(because D/H exchange and/or internal return to rearranged tosylate caused significant deviation from a simple first-order kinetic plot), the rates were extrapolated to zero time.

Product Distributions. These were determined from integration of the 220-MHz spectra with the use of a curve resolver where necessary. The curve resolver was necessary to establish the relative amounts of VI and VIII, for example, since the small difference in chemical shift of the methyl groups of VI and VIII (due to the adjacent deuterium) causes some overlapping of the singlet of VIII with the upfield peak of the doublet of VI. The stability of the products was evident from the constant ratio with which the products were formed.

Acknowledgment. We are indebted to Professor W. A. Gibbons and Mr. P. Zeigler for the 220-MHz NMR spectra and to Dr. C. Angell of Union Carbide for use of the curve resolver. This work was partially supported by the Research Foundation of the City University of New York, Grant PSC-BHE-13120.

The Surface of Silica as a Medium for the Radical and Ionic Decomposition of Diacyl Peroxides

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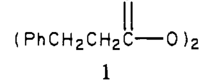
Abstract: The rates of decomposition of β-phenylpropionyl peroxide **1**, β-phenylisovaleryl peroxide **2**, and β-phenylisovaleryl *p*-nitrobenzoyl peroxide **3** are much higher on silica surfaces than they are in solution. The products formed on silica surfaces are derived from both radical and ionic precursors except in the case of **3**, for which the reaction may be entirely ionic. The relationships between the medium effects on the rates and on the products suggest that the ionic and radical parts of the reaction branch from a common polar intermediate.[1a,b,e] Both the ionic and radical products differ significantly from those formed in solution. In the neophyl radical, adsorption inhibits the migration of phenyl to form phenyl-*tert*-butyl radical. In the ionic reaction, there is extensive migration of methyl in competition with phenyl, in contrast to the behavior of neophyl derivatives in solvolysis[9] reactions. Dihydrocoumarin, from **1**, and dimethyldihydrocoumarin, from **2** and **3**, are not formed at all in solution. Esters, which are often formed via carboxy inversion and related reactions when polar diacyl peroxides decompose in solution, appear to arise from electron transfer in radial-pair precursors. There is no evidence of carboxy inversion compounds or carbonic acid esters in the physically adsorbed products, although some RO—C(=O)$^+$ groups (1-2%) appear to be trapped by the silica. Rearranged and unrearranged neophyl cations are trapped more extensively as silyl ethers. Other ion-derived products are one of the phenylisobutylenes, several phenylbutenes, and the carboxylic acids. Coadsorbed oxygen or acetonitrile alters the product distribution partly by trapping radicals and partly by site preemption[3] effects.

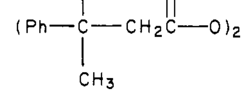
In the decomposition of certain diacyl peroxides, although some of the products can be assigned to radical-pair precursors, others found in the same reaction mixture require ion-pair precursors. Both the proportion of ionic products and the decomposition rate are increased by polar solvents or by suitable polarizable or polar substituents. Even though the proportion of radical products in the fast reactions decreases, the net rate of radical production is often observed to increase. It has therefore been proposed that the radical and ionic branches of the reaction share a common rate-determining step whose transition state is rather polar.[1]

In this paper we report an unusual medium effect and novel products in the decomposition of bis(β-phenylisovaleryl) peroxide (**2**). Peroxide **2**, with its polarizable neophyl group, is a borderline member of the class of polar diacyl peroxides. The related compound **3**, with a much better anionic leaving group, has been shown to give the carboxy inversion (ionic) reaction in solution.[2] Peroxide **1**, with its less polarizable β-phenylethyl group, should be less susceptible to the ionic mode of decomposition. A few experiments with **1** and **3** are included for comparison.



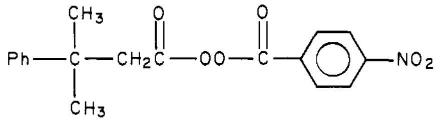
$(PhCH_2CH_2C(=O)—O)_2$

1



$(Ph—C(CH_3)_2—CH_2C(=O)—O)_2$

2



3

Table I. Products from Peroxide 1 (Mol %)[a]

	in benzene[b]	on P_0 silica *c*	with O_2[d]	$h\nu$[e]
R_1COOH	13.1	48.4	45.1	28.4
R_1COOH		0.8[f]	0.7[f]	
R_1COOR_1	12.8	18.2	25.1	2.88
lactone L_1	0	0.63	3.30	0.0
R_1OH	trace	2.04	7.37	trace
R'_1OH	trace	trace		trace
R_1OSi[g]		4.4	7.28	0.5
R'_1OSi[g]		2.4		trace
R_1H	76	9.3	2.5	18.7
R_1R_1	18.7	3.92	9.26	14.8
styrene[h]	0[h]	0.4	1.89	0[h]
dibenzyl	18.5			

[a] Means of several analyses in most cases. [b] 0.1 M at 55 °C. [c] Means of runs at 2.66 and 5.1 wt % at 55 °C. This corresponds to about 0.1 monolayer. The differences were small. [d] 6.0 wt % at 55 °C, with coadsorbed O_2. [e] 6.25 wt % at 25 °C, photochemical. [f] Extracted after acid hydrolysis of the silica. [g] Alcohol extracted after acid hydrolysis of the silica. [h] No attempt was made to isolate the polymer.

Our attention was drawn to peroxide **2** by the discovery that the rate of its decomposition on a silica surface is about 70 times

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(1) (a) Walling, C.; Sloan, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7679-7683. (b) Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnu, C. G. *Ibid.* **1970**, *92*, 4927-4932. (c) Leffler, J. E. *Ibid.* **1950**, *72*, 67. (d) Greene, F. D.; Stein, H. P.; Chu, C. C.; Vane, F. M. *Ibid.* **1964**, *81*, 2080-2081. (e) Leffler, J. E.; More, A. A. *Ibid.* **1972**, *94*, 2483-2487.

(2) Lamb, R. C.; Vestal, L. L.; Cipau, G. R.; and Debnath, S., J. Org. Chem., 1974, 39, 2096-2103.

0002-7863/81/1503-7768$01.25/0

Table II. Products from Peroxide **2** (Mol %)[a]

	in soln			on P_0 silica			on P_1 silica	
	CH_3CN[b]	PhH[c]	PhH[d]	*e,f*	O_2[g]	$h\nu$[h,e]	*e*	CH_3CN
R_2COOH	26.1	27.3	24.6	81.3	85	53.8	87	83.5
R_2COOH[j]				0.8	2.8	3.1	1.9	0.3
R_2COOR_2	2.4	5.96	6.19	0.15	0.18	0.18	0.5	0.5
$R_2COOR'_2$	1.5	3.48	3.30	5.41	2.49	7.53	6.21	6.1
lactone L_2	0	0	trace	7.51	10.4	4.8	7.73	4.9
R_2OH	4.0	3.7	3.65	0.9	2.8	0.45	1.6	3.2
R'_2OH	3.1	7.5	8.38	2.4	5.9	1.10	1.45	2.6
R''_2OH		0.05	0.11	trace	0.55	0.08	0.3	0.8
R_2OSi[k]				0.8	0.25	0.06	0.5	0.5
R'_2OSi[k]				0.8	1.2	0.41	1.8	2.1
R_2H	12.0	1.4	1.01	1.5	0.2	5.3	1.3	1.62
R'_2H	12.1	13.3	13.8	0.19	0.0	0.7	0.14	0.22
R_2R_2	7.6	10.7	11.0	1.03	1.33	13	0.97	3.0
$R_2R'_2$	0.7	2.5	3.35	0.40	trace	0.3	0.45	0.7
$R'_2R'_2$	0.1	1.4	1.12	0.1	trace	0.4	0.15	0.1
phenylisobutylenes								
4	6.6	27.0	29.7	12.6	8.1	14	35.5	22.4
5	0.8	1.98	1.57	28.1	25.7	8.4	4.2	2.3
phenylbutenes								
6		0	0	1.35	1.5	1.20	trace	7.8
7		0	0	0.22	0.9	0.1	3.78	4.6
8		0.03	0.03	5.9	6.5	0.6	2.6	2.3

[a] Means of several analyses. [b] 0.12 M, 55 °C. [c] 0.3 M, 80 °C. [d] 0.1 M, 55 °C. [e] Means of two runs at ca. 3 and 6 wt %, concentration effects small. [f] At 55 °C. [g] 3.4 wt % at 55°, with coadsorbed O_2. [h] At 25 °C, photochemical. [i] 3 wt % with 4.2 wt % coadsorbed CH_3CN. The CH_3CN was put on first. [j] Extracted after acid hydrolysis of the silica. [k] Alcohols extracted after acid hydrolysis of the silica.

that in cyclohexane solution. In contrast, the polar solvent acetonitrile gives a rate only 3.6 times that in cyclohexane. For further comparison, the very polar and unstable isobutyryl peroxide decomposes 14 times as fast in acetonitrile as in cyclohexane.

The high rate of decomposition of **2** on silica led us to expect a high proportion of polar products. Indeed, a high proportion of the products can be assigned to polar mechanisms, but they are very different from those usually found when polar peroxides are decomposed in solution. As in the usual solution experiments the fast reaction on the silica surface continues to give radical products as well as polar ones, but the distribution of radical product is somewhat different. For direct comparison, **1** and **2** were also decomposed in benzene and acetonitrile solutions. The silicas used as reaction media are designated by P_0 and P_1, which refer to two levels of purity. These are the same as silicas P_0H_1 and P_1H_1 used in an earlier investigation of radical reactions on surfaces;[3] in the present work no experiments on dehydroxylated silicas (suffix H_0) were included. Other factors varied in the present work were the use of photolysis at 26 °C as opposed to thermolysis at 55 °C and the effects of coadsorbed O_2 and coadsorbed acetonitrile.

The products are shown in Scheme I and their yields in Tables I–III. Some products can be assigned to radical-pair or ion-pair precursors merely from their structure. Thus the monomeric and dimeric alkanes RH and RR have to be radical, while products in which the neophyl carbon skeleton has rearranged with migration of methyl rather than phenyl have to be of ionic origin. Since acyloxy radicals decarboxylate readily, greater recovery of undecarboxylated COO moieties is another indication of increased ionic reaction. On these bases, **2** is always more ionic then **1** under a given set of reaction conditions. For a given peroxide, reaction on the silica surface is always more ionic than reaction in either of the two solvents. Since peroxide **3** is inherently more ionic than the other two, the increased yield of lactone in the sequence **1** < **2** < **3** indicates that this is probably an ion-derived product.

Radical Products

Neophyl radicals R_2 from **2** can be expected to rearrange to phenyl-*tert*-butyl radicals R'_2 in competition with abstraction and radical combination reactions. Neophyl radicals generated by other means in solution at 130 °C in the presence of good H donors are converted to mixtures of R_2H and R'_2H.[4] The rate constant for the rearrangement reaction in *tert*-butylbenzene solution at 27 °C is about 10^{-3} s^{-1}.[5] In the absence of good hydrogen donors the neophyl radicals can give dimers or esters by radical combination. Once rearranged, they have the additional possibility of giving alkenes, but these can also be formed from rearranged ion pairs.

Table III. Products from Peroxide **3** (Mol % Yields) on P_0 Silica[a]

p-$O_2NC_6H_4COOH$	92.8	R_2H	0.01
p-$O_2NC_6H_4COOH$	1.0[b]	R'_2H	0.00
R_2COOH	0.0	R_2R_2 and other dimers	0.00
R_2COOR_2	0.0		
$R_2COOR'_2$	0.0	phenylisobutylenes	
p-$O_2NC_6H_4COOR_2$	0.0	4	1.32
lactone 2	20.0	5	36.8
R_2OH	1.1		
R_2OSi	1.3[c]	phenylbutenes	
R'_2OH	3.7	6	1.54
R'_2OSi	3.5[c]	7	0.1
R''_2OH	0.0	8	7.55

[a] Mean of two runs at 3.26 and 6.5 wt %. [b] Extracted after hydrolysis of the silica. [c] Alcohols extracted after hydrolysis of the silica.

Constraints on the Motions of Adsorbed Neophyl Radicals. The decomposition of **2** on either P_0 or P_1 silica gives much less alkane than it does in solution, as is to be expected if a larger part of the reaction on silica is ionic. The important differences from solution are in the proportions of dimeric to monomeric alkanes and in the extent of rearrangement of the R_2 groups to R'_2. The increased proportion of dimer on the silica is the result of constraints on the translational motion of the adsorbed radicals. The alkyl groups in these dimers are mainly unrearranged, but this is also true of the dimers formed in benzene. Dimer formation is probably mostly geminate even in benzene. The contrast between the monomeric alkanes formed in the two media is more striking. Despite the greater availability of potential H donors in benzene and the probable shorter lifetime of the radicals, the

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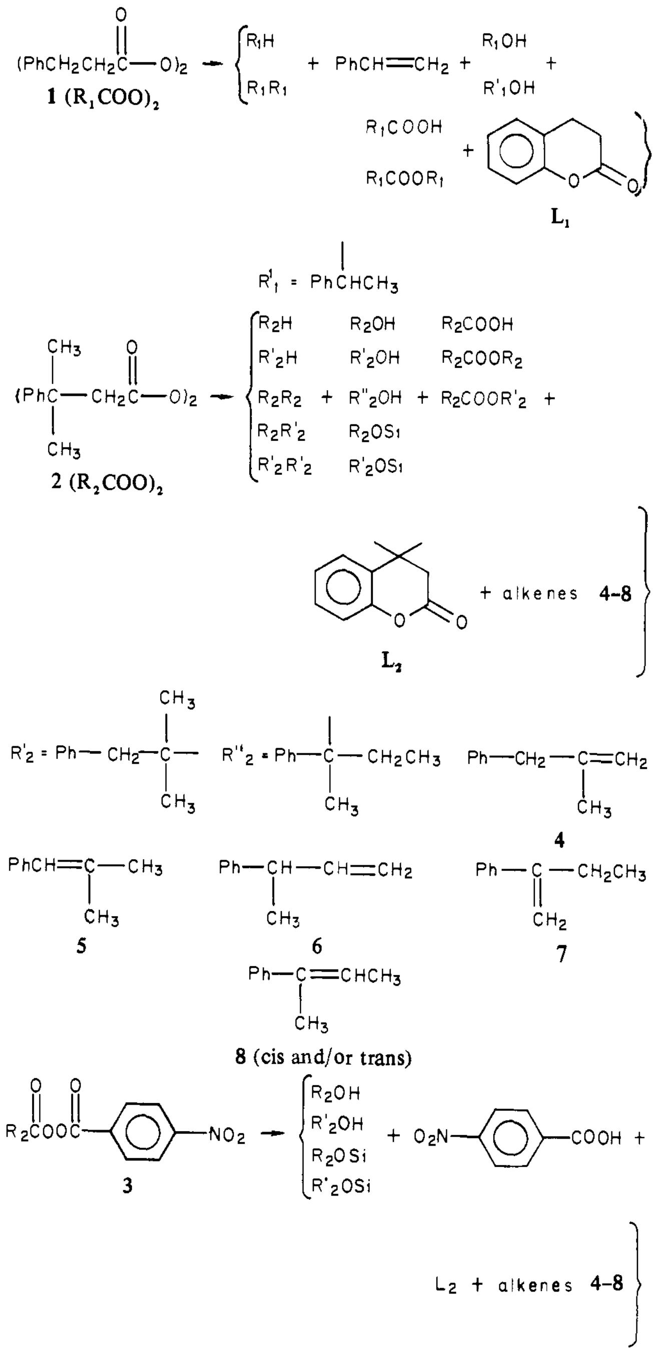
(3) Leffler, J. E.; Zupancic, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 259–267.

(4) (a) Rüchardt, C. *Chem. Ber.* **1961**, *94*, 2599–2608. (b) Rüchardt, C.; Hecht, R. *Ibid.* **1965**, *98*, 2471–2477.

(5) Hamilton, E. J., Jr.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 795.

Scheme I



proportion of rearranged alkyl groups in the R—H formed on silica is actually about 2 orders of magnitude lower than it is in benzene. It can be concluded that adsorption not only constrains the translational motions of the neophyl radicals *but also the internal motions necessary for phenyl migration.*

In the photolysis of **2** on P_0 silica at 26 °C the initial reaction should be mainly radical, although some unknown portion of the peroxide decomposes thermally even at 26 °C. Despite this uncertainty, we find a large increase in the yields of both monomeric and dimeric alkanes and again a very low proportion of rearranged groups.

Effects of Coadsorbates on the Radical Products. Both oxygen and acetonitrile are able to scavenge radicals in solution. In addition, any coadsorbed substance can also be expected to exert a site preemption effect[3] which will alter the proportions of the peroxide adsorbed on various chemically nonequivalent sites. Both oxygen and acetonitrile appear to preempt sites that would otherwise be occupied by the peroxide, or perhaps by intermediates, as well as trapping some of the radicals.

Coadsorbed oxygen very much lowers the yields of the monomeric alkanes R_2H and R'_2H, while simultaneously increasing the yields of the corresponding alcohols. A much more striking result is that the yield of *dimeric* alkanes RR is increased by substantial amounts and the dimers contain less rearranged alkyl than in the absence of oxygen. Very similar results are obtained with peroxide **1** and coadsorbed oxygen.

Apparently some of the alkane formation on silica is nongeminate. Oxygen is able to intercept the nongeminate radicals, both rearranged and unrearranged, and divert them to form the corresponding alcohols. The *increased* yield of dimer despite the trapping of some of the radicals, and the fact that the dimer is composed mainly of unrearranged alkyl groups, means that coadsorbed oxygen is increasing the relative rate of geminate dimer formation. This result suggests a site preemption effect. It also appears that the sites where combination now occurs are able to constrain the motions of the adsorbed neophyl radicals. These constraints encourage geminate recombination and discourage rearrangement.

Coadsorbed acetonitrile increases the amount of alkyl groups recovered as monomeric alkanes but, as in the case of oxygen, increases the yield of dimeric alkanes much more substantially (a factor of 3). At the same time, the extent of rearrangement in the enhanced yield of dimeric alkanes is reduced by more than a factor of 2. Acetonitrile traps those radicals that escape geminate reaction, converts them to RH, and prevents them from contributing rearranged alkyl groups to the dimer. At the same time, the coadsorbed acetonitrile directs the adsorption of the peroxide to sites that will favor the fast geminate recombination of unrearranged radicals.

Radical-Derived Esters. Esters are formed from diacyl peroxides in solution by a radical mechanism (geminate recombination) and by at least two ionic mechanisms.[1d] The fact that the esters formed on silica are almost entirely rearranged, *in contrast to the dimeric alkanes and in contrast to the esters formed in solution*, means that an ionic process is involved at some stage. On the other hand, coadsorbed oxygen decreases the yield of ester from **2**, suggesting that some of the ester passes through a radical stage as well. Photolysis rather than thermolysis increases the ester yield, and again the ester is almost entirely rearranged. Since photolysis is believed to give radicals as the initial intermediates, at least in solution,[6] the ester formed on silica might also be expected to have radicals as the initial intermediate. All of these observations can be reconciled by the hypothesis that neophyl acyloxy radical pairs are converted into ion pairs by electron transfer.[7] A fast or concerted rearrangement of the alkyl cation followed by combination with the carboxylate ion leads to the rearranged ester. Some of the ion pairs may of course be formed directly or by way of intermediates related to the carboxy inversion reaction. However, no esters of any kind were formed in the decomposition of **3** on silica, and we have no evidence for the presence of the carboxy inversion product itself.

Radical-Derived Phenylisobutylenes. The migration of phenyl either in the neophyl radical or in an ionic reaction provides a route to the formation of the phenylisobutylenes **4** (unconjugated) and **5** (conjugated). The relative yields of the two phenylisobutylenes in solution seem to depend at least in part on the radical vs. ionic orgin. Neophyl radicals generated in solution at 130 °C[4] give about equal amounts of **4** and **5**. Ionization of neophyl derivatives in solvolysis gives mainly the conjugated isomer **5**.[9] Our experiments with **2** in benzene and in acetonitrile gave ratios in which the conjugated isomer predominated by a factor of about 9.

On P_1 silica there is no complication from silica-catalyzed isomerization of the alkene, and the product is mainly **4**, suggesting that radical pairs are the major precursors of the phenylisobutylenes formed from **2**. This conclusion is supported by the decreased total yield and decreased proportion of **4** brought about by coadsorbed acetonitrile.

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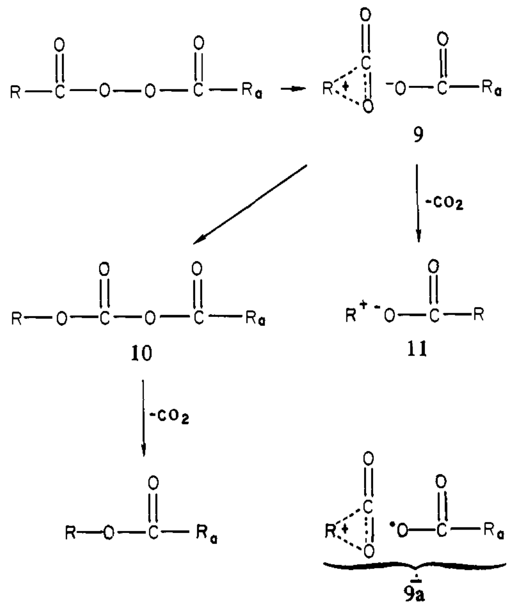
(6) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395–4404.
(7) Lawler, R. G.; Barbara, P. F.; Jacobs, D. *Ibid.* **1978**, *100*, 4912–4914.
(8) Longosz, E. J.; Tarbell, D. S. *J. Org. Chem.* **1961**, *26*, 2161–2169.
(9) Saunders, W. H., Jr.; Paine, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 882.

On P_0 silica the phenylisobutylenes will eventually isomerize to an equilibrium mixture in which the ratio of **4** to **5** is about 0.04. In the thermolysis of **2** on P_0 silica, **4** is the minor isomer but is still found in more than the equilibrium proportion. In the photolysis, **4** is the major isomer. We conclude that part of the reaction leading to phenylisobutylenes when **2** is decomposed on P_0 silica proceeds via radicals even in the thermolysis. In contrast, the decomposition of the more polar peroxide **3** on P_0 silica gives mainly **5**, supporting a predominantly ionic mechanism.

Products Derived from Ion Pairs

Ion-derived products formed from diacyl peroxides in solution can be summarized quickly. The first to be recognized was the carboxyinversion compound **10**,[1c] which may be formed from an ion pair resembling **9**. The hypothetical common intermediate at the point at which the mechanism diverges into separate ionic and radical branches may be a hybrid **9a** in which one of the electrons of the anionic part of **9** is distributed over both moieties or rapidly transferring. Esters are formed by the geminate recombination of radical pairs, by the decomposition of carboxy inversion compounds **10**, from alkyl cation–carboxylate ion pairs **11** and possibly directly from **9** with loss of CO_2 without formation of **10**. An additional route to the ion pair **11** and hence to a variety of ionic products is electron transfer from alkyl to acyloxy radical.[7]



The carbonium ion of **11** can be trapped by suitable nucleophiles such as acetonitrile solvent.[1a,b] It is also possible that the trapped carbonium ion is supplied directly from **9** rather than from **11**; however, no R—OC(=O)$^+$ derivatives, other than the carboxy inversion compound, have been isolated from reactions in solution.

Carboxy Inversion Intermediates. Because the carboxy inversion compound is often the major product of the ionic reaction in solution, we sought evidence of its formation on silica. In solution, even when **10** can not be isolated, it can be detected by transient infrared bands or by the delayed evolution of CO_2 as the inversion product decomposes to ester.[1e] An alternative mode of decomposition given by some carboxy inversion compounds is disproportionation to dialkyl carbonate and acid anhydride.[8] In either case, if the product washed from the silica contained **10** or if it contained dialkyl carbonate, acid hydrolysis should evolve CO_2. No CO_2 was formed from the products extracted from the experiments with **2** or **3** on P_0 silica or **2** on P_1 silica.

In order to detect cationic intermediates that might have been trapped by reaction with *silanol* groups, we hydrolyzed the silica remaining after simple extraction of the merely physically adsorbed products. This procedure gave alcohols and, in the case of **2** and **3** on P_0 silica, 1–2 mol % of CO_2. No CO_2 was evolved from the P_1 silica. If P_0 silica traps acylium ions from the ion pair **9**, it is only a minor reaction, and we do not believe that the carboxy inversion reaction is an important process on silica.

Table IV. Decomposition Rates[f]

temp, °C	concn	medium	10^5k, s^{-1}
		peroxide 1	
55.8	0.0536 M	cyclohexane	0.68
49.4	2.83 wt %	P_0 silica	7.5
		peroxide 2	
55.0	0.0509 M	cyclohexane	0.64
55.0	0.0509 M	cyclohexane[a]	0.84[a]
55.0	0.0502 M	acetonitrile	2.27
26	3.2 wt %[e]	P_0 silica	1.32
40	3.61 wt %[e]	P_0 silica	8.0
40	7.29 wt %[e]	P_0 silica	7.7
40	3.51 wt %[e]	P_0 silica[c]	7.2[c]
50	3.20 wt %[e]	P_0 silica	25.6
50	3.21 wt %[e]	P_1 silica	21.3
55	3.2 wt %[e]	P_0 silica	45[d]
		peroxide 3	
40	0.014 M	cyclohexane	0.083[b,d]
55	0.014 M	cyclohexane	0.79[b,d]
40	3.92 wt %	P_0 silica	13.3

[a] With 0.095 M $ClCH_2COOH$. [b] From ref 2. [c] With 0.84 wt % $PhC(CH_3)_2CH_2COOH$. The acid was put on before the peroxide. [d] Extrapolated from data at other temperatures. [e] A wt % of 3.1 corresponds to about 0.1 monolayer. [f] Based on the first half-life.

Alcohols from Ion Pairs. Alcohols are found both in the extract from the silica and after hydrolysis of the silica. Coadsorbed oxygen increased the yield of unrearranged alcohol R_2OH in the extract before hydrolysis, and as discussed before, part of this effect is due to trapping of alkyl radicals. However, oxygen also increases the yield of rearranged alcohols R'_2OH in the extract, slightly increases the yield of chemisorbed R'_2OH, and slightly increases the yield of R''_2OH. The latter is undoubtedly an ionic product since the rearrangement involves methyl migration. These increases in yield can be ascribed either to site preemption effects or to electron transfer. Coadsorbed acetonitrile, while trapping radicals as monomeric alkane, also increases the yields of R_2OH, R'_2OH, R''_2OH, and chemisorbed R'_2OH. Initiation by photolysis rather than thermolysis decreases the yields of alcohols, both rearranged and unrearranged, both physically adsorbed and chemically adsorbed. The alcohols formed on silica are therefore in large part ionic products. The alcohols formed from **2** in solution may have been formed by way of the carboxy inversion reaction, but we did not hydrolyze the solution products to test for CO_2 evolution.

Alkenes from Ion Pairs. The phenylisobutylene **5** is favored by the ionic reaction and is the major product from **3** on P_0 silica. Besides the phenylisobutylenes, the alkenes include the phenylbutenes **6–8** in which the carbon skeleton has undergone rearrangement with methyl migration. These ionic products are found only in traces or not at all in solution and only to a minor extent in photolysis on silica. The total yield of **6–8** on P_0 is greater from **3** than from **2**, and the yield from **2** is increased both by co-adsorbed oxygen and by co-adsorbed acetonitrile. In the solvolysis of neophyl derivatives, methyl migration is observed, but only to the extent of less than 1% of the phenyl migration.[9] In the decomposition of **2** on P_1 silica with co-adsorbed acetonitrile the amount of methyl migration is about 60% of the amount of phenyl migration.

Lactones. The lactones L_1 from **1** and L_2 from **2** and **3** are not formed in solution. The yields are greater from **2** than from **1**, as might be expected from the gem. dimethyl effect. They are also greater in thermolysis than in photolysis, and greater from the thermolysis of **3** than **2**. Co-adsorbed oxygen increases the yields, but co-adsorbed acetonitrile has the opposite effect.

Kinetics

Rate constants for the decomposition of peroxides **1–3** are given in Table IV. In the nonpolar solvent cyclohexane differences in rate are very small. Chloroacetic acid added to a cyclohexane solution of **2** also gave only a slight increase in rate.

The change in reaction medium from cyclohexane to silica gives very large increases in rate and also magnifies the differences between the peroxides. The rate constants for **2** on P_0 silica is about 70 times that for **2** in cyclohexane, and the rate constant for **3** on P_0 silica is about 160 times that in cyclohexane.

The Question of a Common Intermediate. The products from peroxide **3** on P_0 silica can be attributed entirely to ionic reactions, and the increase in rate as the medium is changed from cyclohexane to silica can be attributed to a change from a radical or mostly radical mechanism to an ionic one. In the cases of peroxides **1** and **2**, however, the formation of hydrocarbons RH and RR puts a lower limit on the proportion of the reaction still giving radicals on silica. If the radical and ionic products are formed by independent initial homolysis and heterolysis rather than in a reaction that branches after the formation of a single polar intermediate, the rate of the homolysis can be estimated from the total rate and the fraction of radical-derived products. If we assume for the moment that the reaction of **2** in cyclohexane is entirely radical, the rate of homolysis in cyclohexane at 55 °C is 0.64×10^{-5} s^{-1}. With use of the yields of RH and RR to estimate the fraction of radical reaction of **2** on P_0 silica, the rate of homolysis is 1.06×10^{-5} s^{-1}. If it is assumed that RH and RR and the phenylisobutylene **4** are radical derived, the homolysis rate on P_0 silica becomes 3.9×10^{-5} s^{-1} and becomes still higher if some of the products that seem to be produced by both radical and ionic processes are taken into account. The ratio 3.9/0.64 is not an impossibly high one for medium effects on a radical reaction but seems to be in the wrong direction if the decreased mobility of adsorbed reagents is considered. In the decomposition of azocumene,[3] the rate on P_0 silica was found to be only half that in solution. We therefore conclude that the Walling hypothesis[1b] of a common intermediate for the radical and ionic reactions applies to the decomposition of **2** on silica.

Kinetic Heterogeneity. Since the different types of adsorption site on a silica surface are not kinetically equivalent and since adsorption prevents equilibration of adsorbate among the different sites on the time scale of our decomposition kinetics, the first-order rate constants decrease somewhat during a run. The decrease between the first half-life and later half-lives ranges from 10 to 20% and is similar to that observed for the decomposition of azocumene on the same silicas.[3]

Adsorption sites on a given type of silica can differ not only as reaction media but also in the rate at which they adsorb the reagent. If the *fast* adsorption sites are *slow* reaction sites, as was the case for azocumene adsorbed on P_0 and P_1 silicas,[3] a low initial surface concentration of reagent will lead to a slower reaction. In the present case, the fast adsorption sites are *fast* sites for the decomposition and the decomposition rate constants are greater at low surface concentrations. At low dosages of the peroxide more of the peroxide can be accommodated by the faster adsorbing and faster reaction sites. This effect can be seen in Table IV, in which weight percentages near 3% correspond to about 0.1 of a monolayer of peroxide on the surface and 6 or 7% corresponds to about 0.2 monolayer.

Since P_0 silica is richer than P_1 silica in the more acidic and more strongly adsorbing sites,[3] the peroxide decomposes more rapidly at a given surface coverage on P_0 silica. The reverse is true for azocumene. Unlike the peroxides, azocumene has a nonpolar transition state.

Interpretation of the Medium Effect. Catalysis of the decomposition of the more polar diacyl peroxides by carboxylic acids can be quite pronounced in solution.[1c,e,15] In the case of our borderline peroxide **2** there is moderate catalysis by chloroacetic acid in cyclohexane and the decomposition in acetonitrile solution shows signs of autocatalysis as the concentration of R_2COOH builds up toward the end of the reaction.

The decomposition of **2** on silica is faster on the more rapidly adsorbing sites and faster on P_0 silica than on P_1 silica. The differences between these silicas can be summarized as follows:[3] P_0 is more acidic and is more active in promoting prototropic reactions, adsorbed substances are slightly less mobile, and P_0 silica has more of the fast adsorption sites. These differences support a transition state in which the peroxide is hydrogen bonded. It may be similar to the acid-catalyzed transition states for the reaction of polar peroxides in solution, although the ultimate products are quite different. Formation of a hydrogen-bonded transition state on the silica surface should have less of an entropy penalty than association with a carboxylic acid in solution, and other polar interactions with the surface should have less of an entropy penalty than interaction with a solvent.

It is were possible to prepare a molecular complex of peroxide plus carboxylic acid on the surface, it may be that this species would also lead to a fast decomposition of the peroxide even though the effect of added carboxylic acid on **2** in solution is small. However, there is no autocatalysis of the decomposition of **2** on the silica even though R_2COOH is a major reaction product. The acid is probably not mobile enough to interact with the remaining peroxide adsorbed at other sites. Added acid placed on the surface before or with the peroxide decelerates the reaction, probably by preempting the strong adsorption sites. The reverse of this kinetic effect is observed in the case of azocumene[3] when the strong adsorption sites are preempted by azobenzene.

Experimental

β-Phenylpropionyl Peroxide 1.[10] A solution of 33.7 g (0.200 mol) of the acid chloride in 500 mL of ether was cooled to 0–5 °C after which a solution of 5.32 g (0.153 mol) of 98% H_2O_2 dissolved in ether was added dropwise with stirring. Next, a solution of 19.1 g (0.242 mol) of dry pyridine in ether was added dropwise during 2 h at 0–5 °C with stirring. Cooling and stirring were continued for 1 h; then the solution was washed with water several times, dried over Na_2SO_4, and stripped of ether by rotary evaporation. The oil was dissolved in a little ether and about 150 mL of petroleum ether. The peroxide was crystallized from this solution by cooling to −20 °C and recrystallized from low boiling petroleum ether: mp 31 °C dec, (lit.[10] 38 °C dec); IR, doublet at 1800 cm^{-1} in CCl_4; NMR (CCl_4), singlet at δ 7.20, multiplet at δ 2.98 and at δ 2.60.

β-Phenylisovaleric Acid. The reaction was conducted in a three-neck flask provided with a magnetic stirrer, reflux condenser, dropping funnel, and an inert atmosphere. To 19 g of Mg were added ca. 200 mL of tetrahydrofuran freshly distilled from $LiAlH_4$ and then 15 mL of neophyl chloride.[11] Introducing a crystal of I_2 and 2 mL of ethylene bromide and warming with a heat gun induced a vigorous reaction. Additional THF (total 700 mL) and neophyl chloride (total 120 g) was added in small portions during 2 h; then the mixture was stirred for another 5 h. Excess Dry Ice was added with stirring and the THF removed by rotary evaporation. The gummy residue was treated with excess 3 N HCl, the solution stirred, and the organic layer dissolved with ether: yield, 110 g (80%); mp 59 °C. Before conversion to peroxide the acid was shown to be free from rearranged isomers by NMR spectroscopy.

β-Phenylisovaleryl Peroxide 2.[12] A solution of 33 g (0.168 mol) of the acid chloride in an equal volume of dry ether was cooled to 0–5 °C, and 9.0 mL of 30% H_2O_2 added dropwise with stirring. Next a solution of 8.64 g (0.216 mol) of NaOH in 11 mL of H_2O was added dropwise with stirring while maintaining the temperature at 0–5 °C. After an additional hour of vigorous stirring, water was added and the ether layer separated, washed several times with water, and dried over Na_2SO_4. The oil remaining after evaporation of the solvent crystallized on standing. It was recrystallized by dissolving it in a minimum amount of $CHCl_3$, adding absolute ethanol, and cooling: needles, mp 36 °C dec (lit.[12] 40 °C); IR (CCl_4) 1810 and 1785 cm^{-1}; NMR (CCl_4) δ 1.47 (s, 6 H), 2.60 (s, 2 H), 7.25 (m, 5 H).

β-Phenylisovaleryl *p*-Nitrobenzoyl Peroxide 3.[2] This peroxide was made from β-phenylisovaleryl chloride and *p*-nitroperbenzoic acid.

Identification of Products. The carboxylic acids were identified by their melting points and NMR and IR spectra. In addition, the *p*-nitrobenzoic acid from **3** was methylated and found to contain less than 1% of R_2COOH by means of GLC. The alkanes R_2H and R'_2H, previously isolated from the products of the decomposition of **2** in benzene by Rickatson and Stevens,[12] were identified by spiking with authentic samples and chromatographing the mixture on a 25-m Supelco SP 2100 quartz capillary column using a flame ionization detector. The peak from the spiked sample increased in relative intensity but did not change in shape or develop a shoulder. The spiking was then confirmed by using

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a 25-m Carbowax 20 M column, which has quite different retention properties.

The alkane $R'_2R'_2$ had also been isolated previously,[12,13a] and we confirmed it by spiking on the two GLC columns using an authentic sample.[16] The alkane R_2R_2 was isolated by LC, and its ^1H NMR at 270 MHZ compared with that of a synthetic sample;[17] the isolated sample had the same peaks but appeared to be contaminated with a small amount of $R'_2R'_2$. The structure of R_2R_2 was confirmed by spiking on two columns with an authentic sample. The peak assigned to R'_2R_2 remained next to that of R_2R_2 on both GLC columns.

The alkenes **4** and **5** had also been isolated previously,[12] but were also isolated from our reaction products by GLC and LC. The ^1H NMR spectra were compared with those of authentic samples and the GLC peaks confirmed by spiking on two columns.

A mixture of the phenylbutenes **6**, **7**, and **8** was isolated from the decomposition products from **2** by GLC and the 270-MHZ ^1H NMR spectrum compared to that of a mixture made by the dehydration of a synthetic sample of the alcohol R''_2OH. The GLC peaks of this mixture were assigned to the isomers on the basis of the intensities in the integrated ^1H NMR spectrum. The synthetic mixture was used to identify these alkenes in various product mixtures by spiking on the two GLC columns.

The esters R_2OOCR_2 and R'_2OOCR_2 have been found in the products from the decomposition of **2** in hexachloroacetone and characterized by Shevlin and Hansen.[13c] The esters were isolated from our product mixtures by GLC and LC and their IR and NMR spectra compared with those reported in the literature and with those of our synthetic samples. The peaks were identified in various product mixtures by spiking with authentic samples on both GLC columns.

The lactone L_2 was isolated by GLC and LC and its ^1H NMR spectrum compared with that of a synthetic sample.[13d] This sample was used to confirm the lactone in various product mixtures by spiking on both columns.

The alcohols R_2OH and R'_2OH were isolated by GLC and LC and the NMR spectra compared with those of synthetic samples.[13b] They were accompanied by traces of the alcohol $R''OH$ identified by peaks corresponding to those of a synthetic sample. Synthetic samples were used to identify GLC peaks by spiking on both columns.

The lactone L_1, R_1OOCR, R_1OH, R'_1OH, styrene, R_1H, $R_1C_6H_5$, and R_1R_1 were identified by spiking with authentic samples.

1-Phenyl-1-methylcyclopropane was synthesized from α-methylstyrene and methylene iodide[14] and characterized by its ^1H NMR (δ) spectrum: aromatic multiplet, 5 H, 7.01; CH_3, 3 H, 1.35; CH_2CH_2, 2 H, m, 0.65; 2 H, m, 0.78. This compound did not correspond to any GLC peak in our product mixtures, although it has been reported as a product from **2** and related peroxides decomposing in solution.[12,13c]

Product Analysis Runs. The peroxide was put on the silica from a hexane solution using either of the two methods of ref 3; the solvent was then removed by tumbling in a rotary evaporation apparatus until the silica was free flowing, and then the silica was transferred to an amplitude for degassing. Degassing was usually continued until the pressure reached 10^{-5}mmHg. For photolysis runs, the ampule was a quartz tube cooled by a stream of water, that was rotated continuously so as to tumble the particles during the photolysis and to ensure uniform illumination.

Products were removed from the silica in two stages. In the first stage, the silica was simply washed with several portions of ether. The ether solution was extracted with bicarbonate to remove the acid, then dried, and concentrated for the subsequent analysis of the neutral products.

In the second stage, the extracted silica was stirred with 5% H_2SO_4 at 50 °C for 1 h, and then this mixture was extracted with ether. This second ether extract was the source of the alcohols identified in the tables as ROSi.

In a few experiments the first and second ether extracts were hydrolyzed with dilute H_2SO_4 while connected to a gas adsorption train to detect evolution of CO_2 during the hydrolysis.

The yields of acid were determined by weighing the isolated acids.

Yields of neutral products were determined by gas chromatography using a Hewlett-Packard computer-controlled GC with a flame ionization detector and a 25-m Supelco SP 2100 quartz capillary column and a glass inlet splitter. The more volatile components, alkanes, alkenes, and alcohols, were determined by using *p*-bromotoluene as the internal standard, an initial temperature of 60 °C, and a temperature program that eluted the last alcohol at about 17 min and a temperature of about 125 °C. The less volatile components, lactone, esters, and dimeric hydrocarbons, were determined by using phenyl benzoate as the internal standard and a temperature program beginning at 160 °C. The less volatile ester emerged at about 16 min at which point the temperature was about 240 °C.

Kinetic Runs. Samples for kinetic runs were prepared as described for product studies except that the silica, after rotary evaporation to the free flowing stage, was partitioned approximately among a number of separate ampules. After the thermolysis or photolysis the ampule was opened and the bulk of the contents quickly transferred to a weighing bottle; this avoids increases in weight due to adsorption of atmospheric moisture. The sample, consisting of a 1–2-g aliquot, was then transferred to a flask, and 15 mL of acetic acid saturated with CO_2 and 1.5 mL of saturated aqueous KI and a pellet of Dry Ice were added. The flask was then heated on the stream bath for 7 min, diluted with 50 mL of H_2O, and titrated to a starch end point, with thorough stirring, by using 0.05 M sodium thiosulfate. A CO_2 atmosphere was maintained by adding small pellets of Dry Ice.

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Sequence-Specific Osmium Reagents for Polynucleotides.
2. A Method for Thymine–Cytosine Pairs

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Abstract: We have modified the dinucleoside monophosphate, deoxythymidylyldeoxycytidine (d-TpC), by replacement of the exocyclic amino group of cytosine with a series of ligands, $H_2N(CH_2)_nN(CH_3)CH_2CH_2N(CH_3)_2$, where $n = 2, 4$, and 6. The kinetics of the reactions of these modified dinucleoside monophosphates with osmium tetroxide were measured. The modified nucleotides react with osmium tetroxide 4200, 7900, and 1200 times faster than the unmodified species for $n = 6, 4$, and 2, respectively. The products of the reactions are macrocyclic oxoosmium(VI) esters for which 360-MHz proton NMR spectra are reported.

Osmium(VIII) reagents add to the 5,6-double bond of pyrimidines to form osmium(VI) esters.[1] The reactivity order for the common pyrimidine residues is thymine > uracil > cytosine. The common purines are unreactive. This kinetic specificity for

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