility of a loose transition structure or intermediate in the dissociation mechanism. The overall weight of the evidence suggests either that a bond energy of 30 kcal/mol for simple diacyl peroxides is too low and that the bond dissociation process is more complicated than a simple and direct one-bond fission or that the symmetry-breaking problem associated with HCO_2 is significantly greater than for NO_2, causing an error of about 3–4 kcal/mol for each alkyloxyl radical.

In summary, G2 and CBS estimates of the average O–O bond energy for the series of peroxides studied suggest that the anticipated average bond energy should be increased from 34 to ~45 kcal/mol. This study further points out the importance of orbital correlation of the ground state of the peroxide with the products of O–O bond cleavage and suggests that processes more complicated than simple one-bond fission may be involved in the O–O bond homolysis in diacyl peroxides.

Supporting Information Available: Cartesian coordinates of structures optimized at the MP2/6-31G* level of theory and total energies for individual species (12 pages). See any current masthead page for ordering and Internet access instructions.

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