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Homolytic Bond-Dissociation in Peroxides, Peroxyacids, Peroxyesters and Related Radicals: *ab-initio* MO Calculations .

Rois Benassi* and Ferdinando Taddei

Dipartimento di Chimica, Università, Via Campi 183, 41100 Modena, Italy.

Abstract: Homolytic dissociation energies for different cleavage paths in a number of peroxides, peroxyacids and peroxyesters and in the radicals formed from these molecules, were calculated from the total MO *ab-initio* molecular energies of the chemical species involved in the bond cleavage reactions and compared with experimental values, where known.

Compounds containing the O-O linkage are very important key species in several chemical reactions, both because they are often crucial intermediates in the oxidation of organic compounds, in view of their use for producing free radicals and for oxidation reactions.

Organic peroxides are widely employed in several branches of synthetic chemistry[1] and have been found to occur as important intermediates in many biological processes[2]. Peroxyacids have found extensive application in the oxidation of organic compounds[1] (mainly olefins, ketones and sulphur compounds) and peroxyester are in most cases very efficient initiators of radical reactions[3]. Hydroperoxides are explosives and do not survive at moderately high temperatures; the same is true for peroxyesters derived from primary and secondary alkyl hydroperoxides [1]. The thermal decomposition of peroxyesters is commonly interpreted as proceeding through initial O-O bond breaking followed by fast decarboxylation of the carboxylate radical[4].

Knowledge of the chemical and physical properties of these molecules thus seems essential in order to elucidate the reaction mechanism of chemical processes occurring at atmospheric and stratospheric level, in biochemistry and metabolism.

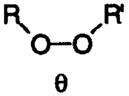
The energy required for homolytic dissociation of the O-O bond in different molecules was estimated by us in preceding papers [5-7] from heats of formation of molecules and of the free radicals formed. These results were obtained by estimating heats of formation through empirical formulations which were based on group contribution additivity, and from schemes introducing total molecular energies from MO *ab-initio* calculations[8,9] which try to overcome the problem of employing energies at correlated levels. Besides the poor approximation level represented, the results are justified only in view of applying these approaches to large molecular systems. Furthermore, the MO energies of radicals from SCF calculations should be employed with caution, especially when localisation of the unpaired electron and symmetry breaking [10] is likely to occur, leading to wrong estimates [6,7] of heats of formation.

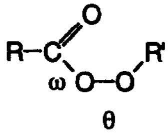
In order to evaluate bond dissociation energies from a more rigorous theoretical approach, total energy changes (DE) for the reaction (1) are evaluated in the present study at the UMP2/6-31g* level.

$$A\text{-}B \rightarrow A\cdot + B\cdot \qquad (1)$$

In order to obtain reliable energy values they should be referred to the most stable conformation of the molecules and radicals. This aim is fulfilled by minimizing the total energy with respect to all geometrical parameters. Furthermore, in order to verify whether the total energy change associated with reaction 1 is really assimilable to a bond dissociation energy, the molecular energy along the bond breaking coordinate in a number of the molecules studied should also be followed.

The compounds examined are:





R = H, CH_3
R'= H, CH3

together with the radicals formed by breaking the O-O, R-O, R-C and O-R bonds.

COMPUTATIONAL METHOD

All *ab-initio* MO computations reported in this paper were performed with the GAUSSIAN-92[11] series of programs on an AIX/RS6000 elaborator. Standard 6-31g* basis sets were employed. It was concluded in previous studies[5,12] that this set satisfactorily reproduces conformational and geometrical features of molecules containing the X-X bond.

The geometries of conformational minima of molecules and radicals were fully optimised with the gradient method at UMP2/6-31g* level (UMP2/6-31g*//UMP2/6-31g*) with all electrons correlated. The corresponding energy values are indicated as EUMP2. Harmonic vibrational frequencies were obtained analytically in order to calculate the Zero-Point-Vibrational Energy (ZPE) and to verify the exact nature of the minima.

In order to remove contamination from higher spin states, spin-projection operators were applied and the energies obtained at this level were labelled EPMP2[13,14]. This step has to be performed since spin contamination may cause significant distortion [13,14] of bond dissociation energy profiles and, in addition to this, the perturbation level introduced for electron correlation does not completely reduce spin contamination.

RESULTS AND DISCUSSION

Geometries and Vibrational Frequencies

Point group, electronic state, total energy at MP2 and PMP2 level and relative energy values, when two conformational minima are present, are collected in Table 1. Geometrical optimised parameters and, when available, experimental data are reported in Table 2. The *cis* and *trans* labelling refers to the conformation around the C-O bond (ω represents the twist angle around this bond).

Tab. 1

Point group, Electronic state, Total energies (a.u) and relative energies (kcal/mol) of rotational ground state conformers

			Point group	Electronic state	EUMP2 a.u.	PMP2 a.u.	ΔE kcal/mol
I	HOOH		C_2	$X\,^1A$	-151.134918		
II	CH_3OOH		C_1	$X\,^1A$	-190.29974		
III	CH_3OOCH_3		Ci	$X\,^1A_g$	-229.465520		
IV	HC(O)OOH	*cis*	C_s	$X\,^1A'$	-264.187820		
		trans	C_1	$X\,^1A$	-264.182734		3.19
V	$CH_3C(O)OOH$	*cis*	C_s	$X\,^1A'$	-303.371855		
		trans	C_1	$X\,^1A$	-303.363328		5.35
VI	$HC(O)OOCH_3$	*cis*	C_1	$X\,^1A$	-303.350044		
		trans	C_1	$X\,^1A$	-303.348939		0.69
VII	$CH_3C(O)OOCH_3$	*cis*	C_1	$X\,^1A$	-342.532678		
		trans	C_1	$X\,^1A$	-342.529589		1.94
VIII	HOO		C_s	$X\,^2A''$	-150.502365	-150.504712	
IX	CH_3OO		C_s	$X\,^2A''$	-189.668018	-189.670404	
X	HO		$C_{\infty v}$	$X\,^2\Pi$	-74.523206	-75.524753	
XI	CH_3O		C_s	$X\,^2A'$	-114.693092	-114.695002	
XII	HC(O)OO	*cis*	C_s	$X\,^2A''$	-263.538258	-263.540611	
		trans	C_s	$X\,^2A''$	-263.541186	-263.543686	-1.92
XIII	$CH_3C(O)OO$	*cis*	C_s	$X\,^2A''$	-302.723031	-302.725310	
		trans	C_s	$X\,^2A''$	-302.723100	-302.725753	-0.28
XIV	HC(O)O		C_{2v}	$X\,^2B_2$	-188.578111	-188.584285	
XV	$CH_3C(O)O$		C_1	$X\,^2A$	-227.765067	-227.771126	
XVI	C(O)OOH	*cis*	C_1	$X\,^2A$	-263.531292	-263.535472	
		trans	C_1	$X\,^2A$	-263.532013	-263.533687	1.12

XVII	$C(O)OOCH_3$	*cis* C_1	$X\,^2A$	-302.698320	-302.702478	
		trans C_1	$X\,^2A$	-302.697983	-302.700646	1.15
XVIII	HC(O)	C_s	$X\,^2A'$	-113.540332	-113.542776	
XIX	$CH_3C(O)$	C_s	$X\,^2A'$	-152.722652	-152.724878	
	CH_3	D_{3h}	$X\,^2A_2''$	-39.673031	-39.675037	
	O_2	$D_{\infty h}$	$^3\Sigma_g^-$	-149.954320	-149.96037	
	CO_2	$D_{\infty h}$	$^3\Sigma_g^-$	-188.118363		

Tab.2

Optimized and Experimental Geometrical Parameters Lengths (Å) and Angles (deg)

		O-O	O-H	O-Csp^3	O-Csp^2	C=O	H-Csp^2	Csp^3-Csp^2	Csp^3-H
I		1.468	0.976						
		(1.464)[a]	(0.965)						
II		1.469	0.976	1.420					1.092; 1.094; 1.093
		(1.443)[b]	(0.967)	(1.437)					
III		1.477		1.419					1.091; 1.093; 1.093
		(1.457)[b]		(1.420)					
IV	*cis*	1.457	0.991		1.349	1.215	1.095		
		(1.445)[c]	(1.014)		(1.332)	(1.208)	(1.090)		
	trans	1.467	0.978		1.376	1.204	1.098		
V	*cis*	1.458	0.992		1.360	1.220		1.498	1.092; 1.092; 1.089
		(1.47)[d]	(1.00)		(1.33)	(1.22)		(1.49)	(1.09)
	trans	1.473	0.978		1.385	1.211		1.498	1.091; 1.091; 1.089
VI	*cis*	1.460		1.427	1.369	1.205	1.100		1.092; 1.092; 1.092
	trans	1.469		1.427	1.375	1.205	1.098		1.092; 1.092; 1.093
VII	*cis*	1.459		1.426	1.382	1.209		1.505	1.091; 1.093; 1.089[e] 1.093; 1.092; 1.092[f]
	trans	1.479		1.426	1.382	1.212		1.499	1.091; 1.091; 1.089[e] 1.094; 1.092; 1.091[f]
VIII		1.325	0.983						

IX		1.311		1.451					1.089; 1.089; 1.089
X			0.979						
			(0.970)^g						
XI				1.387					1.101; 1.096; 1.010
XII	*cis*	1.338			1.419	1.195	1.097		
	trans	1.332			1.425	1.194	1.098		
XIII	*cis*	1.332			1.442	1.198		1.496	1.092; 1.092; 1.089
	trans	1.326			1.445	1.200		1.495	1.091; 1.091; 1.089
XIV					1.260	1.260	1.095		
XV					1.264	1.264		1.489	1.091; 1.091; 1.093
XVI	*cis*	1.433	0.978		1.345	1.191			
	trans	1.462	0.979		1.354	1.195			
XVII	*cis*	1.434		1.428	1.350	1.193			1.092; 1.091; 1.093
	trans	1.465		1.426	1.353	1.196			1.092; 1.091; 1.093
XVIII						1.191	1.123		
						(1.175)^h	(1.125)		
XIX						1.196		1.513	1.093; 1.092; 1.092
CH_3									1.078
									(1.079)^g
O_2		1.246							
		(1.208)^g							
CO_2					1.178				
					(1.162)^g				

	H-O-O	O-C=O	H-C-O	Csp^3-C-O	O-Csp^3-H	H-C-C	Csp^3-O-O	Csp^2-O-O
I	98.66							
	(99.4)							
II	98.40				104.23; 111.29		104.46	
	(99.6)				110.91		(105.7)	
III					104.40; 110.96		103.19	
					110.96		(105.2)	
IV	100.32	124.80	108.22					110.48
	(98.9)	(124.4)	(109.0)					(110.7)
	98.32	120.15	111.95					107.00

V	99.69 (96.6)	122.45		109.97 (110)		109.97; 109.97; 108.59 (108.8)		110.68 (112.9)
	97.06	115.52		117.64		110.58; 110.60 107.42		110.15
VI		127.65	105.58		110.84; 103.33; 111.06		106.07	109.97
		120.46	111.86		110.71; 103.62; 111.17		104.65	107.13
VII		125.05		107.59	110.85; 103.48; 111.05	111.14; 109.04; 108.63	106.08	110.20
		115.86		117.44	110.88; 110.88; 103.69	110.45; 110.45; 107.55	102.60	109.92
VIII	104.55							
IX					105.05; 108.97 108.97		110.13	
X								
XI					104.81; 112.41; 112.41			
XII		125.75	105.75					111.82
		120.21	109.68					109.05
XIII		122.88		107.12		109.81; 109.81; 109.00		112.01
		115.05		116.02		110.63; 110.63; 107.23		112.83
XIV		111.53	124.24					
XV		110.30		124.85		109.76; 109.76; 109.17		
XVI	99.92	131.65						110.18
	95.58	124.21						107.33
XVII		131.29			110.72; 103.48; 110.92		106.34	110.28
		107.38			110.84; 103.39; 111.07		124.69	105.23
XVIII			123.32 (125.5)					
XIX				127.49		111.14; 108.64; 108.64		

	ϑ	ω	H-C-C-O	O-O-C-H	C-C-O-O
I	121.20				
	(111.8)				
II	124.00			177.40; -63.71;	
	(114.0)			58.98	
III	180.			180.0; -61.30; 61.30	
	(119.)				
IV	0.	0.		180.	
	-126.62	-178.18		1.65	
V	0.	0.	59.48; -59.48; 180.		180.0
	-146.09	-179.67	60.69; -58.20; -178.74		-0.19
VI	92.99	-5.28	175.54	57.69; 175.78;	
	120.42	178.45	-1.30	293.71	
				58.85; 177.12;	
				295.75	
VII	92.28	-6.96	57.87; 175.95; 293.92	38.53; -80.69;	172.55
	179.53	180.0	-61.51; 61.45; 179.98	160.34	0.00
				59.34; -59.40;	
				179.97	
VIII					
IX				180.00; -60.63;	
				60.63	
X					
XI					
XII		0.0		180.0	
		180.0		0.0	
XIII		0.0	59.21;-59.21; 180.0		180.0
		180.0	59.53; -59.53; 180.		0.0
XIV					
XV			30.40; 152.01; -88.78		
XVI	-113.32	2.12			
	120.39	177.59			

XVII	95.44	-4.50		57.57; 175.94; -66.10
	104.01	177.26		58.04,;176.23; -65.44
XVIII				
XIX			0.0; -121.61; 121.61	

a) Rif. 15; b) Rif. 16; c) Rif.17; d) Rif. 18; e) Referred to C-CH_3; f) Referred to O-CH_3; g) Rif.8; h) Rif. 19

In the peroxides (I-III) introduction of electron correlation improves the agreement of calculated and experimental bond lengths and bond angles with respect to 6-31g* results[5]. The dihedral angle θ is the parameter least accurately reproduced. This is very likely related to the flat energy profiles associated with the internal rotation around the O-O bond and so the calculated values are strongly dependent on the basis set employed [20]. Attempts to improve the agreement between calculated and experimental dihedral angles were not performed in the present study since the search for the correct dihedral angle in the flat minimum should correspond to small changes in the total molecular energy and this does not significantly influence the aim of determining bond dissociation energies. Implementation of the calculation level makes computer time requirements prohibitive for molecules of larger molecular size and moreover in calculating the energy balance of reaction 1, errors due to the choice of basis set should be of the same order of magnitude for the various molecular species involved.

For peroxyacids IV, V two conformational minima, corresponding to the *cis* and *trans* orientation relative to rotation around C-O bond (angle ω), were found : more exactly, they should be labelled *cis-cis* and *trans-skew,* if the orientation around the O-O bond (angle θ) is also considered. For both peroxyacids, the most stable conformer turns out to be that of *cis* type (Tab 1), in agreement with experimental evidence[17, 18]. For this conformer the calculated geometrical parameters, too, are in good agreement with the corresponding experimental ones: both molecules show a fully planar structure stabilized by an intramolecular hydrogen bond.

For peroxyacids and peroxyesters the same relative order of conformer stability was found , yet the ΔE is smaller: for the latter compounds the presence of intramolecular hydrogen bond in peroxyacids should cause this different behaviour. This conclusion is supported by analysis of the geometrical parameters as well: the C=O bond is in fact systematically longer, the C-O bond shorter and the O-C=O bond angle significantly smaller in peroxyacids with respect to peroxyesters as expected from the presence of intramolecular hydrogen bond in the former compounds.

The data for radical species reported in Tables 1 and 2 cannot be compared with experimental results, since these are lacking. Nevertheless a number of features which can be related to their chemical behaviour is worth mention. For most of these radicals the symmetry of the electronic state, reported in Tab. 1, is the same as that found in a previous study [7] at a lower level of calculation, except for XIV, XV and XVI. In derivatives XIV and XV the problem of symmetry breaking [10] occurs: MO results limited to the SCF treatment of the lowest electronic state [7] show that asymmetric distortion occurs unless molecular symmetry is forced[21]. The problem was tackled [10] for the radical XIV by making use of a series of multiconfigurational SCF (MCSCF) expansions: the ground state at this level turns out to be of σ type and in the optimised structure the two C-O bond lengths are equal. Our calculations at MP2/6-31g* level show that the results are in agreement with those from the MCSCF approach both as regards the symmetry of the electronic ground state and the equilibrium geometry. In radical XV, the introduction of a methyl group lowers the molecular symmetry ($C_{2v}\rightarrow C_s$) and, in the equilibrium structure, small twists of the C-H bonds of the methyl group from the molecular plane further lower the molecular symmetry (from C_s to C_1), nevertheless the two C-O bond lengths remain equal. In the total energy hypersurface a structure with two different C-O bond lengths can be located as a minimum, yet this structure is less stable than that with two equal C-O bonds (3.17 and 5.17 kcal/mole for XIV and XV referring to EUMP2 energies, 5.11 and 7.71 kcal/mole referring to EPMP2 ones).

Symmetry distortion also occurs in XI due to the Jahn-Teller effect [22].

In the radicals, which could exhibit a possible *cis-trans* isomerism, the more stable conformer is of the same type as that found in the molecule from which, in principle, the radicals could have originated, at the level of EPMP2 energies. This is not the case with the radicals XII and XIII: for these molecules the *trans* form turns out to be the more stable one. The higher ΔE for XII should be caused by favourable vicinal H···O interactions, where the O atom is that of the carbonyl group [23].

The O-O bond lengths in derivatives VIII, IX and XII, XIII are shorter than those in the molecules I - VII : this feature could be associated with a marked tendency of these radicals to lose a oxygen molecule. The same conclusion could be reached by pointing out that in radicals XII, XIII the O-C_{sp^2} bond is longer and the C=O bond length shorter than in compounds IV - VII: the latter bond distance reaches a value close to that in the radicals XVIII and XIX, formally derived from XII and XIII by loss of an oxygen molecule.

Experimental evidence[4] has reported that carboxy radicals (XIV, XV) originated by homolytic O-O bond cleavage in peroxyesters, undergo efficient decarboxylation: the large value of the O-C=O bond angle in these molecules was associated [7,21] with their chemical behaviour. The values reported for this angle in Table 2 seem to indicate that, while for XVI and XVII the tendency to eliminate CO_2 should be marked, this should occur to a lower extent in XIV and XV.

The harmonic vibrational frequencies calculated at MP2/6-31g*//MP2/6-31g* level, together with experimental fundamental frequencies and Zero-point Energy value for the compounds examined, are collected in Table 3. Comparison with experimental data, when known, shows a satisfactory agreement, taking into account that calculated frequencies are unscaled and anharmonicity contributions are neglected.

Tab. 3

Calculated and Experimental Harmonic Vibrational Frequencies (cm^{-1})

	MP2/6-31g*//MP2/6-31g*	ZPE kcal/mol
I	337.8 (371)[a] ; 928.7 (877) ; 1323.5 (1266) ; 1464.9 (1402) ; 3738.4 (3599) ; 3740.7 (3608)	16.50

II		156.2; 268.8; 268.8; 450.6; 870.9; 1078.3; 1205.0; 1230.6; 1388.9; 1505.6; 1531.9; 1576.0; 3099.3; 3191.5; 3218.7; 3726.2	35.02
III		21.2; 220.0; 275.7; 307.9; 489.6; 833.9; 1085.9; 1101.5; 1199.0; 1204.4; 1209.9; 1281.9; 1497.4; 1504.8; 1528.0; 1528.0; 1576.0; 1581.4; 3099.0; 3100.4; 3189.8; 3189.8; 3222.1;3222.1	53.57
IV	*cis*	308.7; 362.1; 468.7; 844.0; 873.2; 1016.4; 1191.1; 1392.9; 1518.12; 1809.9; 3183.9; 3506.2	23.55
	trans	194.5; 241.5; 390.4; 606.3; 941.8; 1042.5; 1142.7; 1411.1; 1851.8; 3145.4; 3720.1	23.00
V	*cis*	159.1; 228.2; 258.5; 345.9; 428.5; 524.4; 581.1; 918.3; 1032.4; 1085.5; 1089.2; 1221.0; 1511.0; 1674.0; 1686.3; 1692.7; 2116.1; 3066.5; 3182.3; 3200.2; 3700.1	42.46
	trans	101.1; 154.0; 203.8; 332.5; 496.5; 554.6; 567.6; 812.1; 958.9; 1042.1; 1093.0; 1277.8; 1416.4; 1456.9; 1528.1; 1536.9; 1865.8; 3138.4; 3228.7; 3255.4; 3724.5	41.09
VI	*cis*	97.7; 224.7; 280.0; 338.8; 494.8; 785.8; 848.7; 1028.3; 1051.4; 1114.2; 1202.7; 1241.9; 1408.1; 1500.6; 1532.4; 1568.6; 1847.8; 3110.4; 3117.8; 3212.5; 3227.6	41.79
	trans	61.8; 182.1; 229.8; 381.2; 452.1; 601.3; 901.1; 1043.7; 1059.2; 1145.9; 1208.3; 1245.1; 1400.0; 1503.9; 1529.0; 1572.4; 1845.6; 3108.2; 3137.5; 3208.7; 3229.3	41.52
VII	*cis*	64.7; 105.1; 132.0; 218.8; 326.3; 382.7; 478.6; 606.0; 647.7; 852.1; 931.3; 1032.0; 1059.4; 1094.9; 1202.2; 1234.1; 1262.0; 1451.7; 1499.4; 1532.5; 1535.4; 1537.0; 1569.4; 1873.4; 3108.6; 3130.7; 3210.0; 3221.6; 3224.8; 3250.1	59.72
	trans	18.3; 136.7; 196.4; 225.8; 269.4; 383.7; 507.8; 556.2; 567.2; 827.0; 934.8; 1041.3; 1078.1; 1093.5; 1208.1; 1230.5; 1309.5; 1454.3; 1503.5; 1527.0; 1529.0; 1535.1; 1575.4; 1860.3; 3109.4; 3137.3; 3208.0; 3228.0; 3228.5; 3254.4	59.66
VIII		1238.0; 1476.8; 3607.2	9.05
IX		138.3; 506.8; 964.8; 1171.8; 1221.2; 1276.3; 1502.4; 1540.2; 1550.5; 3138.1; 3254.3; 3263.2	27.92
X		3740.3	5.35
XI		842.6; 1001.0; 1140.9; 1466.3; 1484.2; 1583.2; 3048.5; 3134.2; 3166.9	24.11
XII	*cis*	255.3; 336.2; 799.8; 938.3; 1002.4; 1135.4; 1401.5; 1889.8; 3165.7	15.62
	trans	181.2; 419.7; 605.5; 1012.8; 1027.9;1207.4;1370.1; 1906.0; 3154.2	15.56
XIII	*cis*	90.5; 144.2; 310.7; 422.4; 554.8; 664.9; 779.6; 1025.3; 1086.8; 1153.6; 1215.6; 1456.1; 1531.6; 1531.9; 1924.2; 3130.7; 3218.1; 3256.2	33.59
	trans	130.4; 189.3; 344.1; 507.5; 551.1; 565.6; 768.3; 1023.7; 1083.1; 1178.8; 1250.3; 1454.9; 1525.2; 1532.5; 1942.1; 3142.7; 3253.3; 3258.6	33.86
XIV		668.0; 1171.6; 1309.1; 1533.2; 2321.0; 3184.4	14.56
XV		42.8; 580.8; 598.8; 935.7; 1037.9; 1141.5; 1445.0; 1523.3; 1531.2; 1662.8; 2393.1; 3125.8; 3219.3; 3238.0	32.71
XVI	*cis*	136.1; 299.1; 399.6; 792.1, 966.8; 1442.7; 1606.3; 1903.1; 3710.2	18.83
	trans	174.2; 259.1; 354.4; 606.2; 1073.6; 1158.4; 1433.9; 1893.1; 3708.1	18.05
XVII	*cis*	74.4; 225.1; 315.4; 342.4; 507.0; 790.4; 953.2; 1037.6; 1205.7; 1238.3; 1499.0; 1531.9; 1549.8; 1586.9; 1890.3; 3108.7; 3210.0; 3232.3	34.73
	trans	66.4; 230.9; 239.4; 375.6; 444.6; 607.3; 993.6; 1078.2; 1168.8; 1207.3; 1252.6; 1502.0; 1529.2; 1570.1; 1888.8; 3106.4; 3206.8; 3229.9	33.87
XVIII		1136.1 (1081)^{b} ; 2020.0 (1861) ; 2751.0 (2488)	8.444
XIX		75.8; 468.6; 898.1; 990.4; 1092.0; 1420.3; 1524.7; 1525.1; 1978.5; 3111.9; 3218.2; 3221.1	27.91
CH_3		404.4 (601)^{b}; 1480.7 (1383) ; 1480.7 (1383) ; 3221.3 (3177) ; 3410.2 (3271) ; 3410.2 (3271)	19.2
O_2		1412.8 (1580)^{b}	2.20
CO_2		642.0 (667)^{b} ; 642.0 (667) 1336.4 (1340) ; 2454.5 (2349)	7.25

a) Rif. 24; b) Rif. 25

Homolytic bond dissociation energy (DE)

Homolytic bond dissociation energy (DE) values at various levels of calculation and for different bonds of the compounds studied are reported in Table 4. Comparison with experimental values can be performed only for peroxides I-III.

In peroxides, the O-O bond is the one requiring less energy for homolytic cleavage. Agreement between calculated and experimental DE values referred to the O-O bond is improved by introducing spin annihilation (PMP2) and ZPE corrections. This is true for the C-O bond cleavage as well , but the dissociation energy for O-H bond turns out underestimated at the different levels. This disagreement can be attributed to the basis set employed: for hydrogen peroxide a value of 91.04 kcal/mole is obtained with a larger basis set (TZP) at MP2 level [27] to be compared with 84.3 kcal/mole obtained in this study.

The O-O bond is the one requiring less energy for breaking in peroxyacids and peroxyesters as well. The DE values in peroxyacids are nearly the same as in peroxides, whereas lower values are found for peroxyesters. The higher values in the former compounds are probably related to the presence of the hydrogen bond in peroxyacids , which needs to be broken together with the O-O bond in order to have separate molecular fragments. This is in line with the higher values of DE required for breaking O-H bonds in peroxyacids with respect to peroxides.

Tab. 4

DE values (kcal/mol)

Peroxides

R	*R'*		*RO-OR'*		*R-OOR'*		*ROO-R'*	
H	H	E(UMP2)	55.5	(51)[a]			84.3	(86)[a]
		E(PMP2)	53.6				82.8	
		E(PMP2)+ ZPE	47.8				75.4	
CH_3	H	E(UMP2)	52.4	(45)[a]	78.0	(70)[a]	83.8	(90)[a]
		E(PMP2)	50.2		75.3		82.3	
		E(PMP2)+ ZPE	45.4		68.5		75.1	
CH_3	CH_3	E(UMP2)	49.8	(36)[a]	78.1			
		E(PMP2)	47.4		75.3			
		E(PMP2)+ ZPE	41.8		68.9			

Peroxyacids

R		*RC(O)O-OH*	*R-C(O)OOH*	*RC(O)OO-H*	*RC(O)-OOH*
H	E(UMP2)	54.4	99.3	95.0	91.1
	E(PMP2)	49.2	96.7	93.5	88.1
	E(PMP2)+ ZPE	45.8	89.2	85.5	82.0
CH_3	E(UMP2)	52.4	105.1	94.5	92.1
	E(PMP2)	47.7	101.2	93.1	89.3
	E(PMP2)+ ZPE	43.3	94.0	84.2	83.8

Peroxyesters

R	***R'***		***RC(O)O-OR'***	***R-C(O)OOR'***	***RC(O)OO-R'***	***RC(O)-OOR'***
H	CH_3	E(UMP2)	49.5	96.3	87.1	88.9
		E(PMP2)	44.4	93.7	84.3	85.9
		E(PMP2)+ ZPE	39.3	86.7	77.3	80.4
CH_3		E(UMP2)	46.8	101.2	85.7	89.1
CH_3						
		E(PMP2)	41.8	97.4	83.0	86.2
		E(PMP2)+ ZPE	37.1	91.6	76.1	82.3

a) Rif. 26

As regards the energies for homolytic cleavage of the other bonds in these molecules, the order R-C(O)OOR'> RC(O)-OOR' is found and values 1.5 and 2.5 kcal/mole higher in the peroxyacids than in the corresponding peroxyesters are obtained. Moreover, the DE values for breaking the O-H and O-CH_3 bonds are nearly 9-10 kcal/mole higher than in peroxides, and this should be due to a substituent effect acting on the electronic distribution of the O-O bond.

Bond dissociation in the radicals with O_2 or CO_2 elimination was also examined in accordance with the schemes:

$$ROO\cdot \rightarrow R\cdot + O_2 \qquad (2)$$

$$RC(O)OO\cdot \rightarrow RC(O)\cdot + O_2 \qquad (3)$$

$$RC(O)O\cdot \rightarrow R\cdot + CO_2 \qquad (4)$$

$$\cdot C(O)OOR' \rightarrow \cdot OR' + CO_2 \qquad (5)$$

The DE values calculated for these reactions are collected in Table5. Loss of O_2 is an endothermic reaction and of CO_2 an exothermic reaction. From a quantitative point of view comparison with experimental results is possible only for the loss of O_2 from peroxyl radicals VIII and IX, and the agreement is satisfactory only for the latter. According to a previous work[28], better agreement should be obtained by employing a larger basis set, raising calculations to the third order Møller-Plesset perturbation and higher spin annihilation[13] , especially when the H radical is formed. The endothermic character of the process is nevertheless correctly predicted. Nevertheless, the results provide an indication that the peroxyl and acilperoxy radicals should undergo O_2 loss with a low energy requirement.

Tab. 5

DE values (kcal/mol) [a]

Radicals *R*		*R-OO*		*RC(O)-OO*	*C(O)O-OR*	*R-C(O)O*
H	E(UMP2)	31.3	(47)[b]	27.4	-69.2	-24.2
	E(PMP2)	28.9		23.5	-67.5	-20.3
	E(PMP2)+ ZPE	22.1		18.5	-71.0	-27.6
CH_3	E(UMP2)	25.5	(26)[b]	28.9	-71.0	-16.5
	E(PMP2)	22.0		25.1	-69.6	-14.0
	E(PMP2)+ ZPE	15.4		21.7	-73.0	-20.2

a) For radical H E(HF/6-31g*)= - 0.498233 u.a.

b) Rif. 28

Elimination of the CO_2 molecule is an exothermic reaction for XIV, XV and for XVI, XVII radicals. For the latter radicals bond dissociation with CO_2 loss requires nearly 50 kcal/mole less than in the former ones. At a qualitative level this result was predicted from the geometrical features of these radicals. Experimental evidence shows that CO_2 elimination occurs from radicals XIV, XV [3] and, as a general rule, this turns out to be an exothermic process for carboxy radicals[29].

By employing the results here reported, the energy required for the complete thermal decomposition of peroxyesters through the RC(O)O· radical can be estimated, according to reaction (6).

$$RC(O)OOCH_3 \rightarrow RC(O)O\cdot + \cdot OCH_3 \rightarrow R\cdot + CO_2 + \cdot OCH_3 \qquad (6)$$

At PMP2 level the total energy required for this process amounts to 24.12 and 27.78 kcal/mole for compounds VI and VII, respectively. The first step requires about 2 kcal/mole less for compound VII, whereas the second step (loss of CO_2) is easier for formoxy radical (nearly 7 kcal/mole). Thermal decomposition of the two peresters followed by hydrogen abstraction is thus expected to yield more residual acid in the case of compound VII. This type of comparison was carried out[3] for the thermal decomposition in cumene of *tert*-butyl perbenzoate and *tert*-butyl peracetate but, unfortunately, experimental tests are not available for comparing the reactivity of the perester VI and VII.

In order to assimilate the total energy change for reaction 1 to a bond dissociation energy, the bond cleavage should take place without a transition state (activation energy near to zero). To check the validity of this assumption the dissociation energy profiles as a function of the O-O bond length were constructed for compounds I, III and IV. Calculations at UMP2/6-31g*//UMP2/6-31g* level were performed for fixed O-O bond distances and relaxing all the remaining geometrical parameters. The stability of single-determinant wavefunction was also tested along the reaction coordinate: EPMP2 energy values were employed in order to prevent distortion originating from possible spin contamination. Energy profiles for bond dissociation obtained in this way at fourth-order Møller-Plesset perturbation level with spin projection were found to be [13] close to the more "exact" ones obtained with full CI and MR-CISD calculations: at MP2 level a correct limit for the potential energy was obtained [13], but while the trend in the intermediate region is correct, the potential values are higher than those obtained at higher level. From this comparison an acceptable conclusion seems that at MP2 level the results of calculations can warrant satisfactory dissociation energy values (DE) and the absence of possible transition state can be inferred.

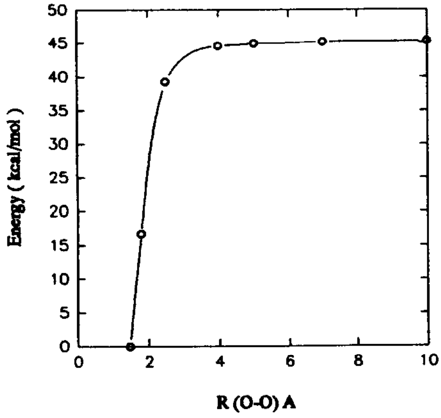


Fig. 1 PMP2 dissociation energy curve of hydrogen peroxide

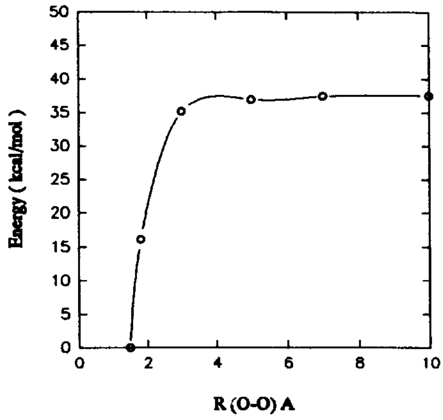


Fig. 2 PMP2 dissociation energy curve of methylhydroperoxide

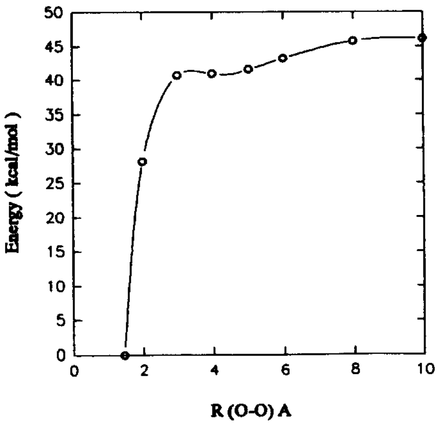


Fig. 3 PMP2 dissociation energy curve of peroxyformic acid

Figures 1,2 and 3 show the EPMP2 energy profiles for compounds I,III and IV at various O-O bond distances. The potential energy curve for hydrogen peroxide is very similar to that obtained at MCSCF level with a larger basis set [27]. The presence of transition states is not evidenced in these profiles, therefore the assumption of assimilating the reaction energy change to a bond dissociation energy (DE) seems reasonably correct. The DE values obtained from the energy profiles of compounds I and II, respectively 45.3 and 37.6 kcal/mole, do not coincide with those reported in Table 3. These differences are due to a problem with size consistency [13] and can be remedied by higher spin annihilation.

A peculiarity is present in the potential energy profile of peroxyformic acid (IV), where two steps are present: one corresponding to a DE value of 41.5 kcal/mole and the other of 46.0 kcal/mole. The energy value of the second step corresponds to complete dissociation of the molecule (DE reported in Table 3), yet the presence of the first step helps in explaining the mechanism of dissociation. In fact while in the first step the O-O bond elongates up to the dissociation limit, the O-H hydrogen bond remains almost constant: to a change of the O-O bond from the equilibrium length to 5 Å corresponds an O---H bond change from 1.91 to 2.07 Å. For this step the energy requirement amounts to 41.5 kcal/mole, close to that found for the O-O bond dissociation in the corresponding peroxyester. On increasing the O-O bond length further, from 5 to 10 Å, the O---H bond increases from 2.07 to 6.8 Å. The energy change corresponding with this second step is associated with the dissociation of the hydrogen bond and amounts to 4.5 kcal/mole.

CONCLUSIONS

The peroxydic O-O bond in all the derivatives here studied is the one requiring the smallest energy contribution for homolytic dissociation, within an interval of 10 kcal/mole for the different compounds examined. The DE values of peroxyacids are higher than those of peroxides and in the former molecules dissociation requires cleavage of the intramolecular hydrogen bond as well, as evidenced from the dissociation energy profiles. Trends of thermal decomposition of peresters and peracids are in agreement with the experimental behaviours so far available only for a limited number of these molecules. Qualitative previsions can thus be made on the compounds most probably generated in the thermal decomposition of the different peresters.

The basis set employed 6-31g* and the calculation methodology utilised (second order Møller-Plesset perturbation theory, MP2 with spin projection) turns out to be a reliable approach for estimating homolytic bond cleavage energy, when the radicals formed are large enough; otherwise extension of the basis set and/or of level of Møller-Plesset perturbation theory becomes necessary. This approach is helpful for studying reasonably large molecular systems, where application of the MCSCF approach becomes problematic and corrections for dynamic correlation effects are difficult to introduce. Nevertheless careful checks should be performed in order to be sure that the single-determinant wave function is a fairly acceptable representation of the electronic state of the molecule under consideration.

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