Interpretation of the Reactivity of Benzyl Free Radical towards Peroxyacids in Terms of Orbital Interactions. Competition between Energy Gap Control and Overlap Control

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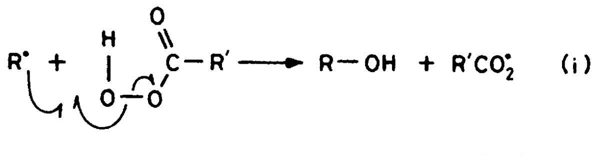
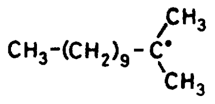
The factors which control the reactivity of alkyl free radicals R$^\bullet$ in reaction (i) are studied. The reactivity



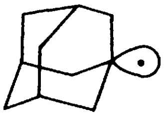
of R$^\bullet$ in (i) depends on the key orbital interaction between the SOMO of the radical and the LUMO of the peroxyacid. This interaction involves two contributions: (i) the energy gap SOMO–LUMO and (ii) the overlap SOMO–LUMO. In reaction (i) the main factor is overlap control which depends on spin delocalisation in the radical R$^\bullet$. This proves that reaction (i) does not involve electron transfer. The energy gap control, which depends on the nucleophilic character of R$^\bullet$, is only observed when the first factor is constant along a series of R$^\bullet$.

Previous work on peroxyacids has shown a correlation between the ionisation potentials, IP, of alkyl-localised free radicals R$^\bullet$ and their reactivity towards the peroxide oxygen of the peroxyacid.[1] Thus, radicals with a low IP such as 1,1-dimethylundec-1-yl (**1**) or adamantan-1-yl (**2**) easily transfer HO from peroxyacids. On the other hand, radicals with the unpaired electron in a highly hybridised orbital, such as bicyclo[2.2.1]heptan-1-yl (**3**),[2] phenyl (**4**),[3] or 2-phenylcyclopropyl (**5**)[4] react slowly or not at all upon the peroxide oxygen.

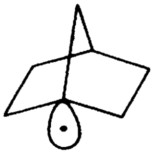


$CH_3\text{-}(CH_2)_9\text{-}\dot{C}(CH_3)_2$

(**1**)

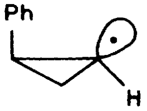


(**2**)



(**3**)

(**4**)



(**5**)

$CH_3(CH_2)_9\dot{C}H_2$

(**6**)

These results are well interpreted in terms of orbital interactions, in which the key interaction occurs between the SOMO of the radical and the LUMO of the peroxyacid, *i.e.* the low lying σ antibonding O–O orbital.[1]

According to the PMO theory[5] the energy effect, Δ*E*(PMO), associated with this interaction is proportional to the square of the overlap integral SOMO–LUMO, $\langle S_{ij}\rangle^2$, and inversely proportional to the energy gap between these two orbitals before interaction, $\Delta\varepsilon = \varepsilon_i - \varepsilon_j$ (Figure).

$$\Delta E\ (\mathrm{PMO}) = \frac{S_{ij}^2(\varepsilon_i - H_{ij}/S_{ij})^2}{\varepsilon_i - \varepsilon_j}$$

i = SOMO, j = LUMO
ε = orbital energy
S_{ij} = overlap integral
H_{ij} = matrix element
$\Delta\varepsilon = \varepsilon_i - \varepsilon_j$

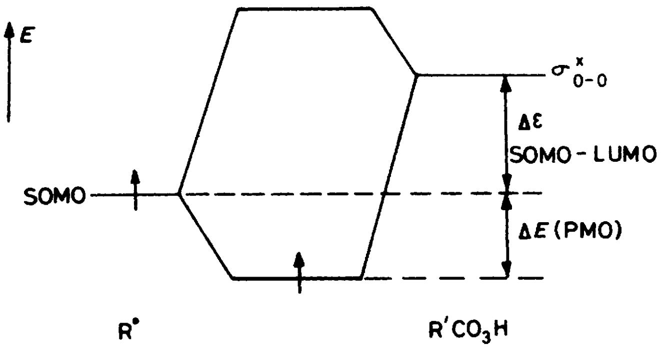
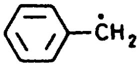


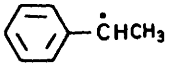
Figure. Schematic representation of the orbital interaction SOMO–LUMO

For localised alkyl radicals a constant overlap $\langle S_{ij}\rangle$ along the series can be assumed, which consequently explains their reactivity differences mainly by the energy gap difference, Δε. The importance of the overlap control can be determined by comparing radicals with different spin density.

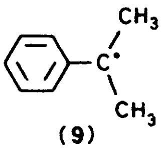
From this point of view, benzyl-type radicals such as (**7**)—(**9**) with the radical centre at a benzylic position are interesting. On the one hand, according to their low IP values (*ca.* 7.2 eV)[6] they should be as reactive as tertiary alkyl radicals, such as (**1**) and (**2**) (IP *ca.* 6.9 eV),[7] and more reactive than primary alkyl radicals, such as (**6**) (IP *ca.* 8.0 eV).[7]



(**7**)



(**8**)



(**9**)

On the other hand, as the spin density on the benzylic carbon is *ca.* 0.6,[8] they should be less reactive than localised radicals having a spin density close to 1. Therefore benzyl-type radicals should be highly reactive in terms of energy gap control ($\Delta\varepsilon$ effect) and weakly reactive in terms of overlap control ($\langle S_{ij}\rangle$ effect).

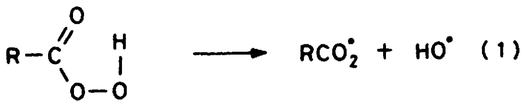
The purpose of this paper is to show the importance of overlap control in peroxyacid HO-transfer reactions. Peroxyacids RCO_3H decompose into alcohol ROH, hydrocarbon RH, and acid RCO_2H. The results of decomposition of adamantane-1-peroxycarboxylic, bicyclo[2.2.1]heptane-1-peroxycarboxylic, and perbenzoic acids, in cyclohexane and in benzene, are first discussed in order to establish how the products are formed simultaneously and how their proportions and the rate of the reaction depend on the nature of R, the solvent used, and the temperature of the reaction.

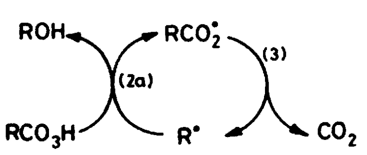
The reactivity of benzyl radicals, $Ph\dot{C}XY$, is studied from the decomposition of $PhCXYCO_3H$ and of peroxydodecanoic and perbenzoic acid in the presence of an alkyl aromatic hydrocarbon PhCXYH used as solvent or cosolvent.

Results and Discussion

In all cases, the radical-producing step is the unimolecular thermal rupture of the weak peroxide bond of the peracid with a bond dissociation energy of *ca.* 47 kcal mol^{-1} [reaction (1)].[9]

(A) *Formation of* ROH: *Adamantane-*1*-peroxycarboxylic Acid* (*Ad*CO_3H).—In our conditions, for most of the radicals (**1**)—(**9**), except $PhCO_2^{\bullet}$, decarboxylation is fast. Reactions (**2**) and (**3**) are a couplet in a chain mechanism, producing ROH and CO_2 and consuming RCO_3H. Kinetic measurements,[1] CIDNP experiments,[10] and the stereochemistry[11] of reaction (**2**) show that ROH is not a cage product. The ester RCO_2R has never been observed, which excludes attack by R on the non-peroxide oxygen of the O–O bond of peracid. When $R^{\bullet}$ is a nucleophilic radical, such as 1-$Ad^{\bullet}$, Cycle 1 describes the most important part of the reaction. Thus, 1-$AdCO_3H$, in cyclohexane as well as in benzene, produces >90% 1-AdOH, the rate being only a little slower in benzene (runs 1 and 2, Table 1).[1]





Cycle 1. ROH Formation in RCO_3H thermal decomposition

Table 1. Decomposition of adamantane-1-peroxycarboxylic acid (0.1M) at 91 °C.[d] Product concentrations are in moles per 100 moles peroxyacid

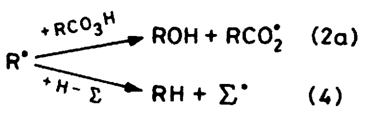
Run[a]	Solvent	k_{exp}[c]	(2)-CO_2H	(2)-OH	(2)-H	SOH + S=O[b]
1	SH[b]	57.8	3	94	3	4
2	PhH	22.0	9	91	0	

[a] Each run is an average at least of three decompositions. [b] SH, SOH, and S=O are respectively cyclohexane, cyclohexanol, and cyclohexanone. [c] k_{exp} is first order (s^{-1} × 10^4) and includes the induced decompositons as well as normal thermal initiation. [d] External oil-bath temperature.

(B) *Bicyclo*[2.2.1]*heptane-*1*-peroxycarboxylic Acid* (**3**)-CO_3H.—For this peracid, the results are different for cyclohexane and for benzene.

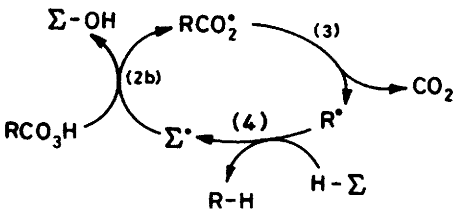
(1) *In cyclohexane* (SH); *formation of* RH. In cyclohexane (**3**)-CO_3H mainly gives the corresponding hydrocarbon (**3**)-H, along with cyclohexanol SOH produced by equimolar hydroxylation of the solvent (run 3, Table 2). This result is explained by the chain mechanism shown in Cycle 2. In this mechanism, the main feature is hydrogen-abstraction from cyclohexane (Σ-H in Cycle 2) by bicyclo[2.2.1]heptan-1-yl [reaction (4)]. The cyclohexyl radical formed reacts easily with peroxyacid producing cyclohexanol [reaction (2)].

Along with (**3**)-H, a little (**3**)-OH is formed *via* Cycle 1. Cycles 1 and 2 have a common step, the decarboxylation reaction (3). The competition between these two processes is due to the choice for $R^{\bullet}$ between HO-transfer from peroxyacid and H-transfer from solvent, respectively reaction (2a) of Cycle 1 and reaction (4) of Cycle 2.

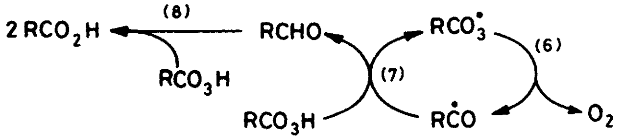


Thus with 1-$AdCO_3H$ the ratio 1-AdOH:AdH is 94:3 illustrating the high reactivity of 1-$Ad^{\bullet}$ *versus* peroxyacid, but the ratio (**3**)-OH:(**3**)-H of 17:79 indicates that (**3**) reacts slowly with peroxyacid. From a general point of view, the ratio ROH:RH gives an estimate of the nucleophilic character of $R^{\bullet}$. This behaviour has been completely explained in terms of frontier orbitals.[1]

(2) *In benzene* PhH: *formation of* RCO_2H. In benzene (**3**)-CO_3H mainly decomposes to the corresponding acid (**3**)-CO_2H. Furthermore the experimental rate constant k_{exp} is much smaller in benzene than in cyclohexane (runs 3 and 4, Table 2). The formation of the acid has been explained by Cycle 3.



Cycle 2. RH Formation and solvent hydroxylation in RCO_3H thermal decomposition. Σ-H Stands for a hydrogen-donor solvent



Cycle 3. Acid formation in RCO_3H thermal decomposition

Table 2. Decomposition of bicyclo[2.2.1]heptane-1-peroxycarboxylic acid (0.1M) at 91 °C.[d] Product concentrations are in moles per 100 moles of peroxyacid

Run[a]	Solvent	k_{exp}[c]	(3)-CO_2H	(3)-OH	(3)-H	SOH + S=O[b]
3	SH[b]	57.8	5	17	79	77
4	PhH	2.9	96	Trace[e]	4	

[a–d] See Table 1. [e] <0.5%.

Table 3. Decomposition of perbenzoic acid (0.1M) in cyclohexane. Product concentrations are in moles per 100 moles of peroxyacid

Run[a]	Cosolvent[e]	θ/°C[d]	k_{exp}[c]	$PhCO_2H$	PhH	Ph_2	SOH + S=O[b]	Cosolvent products
5		105	24.0	60	40	2	95	
6	PhMe	100	4.2	41	nm[f]	2	67	2($PhCH_2OH$), 3(PhC_6H_{11})
7	PhEt	100	6.6	62	nm	1	57	6(PhCHOHMe), 3(PhCOMe)
8	$PhPr^i$	100	10.8	49	nm	2	63	9($PhCOHMe_2$)

[a–d] See Table 1. [e] Cosolvent concentrations are 1M. [f] Non-measured product.

Table 4. Decomposition of perbenzoic acid (0.1M) in benzene at 100 °C. Product concentrations are in moles per 100 moles of peroxyacid

Run[a]	Cosolvent[e]	k_{exp}[c]	$PhCO_2H$	Ph_2	Cosolvent products
9		2.6	98	7	
10	PhMe	2.4	98	5	1($PhCH_2OH$)
11	PhEt	2.4	92	nm[f]	5(PhCHOHMe), 3(PhCOMe)
12	$PhPr^i$	2.8	72	6	7($PhCOHMe_2$), 11(PhCOMe)

[a,c–f] See Tables 1 and 3.

$$E^{\bullet} + RCO_3H \longrightarrow EH + RCO_3^{\bullet} \quad (5)$$

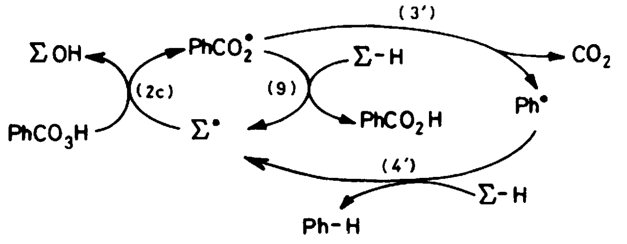
$$E^{\bullet} = HO^{\bullet},\ R\dot{C}{=}O,\ Ph^{\bullet}, PhCO_2^{\bullet}$$

Initially $RCO_3^{\bullet}$ radicals are produced in reaction (5) by hydrogen-transfer of the peroxide hydrogen of the peroxyacid either by $HO^{\bullet}$ radical, or eventually radical (**3**) since some (**3**)-H is formed. The decomposition of peroxyacid into acid, according to Cycle 3, is a slow process.[3] This is mainly due to the reversible character of reaction (6). Furthermore, O_2 formed in Cycle 3 traps other radicals, such as $R^{\bullet}$ and $\Sigma^{\bullet}$ of Cycles 1 and 2, and reduces product formation through these cycles.

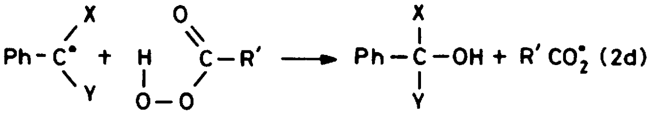
In order to explain this transformation of peroxyacid into acid, two other possible mechanisms have been described in the literature. The first one[12] implies pre-formation of the RCO_3^- anion, but this seems unlikely in a non-polar solvent such as cyclohexane or benzene. The second implies the formation of acids, through an oxenoid-type mechanism, undergoing a stereospecific hydroxylation of Σ-H with retention of configuration.[13,14] In our conditions, in the presence of *cis-* or *trans*-decalin, the stereoselectivity observed[15] is like that for *cis-* and *trans*-decalin-9-yl radicals; this precludes, at least in part, such a mechanism.

The difference between the decompositions of peroxyacid (**3**)-CO_3H in benzene and in cyclohexane explains how cyclohexane induces the decomposition of this peracid. That is due to cyclohexyl radicals formed by reaction (4) of Cycle 2 which react easily with peroxyacids by reaction (2b) of Cycle 2.

(C) *Perbenzoic Acid*, $PhCO_3H$.—(1) *In cyclohexane*. In this solvent perbenzoic acid decomposes into benzoic acid and benzene with almost equimolecular formation of cyclohexanol (run 5, Table 3). This is due to two special features, (i) the decarboxylation reaction of $PhCO_2^{\bullet}$ being slow, this radical abstracts hydrogen from the solvent before decarboxylation and (ii) moreover, phenyl radicals formed by reaction (3′) are very reactive towards hydrogen-transfer from cyclohexane [reaction (4′)]. Consequently they do not react with the peroxide oxygen of peroxyacids, or O_2, to produce phenol.[3,16] Cyclohexyl radicals ($\Sigma^{\bullet} = C_6H^{\bullet}_{11}$) produced either by reaction (9) or (4′) react with perbenzoic acid according to reaction (2c), giving the chain mechanism in Cycle 4.



Cycle 4. Solvent hydroxylation in perbenzoic decomposition. Σ-H Stands for a hydrogen-donor solvent



$$Ph\text{-}\dot{C}XY + H\text{-}C(R')(=O)\text{-}O\text{-}O \longrightarrow Ph\text{-}C(X)(Y)\text{-}OH + R'CO_2^{\bullet} \quad (2d)$$

(2) *In benzene*. In this solvent, perbenzoic acid decomposes quantitatively and slowly into benzoic acid (run 9, Table 4), through a mechanism as in Cycle 3 where R = Ph. Cycle 3 is initiated by $PhCO_3^{\bullet}$ radical formed in reaction (5) where R = Ph and $E^{\bullet} = OH^{\bullet}$, $PhCO_2^{\bullet}$ or $Ph^{\bullet}$ radicals. It should be noted that perbenzoic and bicyclo[2.2.1]heptane-1-peroxycarboxylic acids decompose in benzene quantitatively in acid with roughly the same rate constant (runs 9 and 4). This is an agreement with an identical mechanism, as in Cycle 3, where the $Ph^{\bullet}$ or radical (**3**) is not directly involved in a bond-forming or -breaking process.

From these results with peracids 1-$AdCO_3H$, (**3**)-CO_3H, and $PhCO_3H$ in cyclohexane or in benzene, it appears that the formation of acids, through Cycle 3, takes place mainly when $R^{\bullet}$ reacts slowly with the peroxide oxygen of the peroxyacids and/or does not abstract hydrogen from the solvent. Therefore with all peroxyacids, except $PhCO_3H$, Cycles 1 and 2 are more favoured the smaller is the quantity of acid formed at the end of the reaction. Cycle 2, which needs a good hydrogen donor, is suppressed in benzene: the quantity of acid then formed is a measure of the competition between Cycles 1 and 3, and consequently an indirect evaluation of the facility of the chain mechanism in Cycle 1. As in Cycle 1, reaction (2a) is the limiting step, the quantities of acid formed are also an indirect measure of the reactivity of $R^{\bullet}$ upon the peroxyacid. With perbenzoic acid, the quantities of hydroxylated products, Σ-OH, present at the end of the reaction gives a direct measure of the contribution of Cycle 4 over 3 (R = Ph), *i.e* the reactivity of the radicals issuing from the solvent towards the peroxide oxygen of perbenzoic acid [reaction (2c)]. In all cases, the decomposition rate constants are larger when Cycles 1 or 4 are favoured over 3.

From these considerations, it turns out that the reactivity of benzyl-type radicals towards HO transfer from peroxyacids, can be studied in different ways, either from $PhCXYCO_3H$ decompositions, or from decomposition of peroxyacids, such as (**6**)-CO_3H or $PhCO_3H$, in the presence of PhCXYH.

These alkylaromatic hydrocarbons, used as solvent or

Table 5. Decomposition of phenylperacetic acid (0.1M) at 100 °C.[d] Product concentrations are in moles per 100 moles of peracid

Run[a]	Solvent	k_{exp}[c]	$PhCH_2CO_2H$	$PhCH_2OH$	PhCHO	$PhCO_2H$	$PhCH_3$	$(PhCH_2)_2$	SOH + S=O[b]
13	SH[b]	2.6	52	27	2	3	0	0	13
14	PhH	1.7	60	27	9	5	0	2	

[a–d] See Table 1.

Table 6. Decomposition of peroxydodecanoic acid (0.1M) in cyclohexane. Product concentrations are in moles per 100 moles of peroxyacid

Run[a]	Cosolvent[e]	θ/°C[d]	k_{exp}[c]	RCH_2CO_2H[g]	RCH_2OH	RCH=O	RCO_2H	RCH_3	$R_{is}OH$[i]	SOH + S=O[b]	Cosolvent products
15		85	14.7	24	41	Trace[h]	1	23	12	34	
16		100	38.2	9	53	3	1	17	8	21	
17		140	51.8	7	60	3	2	22	8	19	
18	PhMe	100	6.2	18	42	Trace[h]	4	nm[f]	7	14	3($PhCH_2OH$)
19	PhEt	100	9.9	21	55	1	3	nm[f]	7	16	10(PhCHOHMe), 1(PhCOMe)
20	PhPr^i	100	19.1	16	56	1	3	nm[f]	12	18	8($PhCOHMe_2$)

[a–f] See Tables 1 and 3. [g] R = decan-1-yl. [h] <0.5%. [i] R_{is} = $CH_3(CH_2)_5\dot{C}H(CH_2)_3CH_3$ and/or $CH_3(CH_2)_4\dot{C}H(CH_2)_4CH_3$.[18]

cosolvent, are the source of benzyl radicals $Ph\dot{C}XY$ which can react with peroxyacids *via* reactions (2b) of Cycle 2 or (2c) of Cycle 4. In all cases trapping by O_2 of radicals $R^{\bullet}$ and $\Sigma^{\bullet}$ should be avoided, by elimination of O_2 from the solution, in order to favour Cycles 1, 2, and 4 (*cf.* Experimental section).

(D) *Phenylperacetic Acid.*—The reactivity of benzyl radical $Ph\dot{C}H_2$ was studied in the decomposition $PhCH_2CO_3H$ and was compared with the reactivity of primary and tertiary radicals generated in the same conditions from, respectively, peroxydodecanoic and adamantane-2-peroxycarboxylic acids.

(1) *In cyclohexane* (SH) *and benzene* (PhH) *solutions.* In both solvents (runs 13 and 14, Table 5) $PhCH_2CO_3H$ decompositions give roughly the same final product distribution but the reaction is slightly faster in cyclohexane than in benzene. The presence of $PhCH_2OH$ indicates that $Ph\dot{C}H_2$ radical is formed during these decompositions.

Since $PhCH_2CO_2^{\bullet}$ radical should decarboxylate rapidly, the acid $PhCH_2CO_2H$ cannot be formed by hydrogen-abstraction from cyclohexane. Consequently the high quantities of $PhCH_2CO_2H$ are obtained *via* Cycle 3, and show the weak reactivity of $Ph\dot{C}H_2$ radical in Cycles 1 and 2 ($R^{\bullet}$ = $Ph\dot{C}H_2$). The absence of toluene in the product distribution shows that Cycle 2 is not operative, since $Ph\dot{C}H_2$ does not transfer hydrogen from the solvent by reaction (4). This is explained by an unfavourable enthalpy control, ΔH being *ca.* + 10 kcal mol^{-1}.[17] Therefore cyclohexyl radicals are not formed to induce peroxyacid decomposition; that explains why $PhCH_2CO_3H$ decompositions are alike in benzene and cyclohexane. Furthermore the weak reactivity of $Ph\dot{C}H_2$ towards the peroxide oxygen of peroxyacids can be deduced from the product distributions and from the rate constants in both solvents. In benzene, that is confirmed by the presence of the dimer $(PhCH_2)_2$. If $Ph\dot{C}H_2$ radical was very reactive towards HO-transfer from peroxyacid, the dimer $(PHCH_2)_2$ would not have been formed.

(2) *Comparison with adamantane-*1-*peroxycarboxylic acid.* As IPs of the benzyl radical $Ph\dot{C}H_2$ and a tertiary radical are alike, they should have similar reactivities from the point of view of energy gap control. Therefore it was interesting to compare, under the same conditions, the bridgehead adamantyl radical to benzyl. The bridgehead adamantane-1-peroxycarboxylic acid decomposes more rapidly than $PhCH_2CO_3H$ in benzene (runs 2 and 14) and in cyclohexane (runs 1 and 13). Furthermore, in both solvents, the bridgehead alcohol 1-AdOH is the main product of the reaction.[1] These results show that tertiary radicals are much more reactive than the benzyl radical in peroxyacid HO-transfer reaction.

(3) *Comparison with peroxydodecanoic acid decomposition.* In benzene the rate constant of decomposition of $PhCH_2CO_3H$ is smaller than that observed with the peroxydodecanoic acid and more acid is formed (runs 14 and 22). These results show that $Ph\dot{C}H_2$ must be somewhat less reactive than the undecyl radical in reaction (2a).

In cyclohexane the decomposition of $PhCH_2CO_3H$ is much slower than that observed with peroxydodecanoic acid and much more acid is formed (runs 13 and 16). These differences are well understood in terms of decomposition of peroxydodecanoic acid induced by cyclohexyl radicals. The undecyl radical (**6**) and radicals such as (**3**),[2] (**4**),[3] and (**5**)[4] easily abstract hydrogen from cyclohexane, due to the exothermicity of reaction (4), and therefore give cyclohexyl radical which induces decomposition of the peroxyacid.

From these phenylperacetic, peroxydodecanoic, and adamantane-1-peroxycarboxylic acid decompositions, in benzene and cyclohexane, it can be concluded that $Ph\dot{C}H_2$ radical, in reaction (2a), is slightly less reactive than primary alkyl radicals and much less reactive than tertiary alkyl radicals.

(E) *Peroxyacid Decomposition in the Presence of* PhCXYH.—The reactivity of benzyl-type radicals towards HO-transfer from peroxyacid *via* reactions (2b or c) was also studied by decomposition in cyclohexane or in benzene, of peroxydodecanoic and perbenzoic acid (0.1M) in the presence of an alkylaromatic cosolvent (1M) such as toluene, ethylbenzene, or cumene.

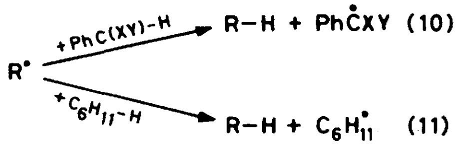
(1) *Peroxydodecanoic acid* (**6**)-CO_3H. (a) In cyclohexane, the presence of toluene, ethylbenzene, or cumene reduces the decomposition rates of (**6**)-CO_3H and raises the quantitites of dodecanoic acid formed (*cf.* runs 18, 19, 20, and 16 in Table 6). Nevertheless going from toluene to ethylbenzene and cumene there is an increase in decomposition rate and of products due to the undecyl radical (**6**), respectively 53, 66, and 72%. These results are well explained by the fact that, in cyclohexane, hydrogen-transfer from solvent by (**6**) competes with hydrogen-transfer from the alkyl part of the aromatic cosolvent.

The hydrogen-transfer is thermodynamically easier from PhCXYH [reaction (10)] than from cyclohexane [reaction (11)]. Actually from product distributions of the cosolvent oxidation, it appears that $Ph\dot{C}H_2$, $Ph\dot{C}HCH_3$, and $Ph\dot{C}(CH_3)_2$ radicals are really formed; however, as they react more slowly with peracid than does cyclohexyl radical, the rate

Table 7. Decomposition of peroxydodecanoic acid (0.1M) in benzene. Product concentrations are in moles per 100 moles of peroxyacid

Run[a]	Cosolvent[e]	θ/°C[d]	k_{exp}[c]	RCH_2CO_2H[g]	RCH_2OH	RCH=O	RCO_2H	RCH_3	$R_{is}OH$[i]	PhR	Cosolvent products
21		90	3.4	60	7	1	4	nm[f]	1	Trace[h]	
22		100	7.1	40	27	2	7	2	4	2	
23		140	nm[f]	47	32	Trace[f]	12	nm[f]	3	Trace[h]	
24	PhMe	100	12.0	38	33	8	6	3	3	1	
25	PhEt	100	16.6	49	33	5	6	nm[f]	5	Trace[h]	8(PhCHOHMe), 2(PhCOMe)
26	$PhPr^i$	100	10.9	38	29	6	6	nm[f]	5	1	12(PhCOHMe)
27	PhMe[j]	130	nm[f]	60	7	2	2	5	2	Trace[h]	9($PhCH_2OH$)

[a,c–i] See Tables 1, 3, and 6. [j] In pure toluene at 0.05M.



of peroxydodecanoic acid decomposition is reduced, and more dodecanoic acid is formed.

(b) When benzene is used as solvent, the competition between reactions (10) and (11) is suppressed because benzene is not a hydrogen-donor to free radicals. Nearly the same results are found in the presence or in the absence of the alkylaromatic cosolvent (runs 22 and 24—26).

Therefore radicals (7)—(9) formed during these reactions, as noted for some oxidised cosolvents, do not induce peroxyacid decomposition, showing that benzyl-type radicals are not more reactive towards HO-transfer from peroxyacid than is the undecyl radical (6).

(c) In pure toluene, the peroxydodecanoic acid decomposition gives mainly the dodecanoic acid (run 27). In this decomposition, toluene acts as a trap for undecyl radicals, and due to its weak reactivity, $Ph\dot{C}H_2$ radicals do not play the same role as cyclohexyl radicals *via* reaction (2b) of Cycle 3, and therefore the decomposition occurs mainly through Cycle 3.

These decompositions of peroxydodecanoic acid in the presence of toluene, ethylbenzene, and cumene show the low reactivity of benzyl-type radicals towards HO-transfer from peroxyacids with, nevertheless, a slight increase along the series (7)—(9).

(2) *Perbenzoic acid* $PhCO_3H$. As noted before, decompositions of perbenzoic acid in cyclohexane lead to 95 mol cyclohexanol per 100 mol peracid (run 5), and in benzene to 98 mol benzoic acid (run 9). When 1M-adamantane, a good H-donor, is added to benzene, up to 60 mol adamantanol per 100 mol peroxyacid is obtained.[15] Therefore it should be possible to study the reactivity of benzyl-type radicals by means of step (2c) of Cycle 4, by decomposing perbenzoic acid in the presence of an alkylaromatic cosolvent. Results are collected in Tables 3 and 4.

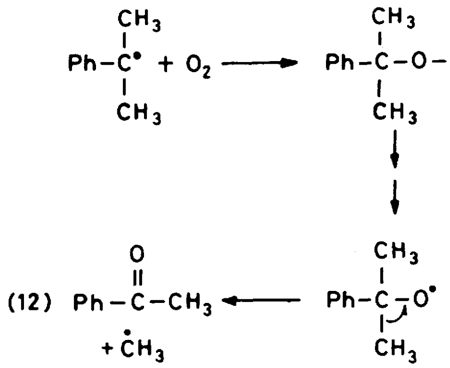
(a) When alkylaromatics are used as cosolvents with cyclohexane, the rate of perbenzoic acid decomposition slows down, as noted before with peroxydodecanoic acid. Furthermore the cyclohexane oxidation products diminish and weak oxidation of the alkylaromatic cosolvents is observed (runs 5—8). These results are explained by a chain mechanism as in Cycle 4, and by a lower reactivity for benzyl radicals than for cyclohexyl radical towards HO-transfer from peroxyacid [reaction (2c)].

(b) The addition to benzene of cosolvents such as $PhCH_3$, PhEt, and $PhPr^i$, does not change significantly the decomposition of perbenzoic acid (runs 10—12). Radicals (7)—(9) are formed as can be seen from oxidised products derived from the cosolvent. Furthermore the formation of $PhCOCH_3$ in run 12 indicates that cumyl radical (9) does not react with peracid, but rather acts as an O_2 trap to lead to acetophenone [reaction (12)].

Table 8. Decomposition of perbenzoic acid (0.1M) in alkylaromatic hydrocarbons. Product concentrations are in moles per 100 moles of peroxyacid

Run[a]	Solvent	θ/°C[c]	k_{exp}[b]	$PhCO_2H$	Solvent products
28	PhMe	130	22.6	75	1($PhCH_2OH$), 2(PhCHO), 10(cresol)
29	PhEt	157	58.4	64	25(PhCHOHMe)
30	$PhPr^i$	172	nm[d]	65	30($PhCOHMe_2$)

[a] Each run is an average of three decompositions. [b] k_{exp} is first order ($10^4 \times s^{-1}$) and includes the induced decomposition as well as normal thermal initiation. [c] External oil-bath temperature. [d] Non-measured.



(c) In pure $PhCH_3$, in spite of the higher temperature, $PhCO_3H$ decomposes at the same rate as in cyclohexane (runs 5, 28). Solvent oxidation seems negligible, but some $PhCO_2H$ can be issued from solvent oxidation. The presence of some cresol shows that a reaction takes place between •OH, formed in the initiation step of the chain mechanism, and the solvent.

With pure PhEt and $PhPr^i$ decompositions are faster, and solvents are respectively oxidised in 25 and 30% yields (runs 29, 30). The increased rate of reaction in PhEt and $PhPr^i$ as compared with that in PhMe is surely just a temperature effect (Table 8).

These decompositions of perbenzoic acid in the presence of toluene, ethylbenzene, or cumene show the low reactivity of benzyl-type radicals towards HO-transfer from peroxyacid with, nevertheless, a slight increase along the series (7)—(9) as with peroxydodecanoic acid.

Conclusions.—First, it should be emphasised that these benzyl-type radicals make few hydrogen-transfers from hydrogen-donor solvents, such as cyclohexane, since hydrogen-transfer mainly depends on thermodynamic control, here unfavourable. Therefore benzyl radicals cannot induce peroxyacid decomposition *via* cyclohexyl radicals as do radicals such as Ph•, $PhCO_2$•, bicyclo[2.2.1]heptan-1-yl, or 2-phenylcyclopropyl, which do not react with the peroxyacid

O–O bond but easily transfer a hydrogen atom from cyclohexane.

From these results it clearly appears that in HO-transfer reactions from peroxyacids, benzyl-type radicals are less or as reactive as primary alkyl radicals, such as undecyl, and much less reactive than tertiary ones. This different behaviour could be explained by the energy effect associated with the SOMO–LUMO interaction which is the key interaction in reaction (i). In view of PMO theory, this interaction is controlled by two factors, the energy gap and the overlap integral SOMO–LUMO. In terms of energy gap control, benzylic radicals should be more reactive than primary alkyl ones, because IPs of the former are lower than those of the latter. In terms of overlap control, benzyl-type radicals **(7)**—**(9)** with a spin density on the benzylic carbon lower than that in localised alkyl radicals, such as the undecyl **(6)**, should be less reactive. Actually, as benzyl-type radicals are less or as reactive as primary radicals, such as **(6)**, it means that HO-transfer from peroxyacids is under overlap control. Consequently, that explains why the energy gap control is masked.

Furthermore, comparing the following series of benzylic radicals **(7)**—**(9)** where the spin density at the reactive carbon is of the same order of magnitude, energy gap control becomes again the determining factor. Correlation with the nucleophilic character of the free radical is found, since methyl groups act as electron donors. As noted before,[1] the steric effect due to methyl groups around the radical centre does not diminish its reactivity towards HO-transfer from peroxyacid.

Experimental

Cyclohexane and benzene were spectroscopic grade, and toluene, ethylbenzene, and cumene were labelled (sample for g.l.c.). G.l.c. analyses were run on a Girdel-75 apparatus with a CR1B recording integrator, and i.r. spectra were obtained in CCl_4 solution with a Hitachi-EPI G2. The purity of peroxide was determined by iodometry.[19]

Preparations of adamantane-1-peroxycarboxylic, bicyclo[2.2.1]heptane-1-peroxycarboxylic, and peroxydodecanoic acids are described elsewhere.[1] For the preparations of perbenzoic and phenylperacetic acids the procedure described by Swern *et al.*[20] was modified as follows.[4,21]

Peroxyacid Preparations.—Perbenzoic acid. Perbenzoic acid (5 g, 41 mmol) was dissolved in a minimal quantity of methanesulphonic acid (10 ml, 154 mmol) at 50—60 °C. The solution was cooled with mechanical stirring to give a malleable homogeneous paste. 85% H_2O_2 (2 ml, 69 mmol) were added dropwise for 20—30 min slowly enough to keep the temperature at *ca.* 10 °C. This temperature was maintained for 30 min after the end of H_2O_2 addition. The mixture was allowed to warm to 18—20 °C to obtain a clear solution after 30—45 min. The mixture was cooled, remaining a clear yellow homogeneous liquid. The mixture was stirred for 1 h to completion of reaction. At the end CH_2Cl_2 (20 ml) cooled at -30 °C was added and then, slowly, ice–water. The mixture was washed with saturated $(NH_4)_2SO_4$ solution[22] and then with ice–water. After fast drying (Na_2SO_4), and evaporation of the solution at *ca.* 0 °C with a rotating evaporator, crystals (4.4 g, 70%) with a purity of 90% were obtained. Perbenzoic acid is kept at -30 °C. The loss of purity is *ca.* 1% a day.

Phenylperacetic acid. To CH_3SO_3H (10 ml, 154 mmol) was added water (1 ml) and $PhCH_2CO_2H$ (2.6 g, 19 mmol) at room temperature. The mixture was cooled (5 °C) and 85% H_2O_2 (2.6 ml, 90 mmol) was added slowly. If foam arose, H_2O_2 addition was slowed. After H_2O_2 addition, the mixture was stirred for 3 h. Work-up, as for perbenzoic acid, yielded phenylperacetic acid (2.4 g, 86%) with a purity of 96%.

Peroxyacid Decomposition.—The procedure has already been described.[4] In a reactor (50 ml) with a condenser was placed the peroxyacid solution (10 ml; 0.1M) to which was eventually added a quantity of toluene, ethylbenzene, or cumene (*cf.* Tables). The reaction was followed by iodometry.[19] At the end of the reaction the solution was treated with diazomethane in order to transform carboxylic acids into their corresponding methyl esters. The product distributions were analysed on two types of g.l.c. column, polar (Carbowax 20 M) and non-polar (SE30).

At equilibrium, the O_2 concentration in the solution depends on the temperature of the solution. But, at non-equilibrium, O_2 elimination from solvent should depend on the importance of reflux, and therefore, on the temperature of an external oil-bath.

Peroxydodecanoic acid was decomposed, in cyclohexane and benzene, at different oil-bath temperatures, 90, 100, 140 °C, *i.e.* respectively 9, 19, and 59 °C above the b.p. of the solution (runs 15—17 in Table 6 and 21—23 in Table 7). It clearly appears from kinetic measurements and from product distributions that Cycles 1 and 2 are favoured at 100 and 140 °C. Consequently, for most experiments the external oil-bath was at 100 °C in order to have better O_2 elimination.

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