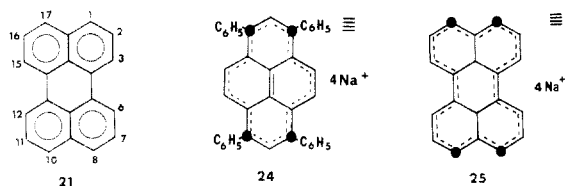
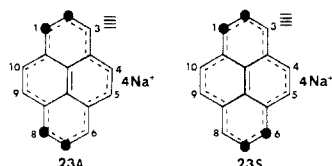


NMR) of 1,3,6,8-tetraphenylpyrene and perylene tetraanions (**24** and **25**, respectively) reveal the expected, simple NMR patterns.



Theoretical calculations ($\omega\beta$ and SCF-MO) performed on the multicharged species suggest a rationale for these unexpected spectral phenomena.²⁸ The calculations assign the largest value of electron density in **23**, **23a**, and **23b** to be located on carbons 2 and 7, while the second highest negative charge density is assigned to carbons 1, 3, 6, and 8. In view of these results we assume that two of the counteranions (Na^+ or K^+) are situated near carbons 2 and 7, while the two remaining cations are in the vicinity of either carbon atoms 1 and 6 or 1 and 8. The lack of symmetry imposed by the positions of the cations is induced on the polycyclic π system to afford two distinct, highly unsymmetric, quadruply charged species, which were dubbed the syn (S) and anti (A) isomers, viz., **23S** and **23A**,²⁹ according



to the locations of the cations. The existence of these two different unsymmetric isomers is revealed by their complex NMR patterns. In contrast, the calculations estimate a symmetrical distribution of the negative charges in the tetraphenylpyrene and perylene tetraanions (**24** and **25**);²⁹ therefore no dissymmetry is expected. ²³Na NMR line-shape studies of these polyions imply the existence of two species with a very low degree of sodium mobility.

Concluding Remarks

Studies of charged polycyclic species provide us with new insights into challenging problems of aromatic chemistry. The charging process leads to an extension of aromatic and antiaromatic series into new homo- and isoelectronic species. Consequently, a better and deeper understanding of the basic relationship between the number of π electrons and their modes of conjugation and aromaticity is obtained. The modes of charge distribution over the π framework (easily deduced from ¹H and ¹³C NMR patterns) and the ways by which these modes are dominated by the aromatic driving force are highlighted through the charging processes. Our studies that demonstrate that highly charged aromatic systems are easily obtained (a fact believed to be linked to the enhanced aromatic stabilization) point to the not yet fully appreciated role of the aromatic nature.

Research on polycyclic systems is almost as old as organic chemistry, and it seems to be far from being exhausted.

(29) The dots on the drawings represent the locations of the cations.

The Role of Local Stress in Solid-State Radical Reactions

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Although synthetic and mechanistic organic chemists have traditionally concentrated on reactions in fluid media, it is not difficult to argue that organic reactions in nonfluid media are at least equally important. Certainly it would be a mistake to regard biochemical reactions, or other reactions that involve rigid or structured phases, as occurring in simple fluids. This is true for a wide variety of processes, including such useful reactions as those of photoresists and heterogeneous catalysts and such deleterious reactions as those involved in the weathering and aging of synthetic or natural materials, including humans. In order to control and exploit organic reactions in nonfluid media, chemists must develop the same sort of intuition about these

processes that they have developed for fluid-phase reactions.

Organic reactions in amorphous solids may have broader practical significance than those in crystals, but a number of research groups have concentrated their efforts on crystals, because highly ordered media offer more opportunities for detailed mechanistic investigation and for sophisticated reaction control. Recent reviews of this work demonstrate an elegant and informative blending of the structural and dynamic techniques of physical chemistry (particularly X-ray diffraction, electron microscopy, solid-state spectroscopy, and computer simulation) with the synthetic and analytical techniques of organic chemistry.¹

J. Michael McBride was born in Lima, Ohio, in 1940. After undergraduate study at the College of Wooster and Harvard College, he stayed in Cambridge for Ph.D. work in free-radical chemistry under the supervision of Paul D. Bartlett. Since 1966 he has been teaching at Yale University. His research has focused on reaction mechanisms in organic solids, using physical methods to study free-radical processes. He has also investigated several topics in the historical development of organic chemistry with particular emphasis on the Palermo school of the 1860's.

(1) (a) M. D. Cohen, *Angew. Chem., Int. Ed. Engl.*, **14**, 386 (1975); (b) D. Y. Curtin and I. C. Paul, *Chem. Rev.*, **81**, 525 (1981); (c) J. D. Dunitz, "X-Ray Analysis and the Structure of Organic Molecules", Cornell University Press, Ithaca, NY, 1979, Chapter 7; (d) A. Gavezzotti and M. Simonetta, *Chem. Rev.*, **82**, 1 (1982); (e) B. S. Green, M. Lahav, and D. Rabinovitch, *Acc. Chem. Res.*, **12**, 191 (1979); (f) I. C. Paul and D. Y. Curtin, *ibid.*, **6**, 217 (1973); (g) J. R. Scheffer, *ibid.*, **13**, 283 (1980); (h) J. M. Thomas, *Pure Appl. Chem.*, **51**, 1065 (1979); (i) G. Wegner, *ibid.*, **49**, 443 (1977).

Differences between reactions in crystalline solids and their fluid-phase analogues are often profound. They have usually been rationalized through the "topochemical principle" of Cohen and Schmidt, which states that reactions in solids should take place with a minimum of atomic and molecular movement.^{1a} With this principle and knowledge of the starting material's crystal structure, it has been possible in many cases to predict both reactivity and product structure. Apparent failure of the principle has sometimes signaled reaction at crystal defects, where the principle still seems to hold, although the initial atomic positions are abnormal.^{1a,b} Lahav's application of this idea in designing syntheses for enantiomerically pure polymers is one convincing example of its utility.²

In applying the topochemical principle it is customary to imagine the reactants cradled in a cavity of fixed structure, which inhibits substantial changes in their conformations and relative position but otherwise lets them behave normally. This Account will suggest that often the environment serves not as a passive cradle but as a press, which biases the "normal" reaction through anisotropic stresses equivalent to tens of thousands of atmospheres. Because of stress generated by reaction the intermediates often follow indirect trajectories rather than least-motion paths, and the mechanical properties of the surrounding medium can become as influential on reaction as its shape is.

Solid-State Chemistry of Radical Pairs

In studying solid-state chemistry our research group has chosen to concentrate almost exclusively on photostimulated reactions in pure crystals of such common free-radical precursors as azoalkanes and diacyl peroxides. In part this choice has been motivated by the practical importance of radical reactions in solids. There is no doubt that radicals play a dominant role in degrading natural and artificial organic solids, particularly when light, air, or ionizing radiation is involved.³ Another practical motivation is that radical intermediates that are synthetically useless in solution, where they are unselective among numerous competing reaction paths, can be constrained by a crystalline environment to react very selectively. Radical systems can also serve as convenient probes for types of lattice control that should influence a broad range of reactions but are difficult to study independently in other cases. Work with radicals has already revealed instances of the following types of lattice control.

(1) *Selection of Reaction Partners.* Molecules in solution usually choose their reaction partners at random, but in the solid a molecule prefers to react with its initial neighbors. Solid-state radical reactions often show quantitative cage effects.^{4,5}

(2) *Control of Product Structure.* This includes constitution (as in disproportionation vs. combination),^{4,6} configuration (as in generation of *E* vs. *Z* olefins,⁶ or of single enantiomers⁷), conformation (as in

generating a neophyl radical without internal rotation),⁸ and choice of one among many nominally degenerate pathways (as in removing one particular member of a set of chemically equivalent hydrogen atoms during disproportionation).⁶

(3) *Control of Intermediate Behavior.* This includes forcing or inhibiting rearrangement or fragmentation.⁹

EPR and Zero-Field Splitting

Another important reason for choosing azo and peroxide systems has been the ease with which they may be studied in detail. Long-wavelength UV irradiation cleanly generates pairs of radicals suitable for single-crystal EPR spectroscopy. EPR spectra can identify very dilute intermediates unambiguously and provide a means for measuring their rates of formation and decay. More importantly, when the spectra are anisotropic, they can be used to determine the orientation of intermediates in a single crystal. Thus single-crystal EPR can supply structural information about solid-state reaction intermediates that is analogous to the information single-crystal X-ray diffraction can supply about starting materials.

For purely spectroscopic purposes it might be easier to generate various radicals with ionizing radiation, but the gentleness of azo or peroxide photolysis has four advantages for mechanistic studies: (1) Since it is usually obvious what radicals an azo or peroxide precursor should give, assigning the spectra is relatively straightforward. (2) Since no other reactive intermediates are formed, interpreting the source of the final products is more reliable than when a variety of ions or other reactive species are generated simultaneously. (3) The first species to be observed is usually a radical pair, which differs from starting material only by the absence of one or more bonds and by subtle motion of the fragments. Such pairs can form product without subsequent long-range motion. (4) The EPR spectra of radical pairs show zero-field splitting (zfs) because of magnetic interaction between the odd electrons. This splitting reduces spectral overlap and provides valuable structural information, as outlined in the next two paragraphs.

The odd electrons in a radical pair can have their spins coupled in a diamagnetic singlet, which would be invisible to EPR, but the paramagnetic triplet state is usually so nearly degenerate with the singlet that it accounts for the statistical 3/4 of the pairs even at very low temperature.¹⁰ Magnetic interaction between the radicals in a triplet-state pair gives rise to zfs, which is familiar in the spectroscopy of molecular triplets.¹¹ Zero-field splitting imposes a doublet structure on the EPR spectrum of a radical pair. The splitting is anisotropic and has a maximum value in gauss of about $55700/r^3$ (where r is the interrational distance in angstroms).¹² The radical pairs we typically observe have

(7) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); M. J. Tremelling and J. M. McBride, *J. Org. Chem.*, **37**, 1073 (1972).

(8) Unpublished work in this laboratory.

(9) D. W. Walter and J. M. McBride, *J. Am. Chem. Soc.*, **103**, 7069, 7074 (1981). Dr. M. R. Gislser found that photolyzing a number of crystalline peresters of 3,3,3-triphenylpropanoic acid gave quantitative yields of ethers with no neophyl rearrangement of the 2,2,2-triphenylethyl radical.

(10) For a case where this seems not to be true, see J. M. McBride and M. W. Vary, *Tetrahedron*, **38**, 765 (1982).

(11) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, NJ, 1969, Chapters 9, 10.

(2) L. Addadi, J. van Mil, and M. Lahav, *J. Am. Chem. Soc.*, **104**, 3422 (1982).

(3) B. Ranby and J. F. Rabek, "Photodegradation, Photo-oxidation, and Photostabilization of Polymers", Wiley-Interscience, London, 1975.

(4) A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Am. Chem. Soc.*, **94**, 8510 (1972).

(5) N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Am. Chem. Soc.*, **97**, 6729 (1975).

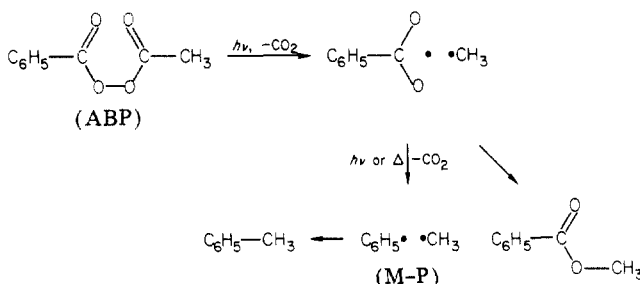
(6) K. J. Skinner, R. J. Blaskiewicz, and J. M. McBride, *Israel J. Chem.*, **10**, 457 (1972).

maximum splittings between 50 G (10.4 Å) and 1300 G (3.5 Å), so it is often possible to choose crystal orientations in which there is no overlap between spectra of different, or differently oriented, species. This has obvious advantages both for assigning the spectra and for measuring kinetics.

The zfs anisotropy of molecular triplets generated in single crystals allowed Hutchison, Closs, and their collaborators to study the structural aspects of solid-state carbene chemistry in unprecedented detail.¹³ More recently Schwoerer and Sixl and their collaborators have used a similar approach to study the bis-carbene quintet states involved in single-crystal diacetylene polymerization.¹⁴ The zfs of radical pairs is much easier to interpret than that of carbenes and other molecular triplets.¹² Correlation between positions of odd electrons within a single molecule makes it difficult to calculate their magnetic interaction, but for radical pairs intramolecular correlation is negligible, because the odd electrons stay on different radicals. To calculate the zfs for a radical pair accurately one only needs to know how spin is distributed within each radical, and how the radicals are arranged relative to one another.¹⁰ When the spin within each radical is localized, or distributed in a way that is easy to calculate, the observed zfs anisotropy of a radical pair gives the average distance between its members to within 0.04 Å and the direction between them to within 1°. These limits are well within normal atomic vibrational amplitudes.

Acetyl Benzoyl Peroxide: Kinetic Anomalies and Forced Rotation

Soon after Lebedev reported observing the EPR spectrum of methyl-phenyl radical pairs in crystalline acetyl benzoyl peroxide (ABP),¹⁵ we began to study the products of its solid-state photolysis.⁵ Decomposition of ABP in solution or as a melt gave more than a dozen products among which no single compound accounted for more than 25%.¹⁶ Partial photolysis of crystalline ABP, however, gave only the simple cage products, methyl benzoate from loss of one CO₂, and toluene from loss of both. Crossover experiments with deuterated material showed that in the solid both products were formed by cage collapse of fragments from single precursor molecules.



A more striking specificity appeared in the ester formed by photolysis of ABP containing ¹⁸O in the

(12) J. M. McBride, M. W. Vary, and B. L. Whitsel, *ACS Symp. Ser.* **69**, 208 (1978).

(13) See for example C. A. Hutchison, Jr., *Pure Appl. Chem.*, **27**, 327 (1971). ENDOR, which also played an important role in the carbene studies, is now being applied to radical-pair systems.

(14) R. Huber and M. Schwoerer, *Chem. Phys. Lett.*, **72**, 10 (1980); W. Neumann and H. Sixl, *Chem. Phys.*, **58**, 303 (1981).

(15) A. T. Koritskii, A. V. Zubkov, and Ya. S. Lebedev, *High Energy Chem. (Engl. Transl.)*, **3**, 355 (1969).

(16) C. Walling and Z. Čekovič, *J. Am. Chem. Soc.*, **89**, 6681 (1967).

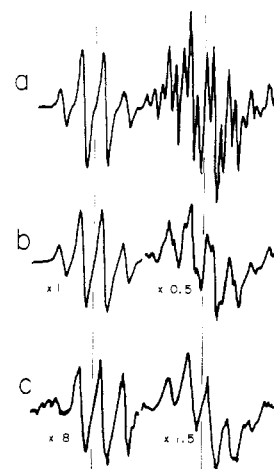


Figure 1. Low-field members of the zfs doublets of MB and MP radical pairs in a photolyzed single crystal of ABP at 77 K. (a) At 28-min photolysis; (b) at 3-h photolysis; note degraded resolution of proton hyperfine structure in both MB quartet and MP multiplet; (c) after 6-min darkness for MB and 40-min darkness for MP following b; note that persistent signals are still more poorly resolved, showing that line width is due to zfs dispersion, not to interaction between pairs. Constancy of the center position of both patterns shows that pairs have the same average zfs in all traces.

peroxide positions. Such ester as was formed in fluid solution showed complete scrambling of ¹⁸O between the carbonyl and ether oxygens, but ester from solid-state reaction had up to 4 times as much label in the ether position as in the carbonyl. The crystalline matrix had thus lifted a degeneracy of reaction paths that prevailed in solution.

Although we were looking for selectivity between the oxygens, we could not confidently predict its sense from the topochemical principle. X-ray diffraction showed that the incipient methyl radical in ABP is slightly closer to the peroxy oxygen of the benzoyloxy group than to its carbonyl oxygen (3.62 vs. 4.07 Å), but that the incipient CO₂ molecule should shield the peroxy oxygen from methyl much more effectively than it shields the carbonyl. X-ray and product studies alone gave no convincing explanation for the observed specificity. EPR provided the additional information needed to understand the reaction.¹⁷

Very brief photolysis of a single crystal of ABP at 77 K in an EPR spectrometer generates the signal of methyl-benzoyloxy radical pairs (MB) with a maximum zfs of 375 G. Continued photolysis converts MB into methyl-phenyl pairs (MP) with a maximum zfs of 259 G. The low-field member of each zfs doublet is shown in Figure 1a.¹⁸ Both features are split into quartets by the methyl protons, and the MP signal is split further by the phenyl protons. Had the structures of MB or of MP pairs varied through the sample, each pattern would be broadened by superposition of sharp patterns centered at different positions because of zfs differences. The sharpness of the MP lines shows that geometric differences among MP pairs in the sample must be less than 0.03 Å. Structural uniformity among the radical pairs is mirrored by their kinetic uniformity.

(17) The explanation in ref 4 is wrong because of the naive assumption that in forming the methyl-benzoyloxy radical pair the smaller radical should move more easily.

(18) B. L. Whitsel, Ph. D. Thesis, Yale University, New Haven, CT, 1977.

MB and MP both showed clean first-order decay with half-lives at 77.4 K of 17 and 134 s, respectively. This contrasts with most observations in glassy matrices, where site variability gives rise to a spectrum of local rate constants.

More extensive photolysis destroys the uniformity in both MB and MP. Figure 1b shows that after 3-h photolysis, which corresponds to a few percent decomposition, the lines in both MB and MP have broadened, although their average positions are unchanged. This indicates a dispersion of radical-radical distances about the single value observed following brief irradiation. As the signals decay in the dark, they appear to broaden further (Figure 1c), because the radical pairs having the original, uniform structure and giving sharp lines decay more rapidly than those with a variety of other structures. Had the breadth been due to magnetic interaction between radical pairs, rather than within them, the lines would have sharpened during decay. The broadest line width for MP corresponds to a dispersion of about 0.06 Å in radical-radical separation among the pairs of variant structure.

The diversity of rates among the radical pairs is more striking than the 1% variation in their structures. Collapse of the pairs with variant structure is some 40 times slower than that of the original, uniform pairs. Even the pairs that continue to give sharp lines decay only about half as fast as the original pairs, from which they are structurally indistinguishable. It is remarkable that the observed rates decrease with increasing conversion, when one might expect the opposite if damage loosened the crystal lattice.^{1f}

How can these species, whose structures are identical within much less than the amplitude of thermal vibration, react at such different rates? We believe that the kinetic anomalies are due neither to the structure of the pair nor to the shape of its immediate environment but rather to the environment's mechanical properties. Of course at high conversion the original lattice loses its structural integrity, but at lower conversion, the effect could be quite different. Since motion in a crystal lattice requires local free volume, the collapse of a radical pair should have a positive volume of activation and be retarded by increasing pressure. When a lattice molecule undergoes homolysis, it must expand to allow the breaking bond to stretch to at least twice its original length. The stress or "pressure" generated by expansion should influence the subsequent behavior of these radicals and also the reactions of surrounding molecules. Stress should fall off rapidly, perhaps with the square of distance from the defect, but where stress is significant the lattice becomes effectively more rigid. Even after MB or MP pairs collapse, their products continue to generate stress because of the new CO₂. Thus reactions in the neighborhood of a previous reacted molecule could exhibit minimal structural alterations but drastic kinetic differences. Reaction further afield could show a small kinetic effect, from the cumulative long-range influence of many previously reacted molecules, without showing any structural effect at all. This interpretation is confirmed by a disproportionate increase in the fraction of drastically retarded pairs with increasing photolysis at low temperature and by the failure of brief additional photolysis to regenerate these pairs after a heavily

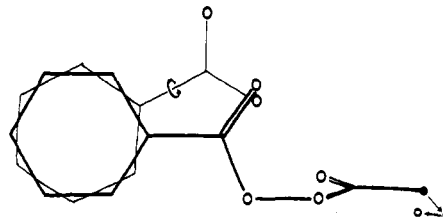


Figure 2. Structure of the ABP molecule (heavy lines) and of the MB and MP radical pairs from it. Small circles in the lower right indicate the methyl carbon positions (from zfs) first in MB and then in MP. Phenyl in MP is assumed to coincide with phenyl in ABP. The benzoyloxy orientation in MB is inferred from ¹⁷O, ¹³C, and *g* tensors.

photolyzed crystal has been annealed to relax local stress.

If the kinetic anomalies of MB and MP are due to stress generated by previous reactions of neighboring molecules in the lattice, the influence of stress should be even more dramatic within the reaction site itself. Careful analysis of the *g* tensor of MB and of the ¹⁷O hyperfine splittings in samples specifically labeled in one or the other of the benzoyloxy oxygens of ABP showed that the benzoyloxy radical undergoes an irreversible 30° in-plane rotation (see Figure 2) and that the CO₂ group of this planar radical rotates to exchange oxygen positions with a half-life of 1 min at 70 K (*E*_a ~ 3 kcal/mol).¹⁹ Both of these rotations are contrary to the hypothesis of least motion, but if one assumes their occurrence, the topochemical principle is consistent with the subsequent preference for forming ester through the original peroxy oxygen and with incompleteness of this selectivity.

Understanding the reaction requires understanding the 30° rotation. We believe the rotation is driven by nonbonded repulsion between the oxygens that were originally linked in the peroxide bond of ABP. If so, the reaction's remarkable specificity is dictated more by stress among fragments of the decomposing molecule than by the shape of the cavity that holds them.

Dibenzoyl Peroxide: Confirmation of the Stress Hypothesis¹⁰

It proved possible to test the hypothesis that stress is more important than cavity shape by studying a system with similar stress but a different reaction cavity. Dibenzoyl peroxide (BPO) crystallizes with a molecular conformation that is quite similar to that of ABP. But aside from the obvious requirement that the sites accommodate groups of similar shape, the arrangement of surrounding molecules is entirely different. Therefore BPO allowed testing whether benzoyloxy rotation might be controlled primarily by the ability of the cavity to accommodate a given change in orientation. Photolysis of BPO at 5 K gives a phenyl-benzoyloxy radical pair (PE) in which the benzoyloxy radical has rotated by 8° in the direction *opposite* that observed in MB. This is the direction one would expect in either compound for fastest relief of repulsion between the formerly peroxy oxygens of benzoyloxy and CO₂ (see Figure 3). However, relaxation ceases temporarily when CO₂ becomes wedged in the O-C-O vee of benzoyloxy. At 15 K benzoyloxy in

(19) J. M. McBride and R. A. Merrill, *J. Am. Chem. Soc.*, **102**, 1723 (1980).

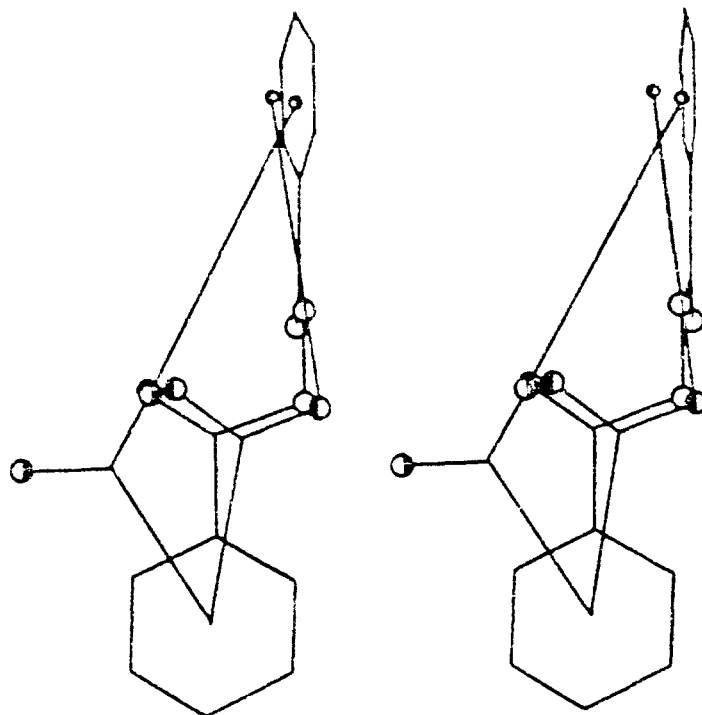


Figure 3. Stereopair view of the structures of the initial and relaxed PB radical pairs relative to the BPO precursor molecule. Large half-filled circles denote oxygens of the benzoyloxy radical, and small ones denote the phenyl carbon with a free valence. Aromatic carbons of the radicals are omitted for clarity, and the carboxyl carbon is joined to the center of the ring. Atoms of the initial PB pair are shaded on the left and those of the pair after 15-K relaxation are shaded on the right. Radical orientations and relative positions within the pairs have experimental significance, but the translation relative to BPO is assumed.

the PB pair rotates by 41° in the reverse direction and gives a more stable PB pair, which has a geometry almost identical with that of MB. At this temperature the benzoyloxy radical can apparently muster enough energy to click past CO_2 and leave behind a hole in which that molecule can more comfortably lodge. In ABP this motion must occur even at 5 K.

Close similarity of the final benzoyloxy orientation in two lattices that are so different supports attributing the motion to pressure from "intramolecular" CO_2 rather than to the detailed shape of the reaction cavity.

3-Methyl-3-phenylbutanoyl Peroxide: Hindered Rotation

Although measuring the barrier that hinders internal rotation of benzoyloxy in MB was relatively straightforward, it is difficult to partition the barrier into intramolecular and intermolecular components. One might suppose that the measured 3 kcal/mol value is an upper limit for the intramolecular contribution to the barrier, but local stress large enough to make the whole radical rotate by 30° might specifically destabilize the radical's favorite conformation and thus facilitate internal rotation. The internal barrier would then be larger than the total.

The zfs in pairs of neophyl radicals generated by photolyzing a single crystal of 3-methyl-3-phenylbutanoyl peroxide (MPBP) promised to provide a convenient means of studying internal rotation in greater detail. Like the type of ^{17}O hfs analysis mentioned above, this approach is suitable for studying rotations that are many orders of magnitude slower than those commonly studied through spectral line shapes.

The molecular conformation in crystalline MPBP is shown in Figure 4.²⁰ As expected, photolyzing a single

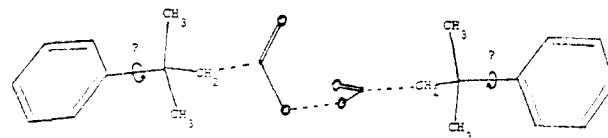


Figure 4. Molecular conformation in crystalline MPBP. Dashed bonds cleave photochemically to generate a pair of neophyl radicals separated by two molecules of CO_2 . Internal rotation that permutes CH_2 and CH_3 locations would alter zfs substantially by changing the interspin vector.

crystal of MPBP at very low temperature yields a pair of neophyl radicals whose zfs indicates an electron-electron vector almost identical with the vector connecting the methylene carbons in the starting peroxide. We had anticipated that as the sample was slowly warmed, nearly degenerate rotamers of the neophyl radicals would begin to interconvert by surmounting barriers similar to those of 3–4 kcal/mol that hinder internal rotation in solid *tert*-butylbenzenes.²¹ Each time an alkyl group takes a rotational step, there should be a change in electron-electron distance or direction, which would change the zfs. It should thus be easy to follow arbitrarily slow rotations, even if there were only one rotational step in a week. If the methylene carbons in each radical could occupy three positions, there would be nine geometries of the pair with different splittings. On warming they should become populated one by one until finally rotation takes less than microseconds, making the signals broaden and coalesce.

In fact, warming the pair of neophyl radicals caused only two subtle, irreversible geometry changes before the radicals reacted with one another at 170 K. It seems surprising that the radical-radical vector never changed

(20) B. E. Segmuller, unpublished work in this laboratory.

(21) J. Yamauchi and C. A. McDowell, *J. Chem. Phys.*, **75**, 1051 (1981).

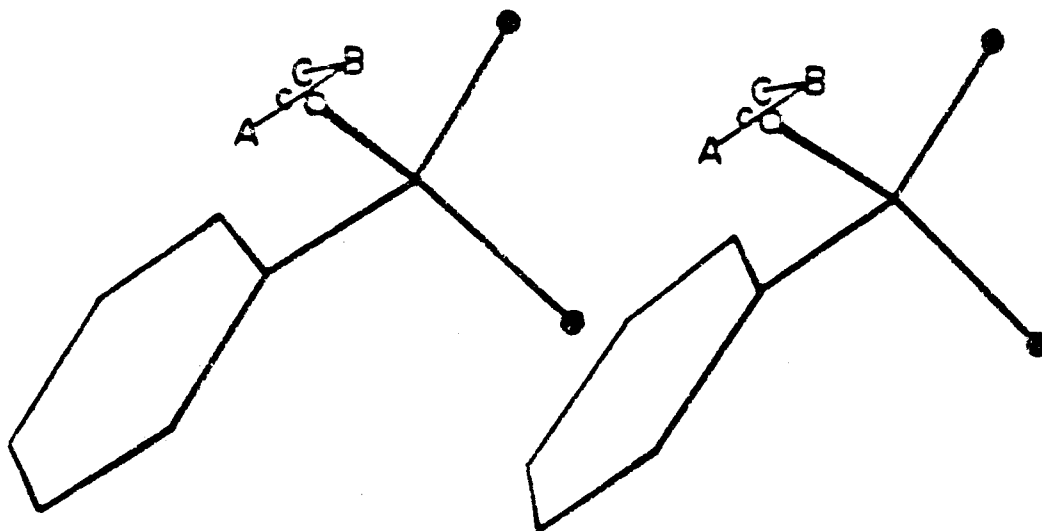


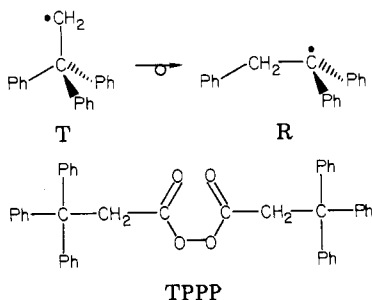
Figure 5. Stereopair view of electron spin location in the more mobile member of the pair of neophyl radicals in crystalline MPBP. The radical is shown in the geometry of the precursor with an open circle denoting the CH_2 carbon. A, B, and C indicate CH_2 positions in the three successive radical-pair structures as measured by zfs (assuming the other radical is stationary). Small c denotes the CH_2 position in the final pair as determined independently through hyperfine anisotropy (assuming a stationary quaternary carbon). CH_2 motion is obviously small and inconsistent with substantial internal rotation.

enough to indicate a single 120° internal rotation (see Figure 5). Even at a temperature where the lattice allows radical carbons to move together from 6 Å to bonding distance, no internal rotation occurs in the surviving radical pairs. How can internal rotation be so slow at 170 K, when the intramolecular barrier should be negligible, and the intermolecular barrier should certainly be smaller than that for 5 Å translation?

Local stress provides a simple solution to this riddle. The radicals are held apart by the pair of CO_2 molecules trapped between them. Apparently these molecules are crammed tightly into the "tert-butyl" rotors of the radicals, locking the whole assembly together so that rotation is impossible. At 170 K a local cataclysm occurs in which the CO_2 molecules shift and unlock the system. Although rotation presumably becomes rapid, it is not observable by EPR because the radical pair quickly collapses.

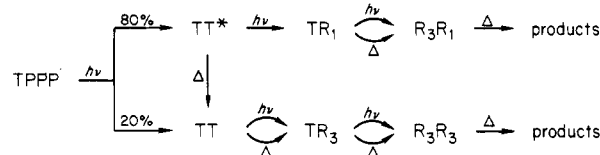
3,3,3-Triphenylpropanoyl Peroxide: Rearrangement⁹

Rearrangement of neophyl radical to phenylisobutyl by phenyl migration is too slow to compete with radical-pair collapse in crystalline MPBP, but the analogous rearrangement of 2,2,2-triphenylethyl (T) to 1,1,2-triphenylethyl (R) can be observed easily in crystals of 3,3,3-triphenylpropanoyl peroxide (TPPP).



Brief photolysis of a TPPP crystal below 160 K gives the EPR spectrum for a pair of T radicals (TT^*) in which the radical carbons have recoiled by a little more

Scheme I



than 0.1 Å from their positions in the intact precursor molecule. This is the kind of motion that would be expected if well-anchored radicals were being pressed apart by the two new CO_2 molecules between them. Subsequent warming or additional photolysis gave five other well-characterized radical pairs as shown in Scheme I. Each of these subsequent pairs is derived by a neophyl rearrangement, except for TT, which comes from simple rapprochement of the unrearranged radicals by about 0.1 Å. The irreversible radical motion that converts TT^* to TT is subtle and presumably reflects a much more substantial relaxation of the CO_2 molecules.

The three thermal migrations of phenyl are slower by perhaps 1000-fold than would be expected in fluid solution at the same temperature, but their specificity and that of the four photochemical rearrangements is much more striking than this retardation. Each rearrangement is specific, giving a single orientation of the radical pair, where three orientations might have been anticipated from the availability of three migratable phenyl groups on the carbon adjacent to the radical center. Rearrangement of one phenyl group leaves the electron spin delocalized across a diphenylmethyl group including the other two phenyls. Each of the three possible diphenylmethyl groups stands in a characteristic spatial relationship to the other radical in the pair. Thus the magnitude and orientation of the zfs reveals which phenyl rearranged. Conformational analysis of the precursor molecule shows that one particular phenyl group has a more favorable torsional angle for rearrangement than the others. The topochemical principle suggests that this phenyl should be the one to rearrange, and it is selected exclusively in three of the four pairs, whether reaction occurs thermally or photochemically.

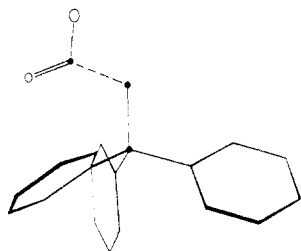


Figure 6. Conformation of half a molecule in crystalline TPPP. Cleaving the dashed bond leaves CO_2 in a position where it presses the radical carbon toward the right. When rearrangement occurs under the influence of this stress, the radical attacks the π system of the phenyl to the right, giving R_1 . Conformationally preferred attack on the phenyl to the left giving R_3 occurs only after CO_2 moves to relax the stress.

In rearrangement of TT^* , however, a different phenyl migrates.

This apparent violation of the topochemical principle is easy to understand in terms of local stress. Figure 6 shows that the location of CO_2 in the precursor molecule is such that after homolysis it should press the radical carbon away from the conformationally favored phenyl and toward the phenyl that does, in fact, rearrange in TT^* . Once this stress is relaxed either by the CO_2 motion accompanying $\text{TT}^* \rightarrow \text{TT}$, or during a preliminary rearrangement, subsequent rearrangement of the pair can take the normal topochemical course.

Undecanoyl Peroxide: Rotational Translation of Long Chains²²

Pairs of triphenylethyl radicals in crystalline TPPP persist almost to room temperature. One might suppose that the immobility of these radicals is due to their girth, but it is not obvious that this is the primary factor determining pair stability. In particular it seems likely that efficiency of lattice packing should be equally important, since pairs of methyl radicals are stable above 30 K in crystalline acetyl peroxide, while many pairs of larger radicals are not stable at this temperature. In order to study mobility when molecular cross-section provides very little resistance to motion, but crystal packing is efficient, we have begun working with diacyl peroxides that yield long, straight-chain alkyl radicals.

Although molecular mobility in crystals of long-chain compounds is often studied in materials science, it is difficult to predict how a single molecule should respond to local stress. Motion perpendicular to the chain axis should be favored by the anisotropy in compressibility of alkane crystals. Compression perpendicular to the chain direction is 70-fold easier than along the chain in the case of polyethylene.²³ On the other hand, motion along the chain axis is an important relaxation mechanism for linear polymers and seems to be dominant in diffusion of smaller molecules in polymeric matrices.²⁴

X-ray diffraction showed that undecanoyl peroxide has an extended conformation in which the incipient *n*-decyl radicals are almost colinear (Figure 7). Adja-

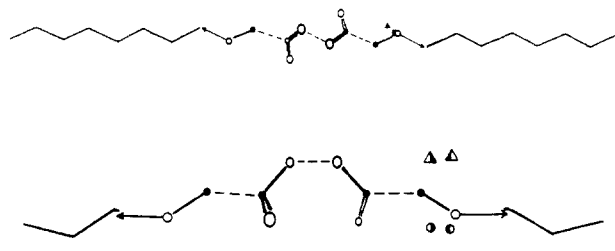


Figure 7. Undecanoyl peroxide. Top: entire molecule viewed along a crystallographic twofold symmetry axis. Dashed bonds break to give a pair of decyl radicals in which the radical carbon on the left is in its original position and that on the right has moved to the position indicated by a triangle. At 33 K the radical carbon on the right moves to the position indicated by a square. At 54 K both radical carbons move to positions indicated by open circles, restoring the crystallographic symmetry. Arrows on the circles point toward the second carbon in the radical chain. Bottom: central portion of the molecule viewed from the side. The circle shaded on the right corresponds to the triangle in the top view, and the circle shaded on the left corresponds to the square. Triangle indicate alternative positions for the radical carbon and cannot be distinguished from the circles by xfs. Vertical positioning of the open circles is not experimentally significant and was chosen to conform with the rotational translation model of Figure 8.

cent hydrocarbon chains are parallel and close packed in the familiar triclinic motif.²⁵ One might anticipate that decyl pairs confined head-to-head in a straight tube should couple to eicosane more easily than they disproportionate, and, in fact, at 0 °C the combination/disproportionation ratio is almost 20-fold higher in the crystal than in pentane solution. It is more surprising that in addition to eicosane, crystal photolysis at 77 K yields 20% of *n*-heptylcyclopropane, formally the product of γ -disproportionation.

EPR has supplied information on radical mobility, even though it has not yet explained the curious formation of a cyclopropane at low temperature. Irradiation below 15 K generates a pair of *n*-decyl radicals, which move irreversibly in two steps at 33 K and at 53 K before collapsing at 134 K. Zero-field splitting gives precise radical-radical vectors for all three pairs. Hyperfine anisotropy from the four equivalent α -hydrogens of the high-temperature pair reveals the direction of the first C-C bond in each chain as an axis of rapid internal rotation.

Although these vectors are known precisely, interpreting them in terms of absolute positions for the radicals in the unit cell is not unambiguous. Only the most stable pair has a radical-radical vector with no component along the crystallographic twofold rotation axis of the precursor molecule. Thus the first two pairs lack the symmetry of their surroundings. Figure 7 shows the result of assuming that one of the radicals remains near its initial position in the first two pairs and then moves, while its partner remains nearly stationary, to form the third pair. The assumption is supported by the similarity in overall motion of the two radicals, which restores twofold symmetry in the final pair. An ambiguity remains, however, because crystal symmetry requires that two radical-radical vectors be present for each of the first two pairs, and experiment cannot distinguish which of them applies when the radical on the left of Figure 7 moves first and which

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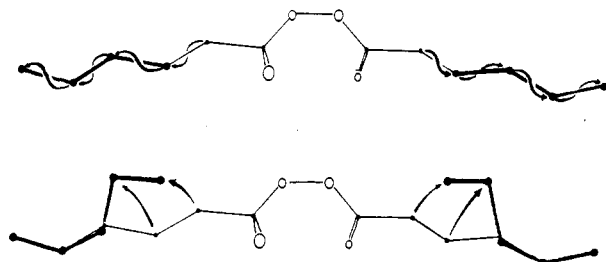


Figure 8. Models for decyl radical motion leading to the most stable pair geometry in undecanoyl peroxide. Top: rotational translation. Initial motion of the radical on the right gives a position near the circles in Figure 7. Subsequent motion of the radical on the left gives the final structure. Bottom: bond rotations that displace only the first three carbons of the chain. Initial torsion in the radical on the right gives a position near the triangles of Figure 7. Subsequent torsion in the other radical gives a final structure consistent with the measured zfs and hfs tensors.

when the radical on the right moves first. Thus even granting the assumption that one radical moves at a time, experiment does not show whether the radicals move to the positions indicated by circles or by triangles in Figure 7.

Figure 8 presents two models for motion of the radicals that are consistent both with the radical-radical vectors and with the direction of their $C_\alpha-C_\beta$ bonds. One involves rotation about the second, third, and fourth bonds of the chain. It leaves the last seven carbons fixed in their original positions but requires the first three carbons to undergo substantial displacement perpendicular to the chain axis. The other model involves rotational translation along the chain axis in which each methylene group replaces its neighbor. The terminal methyl group must move into the interfacial plane where adjacent molecule layers meet. This is the type of screw motion that has been proposed for polyethylene relaxation²⁴ and disputed in crystalline alkanes.²⁶ In the present system parsimony favors the screw model, since otherwise parallelism of the $C_\alpha-C_\beta$ bond in the radical with the C3-C4 bond of the precursor would be fortuitous.

Pressure from the new CO_2 molecules can drive either type of relaxation, but what favors the screw motion? Why should radicals in this crystal respond to the stress by moving parallel to the long molecular axis when the compressibility of most long-chain crystals suggests that they should give more readily in the orthogonal direction? The unusually low melting point of this peroxide may provide an important clue. Fatty acid diacyl peroxides, like other long-chain compounds, have melting points that alternate with chain-length parity,²⁷ and UP is in the low-melting series. Since side-by-side packing of these molecules is insensitive to chain length, a low melting point must be due to inefficient packing at the interface where chain ends from adjacent molecular layers meet. This is precisely where extra room is needed to accommodate the terminal methyl group of the moved radical. Quantitative analysis of free volume distribution in the crystal supports this inference.²⁸

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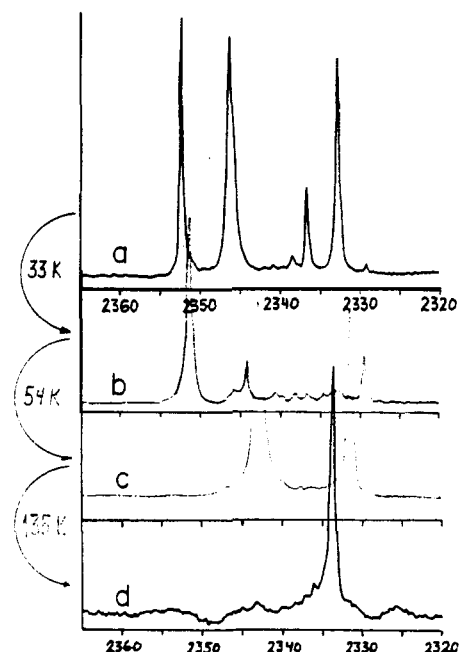


Figure 9. The CO_2 antisymmetric region in FTIR spectra of a single crystal of undecanoyl peroxide after 0.04% photolysis. Spectrum a was generated at 20 K. Successive spectra result from annealing at temperatures where EPR shows radical-pair motion. The steady shift to lower frequency is attributed to relaxation of anisotropic local stresses as large as 40 kbar.

FTIR: Independent Evidence for Local Stress²⁹

This Account has ascribed five phenomena to the influence of local stress generated by photolyzing crystalline peroxides: kinetic anomalies of methyl-phenyl and methyl-benzoyloxy pairs in ABP, driven rotation of benzoyloxy in ABP and in BPO, hindered internal rotation of neophyl radicals in MPBP, nontopochemical neophyl rearrangement in TPPP, and rotational translation of decyl radicals in UP. To be certain that stress is not just a convenient logical device for rationalizing unexpected features of these solid-state reactions, it must be measured independently. Since stress should fall off with the square of distance from the reaction site, a specifically local stress gauge is required. Fortunately the asymmetric stretching vibration of CO_2 is sensitive to pressure,³⁰ has high IR intensity, and occurs at a frequency where the IR spectra of diacyl peroxides have minimal background. Thus an almost ideal stress gauge is specifically generated in the reaction site.

Figure 9a shows the CO_2 asymmetric stretch in an 0.6 mm thick crystal of UP that has been photolyzed to 0.04% conversion at 20 K. Figures 9b-d show the sequence of irreversible spectral transformations that occur after annealing the crystal at temperatures where radical-pair transformations were observed by EPR. Careful kinetic studies show that each transformation takes place at the same rate as the corresponding EPR transformation and that during each transformation all IR peaks grow or decay at the same rate.³¹ The lattice shows no phase transitions that could cause independent phenomena to have fortuitously equivalent rates.

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(31) FTIR shows two metastable intermediates in the lowest temperature transformation, but since they never constitute as much as 20% of the pairs at one time, they are obscured in the EPR spectra.

Thus the kinetic equivalences provide strong evidence that the IR peaks and the EPR signals derive from the same species. This is one of the rare proofs that a species observed by EPR lies on the predominant reaction pathway.

Figures 9a and 9b show more stretching peaks than expected from two CO₂ molecules. This may be due to very rapid equilibration of two structures in a single site. Spectra of ¹³CO₂ in natural abundance show that resonant coupling of the asymmetric stretching in CO₂ pairs causes shifts of less than 3 cm⁻¹ in the observed frequencies. Local electrostatic fields of plausible magnitude cannot explain substantial frequency differences in this system.³²

The most likely interpretation of the successive IR changes is that stress is relieved in each of the structural transformations. Each radical pair has an unstressed CO₂ absorbing near 2333 cm⁻¹ and a stressed CO₂ absorbing as high as 2353 cm⁻¹. A shift of 20 cm⁻¹ corresponds to a pressure between 30 and 50 kbar.³⁰

Since pressures of 1–10 kbar exert strong influence on organic reactions,³³ it is not surprising that anisotropic stresses equivalent to many tens of kilobar in crystalline reaction sites have important chemical consequences.

Conclusion

Local stress caused by CO₂ formation is an important factor in the chemistry of crystalline diacyl peroxides. Because of this stress the simple hypothesis of least motion is incorrect in these systems. The peroxides are unusually easy to study experimentally by single-crystal methods (EPR, X-ray, FTIR) and theoretically by computer simulation, but there is no reason the stress

phenomenon should be unique to them. Analogous effects must influence many other solid-state reactions, particularly when long-range order keeps stress localized, as in crystals. Virtually all reactions, even simple light absorption, cause changes of molecular shape that should create local stress in a solid.³⁴ Subsequent reactions of these species or of their neighbors must occur under influence of the stress.

Dramatic autocatalysis in the thermal polymerization of crystalline diacetylenes has been attributed to lattice strain generated by reaction,³⁵ but theoretical discussions have assumed an overall stress 3 orders of magnitude smaller than the local stress generated by UP decomposition.³⁶ Recent results suggest the importance of local strain for individual propagation steps in diacetylene and distyrylpyrazine polymerization.³⁷

It seems likely that properly understanding reactions in rigid media and fully realizing their synthetic potential will require better insight into the mechanical properties of solids at the molecular level.

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