0.992, $\Delta^{\ddagger}C_p^{\ominus}$ = 3200 J mol^{-1} K^{-1}), in accord with the onset of temperature-sensitive cluster formation. The occurrence of pseudophase separation is further supported by measurements of the Dimroth–Reichardt $E_T(30)$ solvent parameter[13] (Figure 2). There is a steep decrease of $E_T(30)$ going from n_{H_2O} = 0.996 to n_{H_2O} = 0.98, indicative for a large change in micropolarity experienced by the probe molecule and fully consistent with clustering of CHP. At still higher concentration of CHP only a modest further decrease of $E_T(30)$ is observed. Comparison of the *chic* at 0.28 ± 0.05 M for CHP–H_2O (30 °C) with that for the *t*-BuOH–H_2O system at 1.4 ± 0.3 M (25 °C)[5] illustrates the strongly hydrophobic character of CHP. Thus the present results characterize water-rich CHP–H_2O as an extreme case of a TA solution with significant overlap of hydrophobic hydration shells occurring already at concentrations well below 1 mol % of CHP.

Experimental Section

Materials. Sodium 6-nitrobenzisoxazole-3-carboxylate was prepared according to a literature procedure.[14] *N*-Cyclohexyl-2-pyrrolidone (obtained both from GAF Corp. and Janssen Chimica) was distilled twice (bp 96 °C (0.04 mm); n^{20}_D = 1.4980, lit.[15] n^{20}_D = 1.4975). Demineralized water was distilled twice in an all-quartz unit. 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide (the $E_T(30)$ probe) was kindly supplied by Prof. Ch. Reichardt, Marburg, West Germany. All solutions were made up by mass and contained 10^{-3} M of NaOH to prevent protonation of the kinetic and spectroscopic probe.

Kinetic Measurements. These were performed by monitoring the increase of absorption as a function of time at 490 nm. All first-order rate constants (determined at least in duplicate) were reproducible to within 3%. A Perkin-Elmer λ5 spectrophotometer, equipped with a Perkin-Elmer 3600 data station, was employed. Isobaric activation parameters were obtained for the temperature ranges given in Table I. Linear Eyring plots were found, except just above the *chic*, where $\Delta^{\ddagger}C_p^{\ominus}$ was calculated by using the Valentiner equation.[16]

Spectroscopic Measurements. $E_T(30)$ values were calculated from $E_T(30) = Nhc\lambda_{max}^{-1}$ in which N = Avogadro's number, h = Planck's constant, and c = velocity of light. The λ_{max} values (±0.5 nm) were measured with the Perkin-Elmer λ5 spectrophotometer.

Acknowledgment. We thank A. van Warners for preliminary measurements on the CHP–H_2O system.

Supplementary Material Available: First-order rate constants at different temperatures for decarboxylation of 1 in CHP–H_2O at n_{H_2O} = 0.992, 0.960, and 0.940 (1 page). Ordering information is given on any current masthead page.

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Polar Effects in the Decomposition of Diaroyl Peroxides. Benzoyl Peroxide on Silica Gel

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Introduction

Many diacyl peroxides are known to give both ion pairs and radical pairs on thermal decomposition. In the Walling model,[1] the bifurcation of the reaction path occurs at a common intermediate rather than at the peroxide itself. The transition state leading to this intermediate is sufficiently polar for the disappearance of the peroxide to be accelerated both by polar solvents and by electron-releasing substituents. Since the rate- and product-determining steps are decoupled, the polar substituent or solvent can increase the rate of formation not only of the ion pairs but also of the radical pairs.

Since the rate-determining transition state and the common intermediate are represented as resonance hybrids of singlet radical pair and ion-pair structures, a continuum rather than a duality of mechanisms is possible. At one extreme the rate is insensitive to small polar perturbations and the products are almost entirely radical. At the other extreme the rate is very sensitive to polar effects, and the products are derived almost entirely from ion pairs. In general, polarizing substituents and polar solvents will increase both the overall rate and the proportion of products derived from ion pairs.

The best evidence for a Walling mechanism is the isolation of a mixture of ionic and radical products, but products have been thoroughly characterized only for a few peroxides. Increased rates in polar media are also indicative, although they may be due in part to induced decomposition. For alkanoyl peroxides with branches at the α-position, the formation of ion pairs is well established by product studies; these peroxides are also very sensitive to the polarity of the solvent. For unbranched alkanoyl peroxides, the product data are insufficient, but a moderate sensitivity to the polarity of common solvents supports a Walling mechanism. For the acetyl peroxide, a similar but not identical series of solvents shows almost no sensitivity to solvent polarity.[2] This extremely dangerous peroxide is therefore either an exception[3] or a representative of the radical extreme of the Walling continuum, although its behavior on silica has not been studied.

Aroyl peroxides are a special case in which an important ionic contributing structure should be like 1 of eq 1. The Walling mechanism is well established for benzoyl peroxides with *p*-methoxy substituents, for example *p*-methoxy-*p*′-nitrobenzoyl peroxide decomposing in thionyl chloride[4] and anisoyl peroxide decomposing on silica gel.[5] These reactions gave the carboxyinversion compound **2**, formed by the collapse of the intimate ion pair **1**, as a major product accompanied by minor amounts of radical products.

For benzoyl peroxide itself, however, no products analogous to **2** have ever been observed, and the use of more polar solvents has produced only moderate increases in rate. For example, the rates of the styrene-inhibited reaction in acetic anhydride,[6] and the 3,4-dichlorostyrene-inhibited reaction in acetonitrile,[7] were less than 1.7 times the rates in carbon tetrachloride. Although induced decomposition was suppressed as much as possible in obtaining those rates, it is not certain that the entire effect of the change in solvent was due to an increase in the unimolecular rate constant. The rate is also insensitive to the presence of strong carboxylic acids and even sulfuric acid.[8]

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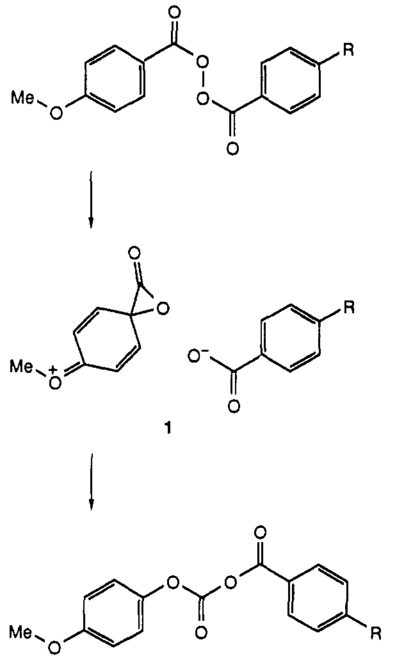

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2

(1)

The effects of a variety of substituents on the thermolysis rate, reported for the reaction in dioxane[6] and in acetophenone,[9] are consistent with polarized transition states. In the dioxane experiments the Hammett plot of the rates in the presence of 3,4-dichlorostyrene against ($\sigma_1 + \sigma_2$) was roughly linear and had a slope of −0.38. Rates for *p*-methoxy and *p*-cyano substituents were greater than predicted by the least-squares line, suggesting that the relationship might be slightly concave-up rather than linear. The concave-up appearance of the curve was much more pronounced for the acetophenone data. *p*-Methoxy and strongly electron-withdrawing groups again gave rates greater than expected. These results suggest polarized transition states at both ends of the Hammett series, but not necessarily for benzoyl peroxides with weakly polar substituents.

From the evidence cited above, the transition state for the unimolecular thermolysis of benzoyl peroxide might have some polar character, but the products could still be benzoyloxy radicals rather than ion pairs. The behavior of benzoyl peroxide on silica is the object of the present paper. Silica[10] as a reaction medium is not only extremely polar but also affords the advantages of lower mobility for radicals that might induce the decomposition of the peroxide, and complete absence of chain transfer. We used the radical products from the photolysis on silica to help sort out the radical versus ionic origins of the thermolysis products.

Results and Discussion

Kinetics. First-order plots for the thermolysis of benzoyl peroxide on silica show a decrease in k_{obsd} during the runs. This is consistent with a surface reaction in which some sites are faster than others and the reagent cannot readily move between sites.[10] The apparent first-order rate constant at 80 °C is 10.1×10^{-5} s^{-1} in the first half-life, decreasing by about 20% in the second half-life. Rate constants for the reaction on silica are compared with those from conventional solvents in Table I. As can be seen from the table, in conventional solvents there is some uncertainty in the rate, probably reflecting difficulties in separating the unimolecular part of the rate from the induced part. At 80 °C the reaction on silica is about 3 times as fast as in benzene or styrene, a ratio that merely begins to suggest incursion of the ionic reaction mode. When the temperature is lowered to 40 °C, the reaction on silica is slow but can still be followed conveniently; the rate is now approximately 15 times that in benzene or styrene. This ratio is about the same as that reported for the very solvent-sensitive isobutyryl peroxide for the solvent change from cyclohexane to acetonitrile.[1]

Table I. Benzoyl Peroxide Rates

medium	t, °C	k_1, s^{-1} $\times 10^5$
benzene	80	4.28,^{a} 2.19,^{b} 3.4^c
styrene	80	2.71^d
P_i silica	80	8.43^e

medium	t, °C	k_1, s^{-1} $\times 10^8$
benzene	40	7.61^f
styrene	40	6.0^d
P_i silica	40	100.^{e,g}

^{a}From ref 6, styrene inhibited. ^{b}From ref 19, in presence of galvinoxyl, corrected for small temperature difference. ^{c}From ref 20, first-order part of k_1, corrected for small temperature difference. ^{d}From ref 11, derived from styrene polymerization. ^{e}Mean of one titrimetric and one NMR run. Rate decreases during the run. Nominal surface coverage 0.2. P_i silica is the P_1H_1 of ref 10a. ^{f}Calculated from the mean 80 °C rates and the activation energy from ref 20. ^{g}The rate for anisoyl peroxide on silica (at 25 °C rather than 40 °C) is greater than this by several orders of magnitude (ref 5).

The enthalpy and entropy of activation for the decomposition on silica are approximately 24 kcal mol^{-1} and −10 cal mol^{-1} deg^{-1}. In styrene[11] the corresponding parameters are 32.9 kcal mol^{-1} and +13.5 cal mol^{-1} deg^{-1}. Activation enthalpies near 33 probably correspond to the peroxide O–O bond strength and a homolytic reaction.[12] Low activation enthalpies and entropies for the decomposition of peroxides are associated with the ionic decomposition mode, both for reactions in solution[8] and on silica. A lower activation enthalpy for the process leading to ions accounts for the increase in the importance of the ionic mode of decomposition of various peroxides at lower temperatures.[13]

Products. Products are listed in Table II for various reaction conditions in the order in which the extent of ionic reaction should increase. These conditions are photolysis at 25 °C, thermolysis at 80 °C, thermolysis at 40 °C with high monolayer coverage, thermolysis at 40 °C with low monolayer coverage, and thermolysis at 40 °C on P_0 silica.[14] Photolysis, even of highly polar peroxides, is known to give radicals rather than ion pairs. Thermolysis at the higher temperature should favor the radical reaction because of the higher activation energy. Thermolysis at higher monolayer coverage should favor radical products, since the catalytically most active sites are too few to accommodate all of the peroxide molecules. Thermolysis on P_0 silica should favor the ionic reaction, because this silica is catalytically more active.[10]

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Table II.[a] Benzoyl Peroxide on Silica

product	photolysis 25 °C[f]	thermolysis 80 °C[b,f]	thermolysis 40 °C[c]	thermolysis 40 °C[b,f]	thermolysis 40 °C[e]
biphenyl	0.87	0.60	0.15	0.03	0.00
phenyl benzoate	9.5	4.0	3.4	1.7	2.5
acids[d]	134	115	173	156	105
dibenzo-α-pyrone	1.2	0.8	0.30	0.2	0.12
phenol	1.8	15.0	7.6	8.5	43.
diphenyl carbonate	0.0	0.0	0.07	0.08	0.44
hydroxyphenyl benzoates	0.0	4.1	1.5	4.3	4.8
benzene	–	trace	–	–	–

[a] Percent moles product/moles of peroxide. From left to right, the total percent recoveries of phenyl groups from ^{12}C and ^{13}C (in parentheses) were 92 (67), 78 (70), 96, 88 (90), 82. [b] 2.2 wt % benzoyl peroxide on P_i silica, approximately 0.2 monolayer relative to N_2 area. [c] 10.6 wt %, approximately 1.0 monolayer relative to N_2 area. [d] Mostly benzoic acid. [e] On P_0[14] silica, low monolayer fraction. [f] Mean from benzoyl peroxide and 90% ^{13}C carbonyl-labeled peroxide.

Biphenyl, a radical product, was formed in greatest yield in the photolysis. In the thermolysis at low coverage, the biphenyl yield decreased by about a factor of 30, while on the more catalytically active P_0 silica it was no longer detectable.

Esters can be formed from diacyl peroxides in several ways: from radical pairs, from ion pairs, and in some cases as one of the products of decomposition of a carboxyinversion intermediate. Phenyl benzoate was isolated in lower yield from the thermolyses, particularly at 40 °C, than from the photolysis, where it is probably formed by geminate recombination of singlet phenyl and benzoyloxy radical pairs.

Phenol is a very minor product in the photolysis, but is an important product in the thermolyses. The probable source is thermolysis to a carboxyinversion intermediate (analogous to **2**), or the corresponding ion pair. Either of these could react with adsorbed water or with surface hydroxyl groups to give phenol. Part of the phenol and part of the benzoic acid were recovered from the silica only after hydrolysis with aqueous sulfuric acid.

In the thermolysis of benzoyl peroxide followed by ^{13}C NMR, the benzoic acid carbonyl signal appears at about the same rate as the disappearance of the peroxide signal, and no signal from the carboxyinversion compound is seen. The carboxyinversion product corresponding to benzoyl peroxide is reported to decompose at room temperature into phenyl benzoate, carbon dioxide, benzoic anhydride, and diphenyl carbonate.[15] The expected decomposition products on silica, by analogy with the behavior of the carboxyinversion product from anisoyl peroxide,[5] are phenol and benzoic acid.

Although the carboxyinversion intermediate is easily seen in the thermolysis of bis(*p*-methoxybenzoyl) peroxide, in that system the lifetime of the carboxyinversion product is about 10 times that of the peroxide. On silica at 40 °C the lifetime of benzoyl peroxide is orders of magnitude greater than that of bis(*p*-methoxybenzoyl) peroxide, and the carboxyinversion compound cannot accumulate.

Hydroxyphenyl benzoates are formed in solution by the reaction of phenols with benzoyl peroxide.[16] In the thermolysis of the peroxide on silica, the probable source of these compounds is reaction of the phenol with undecomposed peroxide. The presence of phenol early enough to react with the peroxide is consistent with its formation from the unstable carboxyinversion compound. Decomposition of the peroxide at 40 °C on silica containing adsorbed phenol gave about 23 mol % of the hydroxyphenyl benzoates, and also increased yields of phenyl benzoate (3.4 mol %) and diphenyl carbonate (0.42 mol %). Carbonates are also sometimes formed in the decomposition of carbonic ester anhydrides.[17]

Dibenzo-α-pyrone, formed in greatest yield in the photolysis, corresponds in structure to a cyclization product of phenyl benzoate.

Conclusion

The best model for the decomposition of diaroyl peroxides is a Walling mechanism in which the importance of ion-pair structures in the rate-determining transition state and in the hybrid intermediate vary continuously with the substituents and the reaction medium. Benzoyl peroxide is evidently near the radical extreme in ordinary solvents, but not on the surface of silica.

Experimental Section

Sample Preparation. P_1 silica is the same as the P_1H_1 silica of an earlier paper.[14] It was dried at 140 °C and stored in a desiccator overnight. This treatment removes most of the adsorbed water without conversion of surface Si–OH groups into Si–O–Si groups. A weighed amount of the peroxide was dissolved in cyclohexane and added to a rapidly stirred cyclohexane slurry of the silica gel. Solvent was removed on a rotary evaporator and the silica again slurried with cyclohexane for transfer to another vessel. The solvent was then removed by evaporation in vacuo until the silica was free-flowing. Portions were then transferred to ampoules and outgassed to 10^{-4} Torr. The vacuum system was protected from silica by glass wool plugs directly above the ampoule, and by oil-wetted glass wool plugs in the liquid nitrogen traps.

Labeled Benzoyl Peroxide. Peroxide labeled with 90% ^{13}C in the carbonyl group was made from the labeled acid and ethereal H_2O_2 by the dicyclohexylcarbodiimide method:[18] mp 103–104 °C dec; IR (methylene chloride) 1747 (m), 1724 cm^{-1} (s).

Solid-State ^{13}C NMR. Magic angle spinning at 5 kHz was used without cross polarization. The spectrometer frequency was 50.325 MHz, pulse width 5.0 μs, delay time 3 s, number of signal acquisitions 400. Rates were obtained from the integrated absorption of the peroxide rather than from peak heights, since the line shapes varied during the run. This is to be expected in view of the nonequivalence of adsorption sites. Using integrated absorptions, the rates from the disappearance of the peroxide agreed well with those from the appearance of the benzoic acid. No peaks corresponding to the carboxyinversion compound could be seen.

Photolysis. A quartz ampoule containing the sample was suspended horizontally in a stream of water 12–13 cm from a 200-W medium-pressure UV lamp. The ampoule was rotated about its horizontal axis at 10 rpm during the photolysis.

Product Analysis. Products were recovered from the silica gel by slurrying three times with 50–75 mL of ether. In the photochemical and 80 °C runs small additional amounts of phenol

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and acid (mostly benzoic acid) were obtained by heating the silica with 10% H_2SO_4 at 50 °C for 4 h. Yields were determined by GLC using on-column injection, H_2 carrier gas, a flame ionization detector, temperature programming, and a dibenzyl internal standard. The column was a 30 m × 0.25 mm i.d. quartz capillary with a 0.25-μm film thickness. The packing was a DB-1701 bonded phase consisting of polysilanes with 86% dimethyl and 14% cyanopropyl substituents. Identification was by retention times, spiking with authentic samples, and low-resolution GC/mass spectrometry.

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Registry No. Benzoyl peroxide, 94-36-0.

A Convenient Synthesis of a Macrocyclic Dioxo Pentaamine and X-ray Crystal Structure of Its Monohydrazoic Acid Salt

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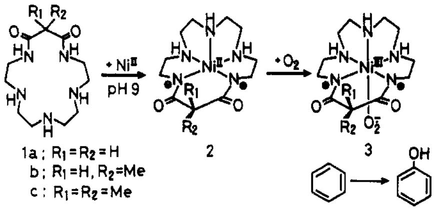
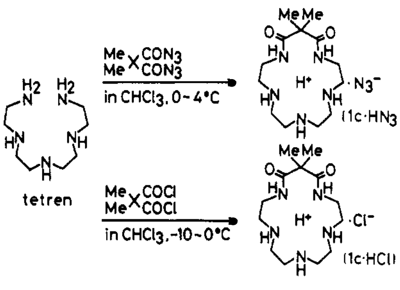
Sixteen-membered dioxo pentaamines **1a** and **1b** form a square-pyramidal complex **2** with high spin Ni^{II},[1,2] which possesses just the right redox potential ($E°$) of +0.24 V (vs SCE in H_2O) for Ni^{II}/Ni^{III} in **2** to permit interaction with O_2, yielding **3**,[3] whereupon the Ni^{II}-bound O_2 becomes activated so as to directly oxygenate benzene into phenol;[4]



1a (as monoprotonated species) also becomes a receptor molecule for anions (e.g. phosphate or ATP) at neutral pH.[5] Despite such novel properties, the ligand synthesis involving condensation of dimethyl (or diethyl) malonate with 1,11-diamino-3,6,9-triazaundecane (**tetren**) is very tedious, requiring more than a few weeks in refluxing methanol.

We now have discovered a much more practical synthetic route to **1c** (with $R_1 = R_2 = CH_3$), whose Ni^{II} complex **2c** shows an even lower $E°$ value of +0.17 V vs SCE,[6] indicating more promising properties for O_2 activation. The new synthesis is depicted as follows: The cyclization took place within a few days. The crystalline products, obtained after purification by silica gel chromatography (eluent, CH_2Cl_2–CH_3OH–28% aqueous NH_3 = 100:20:1 in volume), followed by recrystallization from CH_3CN/CH_3OH, were formulated as **1c**·HX on the basis of X-ray crystal analysis or the pH-metric titrations. The yields of **1c**·HN_3 and **1c**·HCl were 16% and 7%, respectively. These sticking HX were removed only after passing through a strong anion exchange resin column (Amberlite IRA-400) to yield free **1c**, which shows two different modes of ν_{CO} (KBr pellet) at 1663 and 1640 cm^{-1}. The IR spectrum (KBr pellet) for **1c**·HN_3 shows the similar C=O stretchings at 1663 and 1637 cm^{-1}, through a little wider. A N_3^- stretching peak occurs at 2037 cm^{-1}, appreciably deviated from 2110 cm^{-1} of ionic N_3^- (NaN_3) to suggest some interaction of N_3^- with **1c**·H^+. The pH-titration of **1c**·HN_3 has established the pK_a values of 9.4, 8.4, and <3 for the three secondary amines and a normal value[7] of 4.7 for the azide ion at I = 0.2 ($NaClO_4$) and 35 °C. Meanwhile, the free base **1c** showed the pK_a of 9.4, 8.4, and <3.



We were particularly interested in the structure of the **1c**·HN_3 product, since there were few examples[8] of HN_3 polyamine salts structurally characterized, and we were curious about where its H^+ is coordinating to (or which amine is the most basic) and how the N_3^- exist in the monoprotonated macrocycle that can often become an anion receptor.[5] We have thus conducted an X-ray crystal structure analysis of **1c**·HN_3.

The perspective view of **1c**·HN_3 with the atom-numbering system is shown in Figure 1. The complex consists of two macrocyclic cations and two N_3^- anions, which, respectively, are related by inversion point in the crystal. The difference electron density map has revealed that *the protonation is occurring at the N(4) atom*, which might be the most basic nitrogen in **1c**. The ionic proton serves an intraannular hydrogen bonding with amide O(18) pointing into the macrocyclic hole. As a result, this amide hydrogen HN(1) is exposed to N_3^-, which is of an ionic nature in view of the equidistances (1.136 Å) of the two N–N bondings. The N_3^- anion strongly hydrogen bonds with three neutral NH's; N(21′)···HN(1) 2.00 Å, N(23)···HN(7) 2.21 Å, and N(23)···HN(13) 2.07 Å (see Table I), which would be energetically more favorable than a direct interaction with the ionic $H^+N(4)$, as revealed by the longer distance 3.16 Å of N(23)···$H^+N(4)$. We now assign the C=O stretchings of 1663 and 1637 cm^{-1} to the non-hydrogen bonding amide C(14)=O(17) and the hydrogen bonding amide C(16)=O(18), respectively.

The measurements of the ^1H NMR chemical shifts of **1c** in D_2O by varying pH (pD = 12–2, see the Experimental

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