Solvent Steric Effects. II. The Free-Radical Chemistry of Azobisisobutyronitrile and Azobis-3-cyano-3-pentane in Viscous and Crystalline Media[1]

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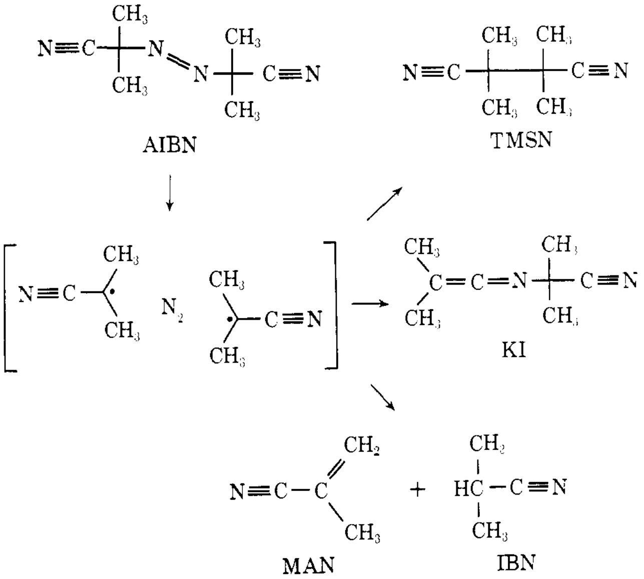
Abstract: Product distributions have been studied for photolysis of azobisisobutyronitrile (AIBN) in fluid solution, in glassy benzyl benzoate, in frozen mixtures, and in two pure crystalline modifications. Azobis-3-cyano-3-pentane (ACP) was similarly studied in benzene solution and in the pure crystal. For ACP the fluid and crystalline products were similar with a ketenimine predominating and somewhat less tetraethylsuccinodinitrile, but for AIBN the crystalline products (95% disproportionation, 5% tetramethylsuccinodinitrile (TMSN)) differed dramatically from those in solution (5% disproportionation, 40% TMSN, 55% ketenimine). A number of alternatives to explaining the product distribution for AIBN crystals in terms of a very specific influence of the ordered environment on the behavior of the intermediate radical pair are considered and excluded. The transition between the crystalline phases of AIBN was studied thermochemically (ΔH monoclinic → triclinic, 0.32 ± 0.04 and 0.26 ± 0.04 kcal/mol for AIBN and AIBN-d_{12}, respectively). The cage effect in crystalline AIBN is greater than 91%.

Intermolecular polar effects have been extensively studied,[3] but analogous steric effects are much less familiar. Such rudimentary examples of solvent steric influences as diffusion control of bimolecular reaction rates,[4] solvent cage effects,[5] and matrix isolation of reactive species[6] are well known and in some measure understood, but more sophisticated solvent steric control over the partitioning of reactive intermediates among reaction pathways has been relatively little studied.[7,8] This is surprising both because of the synthetic potential of such control and because of the commercial and biochemical importance of reactions in nonfluid media.

In this paper we report chemical studies of the fate of cyanoisopropyl radicals generated in pairs by photolysis of azobisisobutyronitrile (AIBN) in fluid, glassy and frozen solutions and in the pure crystalline state and contrast these results with those for the homologous 3-cyano-3-pentyl radicals from azobis-3-cyano-3-pentane (ACP). In subsequent papers we show how the physicochemical techniques of X-ray diffraction,[9] intermolecular potential calculation,[10] and epr spectrometry[10] can be used to study the reaction in the crystalline matrix.

Results

AIBN, one of the earliest[11] and most extensively studied[12] free-radical initiators, undergoes thermal or photochemical homolysis[13] to yield a nitrogen molecule and a pair of cyanoisopropyl radicals. In relatively inert solvents these radicals have long been known to react in cage and noncage processes to yield combination products, tetramethylsuccinodinitrile (TMSN) and dimethyl-*N*-(2-cyano-2-propyl)ketenimine (KI), and disproportionation products, isobutyronitrile (IBN) and methacrylonitrile (MAN). MAN and KI are often not observed, because the former is susceptible to polym-



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(1) (a) Part I: J. M. McBride, *J. Amer. Chem. Soc.*, **93**, 6302 (1971); (b) presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN 118, and at the Second International Symposium on Organic Solid-State Chemistry, Rehovot, Sept 1970, Abstract Ic.

(2) (a) National Institutes of Health Predoctoral Fellow, 1968–1971; (b) Alfred P. Sloan Foundation Fellow.

(3) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York, N. Y., 1966.

(4) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 59.

(5) R. M. Noyes, "Progress in Chemical Kinetics," Vol. 1, Pergamon Press, New York, N. Y., 1961.

(6) A. M. Bass and H. P. Broida, Ed., "Formation and Trapping of Free Radicals," Academic Press, New York, N. Y., 1960.

(7) G. M. J. Schmidt, "Reactivity of the Photoexceted Organic Molecule," Interscience, New York, N. Y., 1967.

(8) C. A. Hutchinson, Jr., "Organic Solid State Chemistry-2," M. D. Cohen, Ed., Butterworths, London, 1971.

(9) A. B. Jaffe, D. S. Malament, E. F. Slisz and J. M. McBride, *J. Amer. Chem. Soc.*, **94**, 8515 (1972).

(10) A. B. Jaffe, K. J. Skinner, and J. M. McBride, to be submitted for publication.

(11) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(12) See, for example, G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **82**, 5394 (1960), and references therein.

(13) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969), have demonstrated that irradiation of azoisobutane solutions at low temperature leads to an isomer with *cis*-azo configuration, which thermolyzes on warming to room temperature. We have not thus far been able to observe a similar phenomenon with AIBN and for the present prefer to think in terms of its direct photochemical decomposition.

erization[14] and the latter to thermal and photochemical homolysis.[12,15]

The product distribution and extent of decomposition can be determined readily by pmr. The data of Tables I–III were obtained from ∼10% solutions of AIBN in benzene or benzyl benzoate degassed and sealed under vacuum in nmr tubes and irradiated in an unsilvered Pyrex dewar with light from a 450-W Hanovia L lamp in a Pyrex cooling jacket. Authentic KI was less than 1% decomposed by 16 hr of this irradiation at 23° in benzene solution.

Fluid Solution. Table I presents results from photolysis of fluid solutions of AIBN. The product distribution, ∼55% KI, ∼40% TMSN, ∼5% IBN (and presumably of unstable MAN), varies little with solvent or temperature and is stable to further irradiation at high or low temperature. The results confirm those of earlier studies of thermolysis and photolysis in other solvents[12] and are consistent with the hypothesis that photolysis has become equivalent to thermolysis by the time product determining competitions occur.[12,16]

Table I. Photolysis of AIBN in Solution

Solvent	T, °C	Total time, hr	% decomp	Product distribution, % KI	TMSN	IBN[a]
Benzyl benzoate	30–40	2	100	53	42	5
	21–24	1	88	52	41	7
	21–24[b]	3	100	52	43	5
Benzene	10	0.5	>95	58	40	4
	10[b]	1.5	100	55	40	5
	−78[b]	6	100	55	40	4
Chloroform[c]	−78	6.5	100	51	43	6

[a] Much less MAN was observed because of polymerization. [b] Continued irradiation of the sample in the preceding line to demonstrate product stability. [c] Containing about 10% pyridine.

Glassy Solution. Benzyl benzoate solutions of AIBN could be glassed by rapid cooling to Dry Ice temperature. The data of Table II show that photolysis is still rapid in such glasses at −62 to −78° but slows appreciably at liquid nitrogen temperature. Persistence of the glassy state at the higher temperatures was difficult to confirm because of clouding caused by nitrogen evolution, but blanks at −65° showed only a small amount of solute crystallization during the time required for photolysis. It seems quite unlikely that the low-temperature sample should have devitrified.

Table II. Photolysis of AIBN in Benzyl Benzoate Glass

T, °C	Total time, hr	% decomp	Product distribution, % KI	TMSN	IBN[a]
−62	0.8	72	38	45	17
−66	1.8	82	38	51	12
−66[b]	1.8	82	41	50	10
−78	2	∼96	34	49	17
−196[c]	6.8	76	36	36	27
−196	16.3	97	34	37	29

[a] Equivalent amounts of MAN were observed. [b] Photolyzed simultaneously with the sample in the preceding line but thawed and reglassed at 30-min intervals. [c] Continuing irradiation of the sample in the preceding line after warming for pmr analysis and reglassing.

Again the product distribution is only moderately sensitive to temperature. The glassy-state product distribution differs from that in solution primarily in that TMSN and IBN increase at the expense of KI, and that MAN survives without polymerization. Decomposition in the glass at −66° gives more TMSN than fluid, frozen, or crystalline photolysis and thus does not occur in a combination of liquid-like and crystal-like regions. Simultaneous duplicate runs at −66° differing only in that one was warmed to room temperature and reglassed at 30-min intervals gave essentially identical results.

Frozen Mixtures. Differential scanning calorimetry showed that AIBN and benzene give a eutectic mixture containing 2.5 mol % AIBN and melting at 4°, 1.5° below benzene itself. Rapid cooling of benzene solutions to lower temperatures gives a polycrystalline mixture of AIBN and benzene. AIBN also crystallized in benzyl benzoate when cooling was slow.

Photolysis of such frozen mixtures containing small crystals of AIBN gave product distributions entirely different from those found in fluid or glassy solutions. Table III shows that over a range of temperatures and conversions KI and TMSN each account for less than 10% of the product, while IBN and MAN, which again is stable to polymerization, account for more than 80% and sometimes more than 90%.

Table III. Photolysis of AIBN in Frozen Solutions

Solvent	T, °C	Total time, hr	% decomp	Product distribution, % KI	TMSN	IBN[a]
Benzene	−24	2	43	<10	7	88
	−24[b]	6	85	6	9	85
	−78	3	67	10	12	78
	−78[b]	5.1	90	10	10	80
	−78	5	64	9	10	81
	−196	1.5	3	*c*	*c*	*c*
	−196[b]	11.7	22	*c*	∼5	∼90
	−196[b]	33.7	50	5	5	90
	−196[b]	83.2	94	5	8	87
Benzyl benzoate[d]	−65[e]	10	32	<2	6	94
	−65[f]	10	44	<5	7	93
	−65[g]	6	45	<5	7	93

[a] An equivalent amount of MAN was observed and interfered with KI analysis. [b] Continuing irradiation of the sample in the preceding line after melting for pmr analysis and refreezing. [c] Not measured. [d] Samples photolyzed simultaneously. [e] Photolyzed without melting. [f] Melted and refrozen at 100-min intervals. [g] Melted and refrozen at 45-min intervals.

Photolysis of the frozen solutions proceeded much more slowly than for glassy or liquid samples at comparable temperature. A substantial part of this retardation may be due to inefficiency of the light penetrating the sample,[17] since runs that were periodically thawed and refrozen gave higher conversion from a given period of illumination. Such comparisons are strictly valid only for simultaneous runs, since no at-

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(14) A. F. Bickel and W. A. Waters, *Recl. Trav. Chim. Pays-Bas*, **39**, 1490 (1950).

(15) J. R. Fox and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4031 (1964).

(16) G. S. Hammond and J. R. Fox, *ibid.*, **86**, 1918 (1964).

(17) A crude calculation using the solution extinction coefficient and the crystal density predicts that 90% of 350-nm light will be absorbed by a crystal 0.15 mm thick, 50% in the first 0.05 mm.

tempt was made to monitor variations in lamp intensity. The periodic melting did not affect the product distribution significantly.

Crystalline Solid. Crystalline AIBN without solvent was photolyzed in sealed, degassed tubes at temperatures from 5 to −78° and to conversions of 8–100%. The product distribution determined by pmr after adding solvent (Table IV) parallels that found for frozen mixtures although the selectivity toward disproportionation is attenuated at high temperatures and conversions, since liquid products[18] can serve as solvent during the latter part of the reaction. The highest selectivity observed was for a run to 35% conversion in a Dry Ice–acetone bath which gave 96% disproportionation, 4% TMSN, and <0.5% KI.[19]

Table IV. Photolysis of Crystalline AIBN

State	T, °C	Total time, hr	% decomp	Product distribution, % KI	TMSN	IBN[a]
b	4–5	10	34	14	14	72
c	3–4	6.8	100	20	21	59
b	0	4	17	0	10	90
Coarse plates	0	2	8[e]	12	10	78
Fine needles[d]	0	2	23	12	13	75
Fine needles	0	4	70	17	17	66
Powdered plates	0	4	26	11	12	77
Powdered needles[d]	0	4	23	14	13	73
Powdered plates	0	4	13	0	16	84
Powder	−10	6	51	10	10	80
b	−65	10	18	0	7	93
Coarse powder	−78	12	35	0	4	96
Coarse powder	−78	15	73	~0	6	94
Triclinic[f]	−78	12	32	11	8	81
Monoclinic[d,f]	−78	12	36	10	8	82

[a] An equivalent amount of MAN was observed and interfered with KI analysis. [b] Not noted. [c] Solid sample liquified during photolysis. [d] Photolyzed simultaneously with sample of preceding line. [e] This may represent decomposition of a little powder included with the larger crystals. [f] Modification determined by X-ray powder photographs of a small sample.

Parallel runs in a Dry Ice–acetone bath using monoclinic and triclinic modifications of AIBN[9] for which phase purity had been established by X-ray powder photography gave nearly identical results. Runs at 0° with needles or plates, which were probably the different crystalline modifications, also gave quite similar results.

As in the case of frozen solutions the rates of photolysis were much slower than for fluid or glassy solution. The rates also seemed to vary with crystal size, perhaps in part because of inefficient light penetration.[17]

Phase Stability. The observation that monoclinic and triclinic modifications of AIBN give indistinguishable product distributions on solid-state photolysis suggests that one phase may convert to the other during photolysis. The transformation from monoclinic needles to triclinic plates can be observed on a hot stage microscope at 65–80° before melting with decomposition at 100–104°. Plates sublime rapidly above 75° but undergo no such visible phase transformation. The transformation from needles to plates seems to occur independently of sublimation, since a phase boundary can be observed moving rapidly along the length of the needles before appearance of the well-defined plates which stack to give an image of the original needle.[9] Differential scanning calorimetry showed the monoclinic → triclinic transition to be exothermic by 0.32 ± 0.04 and 0.26 ± 0.04 kcal/mol for AIBN and AIBN-d_{12}, respectively. In one calorimetric experiment X-ray powder photographs were taken before and after the transition to confirm that it represented this transformation.

Irradiation of a sample of powdered triclinic plates in a quartz capillary with an Osram HBO 200-W mercury arc and copper sulfate filter gave enough decomposition that the triclinic X-ray powder pattern became quite weak, but no trace of the monoclinic pattern appeared. Similar irradiation of monoclinic powder gave rapid and complete conversion to the triclinic modification if the sample were not cooled, but when room temperature air was blown over the sample no triclinic pattern appeared after about 75% decomposition. It thus seems quite unlikely that phase transformation precedes photolysis under the conditions of Table IV.

Microscopic observation (200×) of small (~0.3 × 0.1 × 0.02 mm) single crystals of both modifications during irradiation on a microscope slide at room temperature showed homogeneous white clouding in the irradiated region followed by apparently random appearance of many tiny bubbles about 1 μ in diameter. Continued irradiation caused the crystals to become completely opaque and ultimately to fracture and disintegrate. With larger crystals it could easily be seen that clouding began in the part of the crystal nearer the light source.[17]

Cage Effect. Since the unusual crystalline-state product distribution could have resulted from a special mode of induced decomposition, the fraction of geminate disproportionation in the crystal was estimated. Two samples were prepared by dissolving AIBN and AIBN-d_{12} (99.6 atom%d) in methanol in the molar ratio 1.1:1 and removing the solvent under vacuum to give a crystalline powder. One sample was photolyzed for 6.8 hr at 3–4° (Table IV, entry 2); the other for 6 hr at −9 to −12° (Table IV, entry 10). In both cases pmr analysis of the IBN methyl signal showed no trace (<3%) of the triplet for IBN-α-d_1, a cross-disproportionation product between d_6 and d_0 radicals. Because of the kinetic isotope effect on disproportionation only one-third of crossed disproportionation events should have given this product.[20] We may conclude that less than 9% of the disproportionation involves isotopically mixed radical pairs.[21] It is highly unlikely that the isotopic molecules should have segregated in the crystal,[22] and the conceivable complication that they might photolyze at markedly different rates[23] was discounted on the basis of an approximately 21% yield of TMSN-d_6

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(18) MAN mp −36°, IBN mp −72°.

(19) Experiments are under way to measure the selectivity at very low conversions using isotope dilution analysis.

(20) J. M. McBride, *J. Amer. Chem. Soc.*, 93, 6302 (1971).

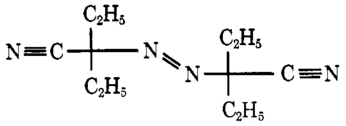
(21) We are currently using mass spectrometry to refine this measurement and test the other products as to cage or noncage origin.

(22) The spectrum of 0.043% C_6H_6 in C_6D_6 at 4.2°K shows nearly equal intensity for natural abundance $^{13}C_2{}^{12}C_4H_6$ and resonance pairs of C_6H_6 implying that the concentration of those pairs is nearly statistical: E. R. Bernstein, S. D. Colson, D. S. Tinti, and G. W. Robinson, *J. Chem. Phys.*, 48, 4632 (1968). We thank Professor Colson for bringing this reference to our attention.

(23) It has been reported that the thermolysis rate of AIBN is some 20–25% faster than that of AIBN-d_{12} and that its cage effect is 5% smaller: S. Rummel, H. Hübner, and P. Krumbiegel, *Z. Chem.*, 7, 351, 392 (1967).

from photolysis of a similar mixture in methanol solution at 25°.[24] It thus seems certain that the solid-state process which results in the selective formation of disproportionation products involves geminate radical pairs.[26]

Azobis-3-cyano-3-pentane (ACP) was studied briefly in hopes that it would reveal matrix influence over disproportionation stereochemistry.[27] Its behavior on thermolysis and photolysis in solution was quite analogous to that of AIBN. Photolysis in benzene at 25–35° gave 25% succinodinitrile and 75% ketenimine with a trace of disproportionation (<5%). Photolysis of the solid at −24° gave 33% succinodinitrile, 67% ketenimine, and, as in solution, only a trace of disproportionation. The solid melted during this photolysis to completion. The product distribution contrasts sharply with that from solid AIBN, which also melted during complete decomposition at −24°.



$N{\equiv}C{-}C(C_2H_5)_2{-}N{=}N{-}C(C_2H_5)_2{-}C{\equiv}N$

ACP

The heat of fusion of ACP was found to be 6.5 kcal/mol and its heat of decomposition 39 kcal/mol. The latter value is in reasonable agreement with that reported for AIBN in which fusion and decomposition are inseparable.[28]

Discussion

The product distribution from cyanoisopropyl radical pairs generated in crystalline AIBN is quite distinctive when compared with those from fluid or glassy solutions. Several explanations of this behavior which would not require some very specific mode of influence from the structured environment in which the pair is born can be excluded by the experimental observations.

The results in fluid, glassy, frozen, and crystalline samples all show remarkably little sensitivity to temperature, except when temperature variation results in a change of phase.

A reasonable argument can be made for increases in disproportionation at the expense of symmetrical coupling to TMSN as medium viscosity is increased, since only the nitrogen molecule and one methyl group would need to move appreciably for disproportionation, while motion of the nitrogen molecule and of all the atoms of at least one radical would be required for coupling.[27,29] The increase in disproportionation in glassy benzyl benzoate over that found in the fluid solvent may be due in part to such an effect,[30] although it is difficult to see why the yield of KI is reduced relative to that of TMSN, since the formation of KI could require motion of no more atoms than does disproportionation.[31] However difficult it may be to assign an appropriate pseudoisotropic "viscosity" to crystalline AIBN, it is hard to believe that its viscosity at 0° exceeds that of glassy benzyl benzoate at −196° by enough to explain the dramatically higher disproportionation yield.

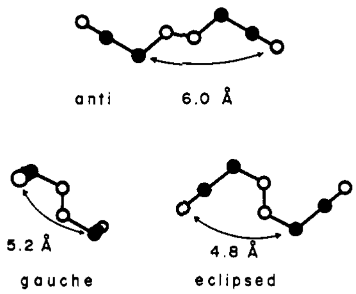


Figure 1. Backbone geometries for AIBN rotamers showing coupling distances for KI formation: open circles, nitrogen; filled circles, carbon.

The differences between glass and crystal might be reconcilable in terms of differing initial geometries for the radical pair. If the pair were generated from a molecule of *anti* conformation, it would require more drastic motion to form KI than if it were generated from a molecule of *gauche* or eclipsed conformation (see Figure 1).[13] Thus an isotropic viscosity alone could explain the differences if the molecular conformation of AIBN were *anti* in the crystal and *gauche* or eclipsed in the glass. However, X-ray diffraction shows the nitrile groups to be within 5° of the eclipsed conformation in both crystalline modifications.[9]

The high yield of disproportionation products from cyanoisopropyl radical pairs generated in crystalline AIBN must result from a very specific mode of interaction with the matrix. In following papers[9,10] we report an analysis of the crystal packing which indicates the importance of intermolecular dipolar interactions in determining the crystal structure, and we show how such forces provide a qualitative explanation of the behavior observed here. Even in this system chosen to exemplify the importance of solvent steric effects, the influence of solvent "polarity" is crucial.[32]

The failure of ACP to yield disproportionation products in solid-state photolysis demonstrates the danger at the present level of our knowledge of solid-state chemistry of extrapolating from one system to a homolog. In the following papers we present an *a posteriori* rationalization of the behavior of ACP in terms of differences in dipole packing between its lattice and those of AIBN.

While visual inspection of irradiated crystals suggests

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(24) Analysis was by *p*-methyl in the mass spectrum of TMSN assuming that fragmentation isotope effects largely cancel in comparing TMSN-d_6 with the sum of TMSN and TMSN-d_{12}. If the compounds had identical decomposition rates and cage effects,[23] the result would translate crudely to a 58% cage effect, a not unreasonable value.[25]

(25) *Cf.* R. D. Burkhart and J. C. Merrill, *J. Phys. Chem.*, 73, 2699 (1969), and references therein.

(26) The remote possibility that these products result from some bizarre nonradical reaction will be tested in another connection.

(27) This has subsequently been achieved with azobis-3-phenyl-3-pentane: K. J. Skinner, R. J. Blaskiewicz, and J. M. McBride, *Isr. J. Chem.*, 10, 457 (1972).

(28) P. Ambrovič and M. Lazár, *Eur. Polym. J. Suppl.*, 361 (1969).

(29) We have observed such an effect for other azoalkanes: K. J. Skinner, M. Lasky, and M. J. Tremelling, unpublished work.

(30) From −50 to −75° the "molecular level" viscosity of benzyl benzoate varies from 1 to 15 P as measured by the rotational relaxation rate of nitroxide spin labels: M. J. Tremelling, unpublished work in this laboratory.

(31) Hindrance of the nitriles by solvation is, of course, a possibility as is most probably the explanation for >90% TMSN from photolysis of AIBN in a benzene–silica gel matrix: P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *J. Amer. Chem. Soc.*, 88, 5075 (1966). A remote possibility which is almost impossible to exclude experimentally is that KI, while photostable in solution, is sometimes in glassy benzyl benzoate and always in crystalline AIBN created and held in a geometry particularly susceptible to photosensitized homolysis.

(32) While polar effects seem to inhibit coupling reactions, it is likely that steric effects are predominant in limiting the rate of disproportionation.[20]

uniform photolysis, it is quite difficult to establish by chemical means that the reaction whose products we observe takes place in the bulk crystal and not at lattice imperfections. The azo chromophores in our crystals are so well separated[33] and have such weak oscillator strengths that exciton hopping to channel excitation to such imperfections from the initial site of photoexcitation should be negligibly slow.[34] However, in view of the longer photolysis times required for crystalline samples, it is possible that decomposition occurs only after excitation of a molecule near a lattice defect and that other excited molecules are deactivated without reaction. If reaction occurred only at imperfections, the reaction rate might have been expected to show the acceleration with conversion characteristic of many solid-state thermal reactions.[35] But samples in which crystals were renewed by periodic dissolution and recrystallization in fact showed faster overall decomposition than those in which "imperfections" were allowed to accumulate.[36] Experiments in progress involving epr spectroscopic investigation of the geometry, concentration, and lifetime of the radical pairs coupled with isotope dilution product analysis are likely to give the most conclusive answer to this question for low conversion. It is clear that at higher conversion, reaction must begin to take place near sites damaged by previous decompositions or on the surface, unless damage can anneal out of the crystal during the photolysis. Since the lattice of ACP is disordered, it is possible that photolysis of this solid always occurs near defects and so differs fundamentally from that of AIBN.

Several generalizations from this investigation are worth emphasizing because of the potential they suggest for synthetic and mechanistic chemistry. Photolytic product distribution can vary quite dramatically, though not always predictably, from fluid to glassy to crystalline samples. Glassy and crystalline matrices give very high cage effects and can preserve products (*e.g.*, MAN) which would not have been stable to the reaction conditions in solution. Photolysis of frozen solutions may proceed more rapidly if the sample is periodically melted and refrozen. Although we made no attempts at accurate actinometry, it seems that in our case photolysis in the glass was significantly more rapid than for frozen or crystalline samples. While this effect may have been due solely to inefficient illumination of the latter samples, it is also conceivable that decomposition in the crystalline matrix is reversible suggesting that solid-state reactions are one of the more promising areas for studying the possibility of such reversibility.[37]

Experimental Section

Solvents were commercial reagent grade and were not purified further.

AIBN was purchased or prepared by standard methods[38] and recrystallized from methanol several times before use. Both triclinic and monoclinic modifications could be grown from methanol solution at room temperature, and no very reliable method was found to favor growth of one or the other, although rapid crystallization usually gave the less stable monoclinic form. The easiest sure way to distinguish between the modifications is by X-ray diffraction.

AIBN-d_{12} was prepared by the same method using acetone-d_6 (99.6 atom %, Stohler), hydrazine sulfate which had been exchanged three times with D_2O in a Soxhlet extractor, sodium cyanide dried over P_2O_5 under vacuum, and D_2O solvent. This material was analyzed by the mass spectrum of TMSN from its photolysis which showed *p*-methyl peaks in the ratio 95.0% d_9 to 5.0% d_8. This implies an atom % enrichment of $0.95^{1/9} = 99.4\%$.

Temperature control during photolysis was achieved with cooling baths of ice water, Dry Ice–acetone, liquid nitrogen, circulating tap water, or dimethyl ether refluxing under controlled pressure. The temperature was monitored with a copper–constantan thermocouple.

Product analysis was by multiple integration of pmr spectra taken with Varian A-60, A-60A, and HA-100 instruments. The products gave signals at the following positions in ppm upfield from solvent benzene: AIBN, 6.013 (s, 12H); TMSN, 6.254 (s, 12H); KI, 5.735 (s, 6H), 5.970 (s, 6H); IBN, 5.23 (septet, J = 7.5, 1H), 6.49 (d, J = 7.5, 6H); MAN, 1.98 (m, 1H), 2.28 (m, 1H), 5.89 (m, 3H). Analysis of ACP products is described below.

X-Ray powder photographs were made using Ni-filtered Cu Kα radiation and a Weissenberg camera with rotating samples of AIBN ground at liquid nitrogen temperature and contained in 0.5-mm quartz capillaries. Distinctive rings were found at the following 2θ angles and agreed with patterns calculated from single-crystal data:[9] monoclinic modification, 13.6, 16.2, 19.3, 26.9, 30.6, 32.8; triclinic modification, 11.9, 15.3, 17.5, 19.7, 23.1, 25.0, 27.0, 28.7, 30.4.

Phase transformations were studied thermochemically with a Perkin-Elmer DSC-1b instrument using samples sealed in aluminum volatile-sample capsules. Sample size was 5–7 mg for the phase transition measurements. Optical observation of the phase transition was with a Reichert polarizing hot-stage microscope.[39]

Mass spectra were recorded from a Hitachi-Perkin-Elmer RMU-6 at 70 eV with a potentiometric strip chart recorder. Slits were adjusted to give flat-topped peaks.

Azobis-3-cyano-3-pentane (ACP) was prepared from 3-pentanone by the procedure of Dox.[38] Differential scanning calorimetry runs at 5°/min showed a 6.5 kcal/mol melting endotherm peaking at 70°, width at half-height 2.5° (lit.[35] mp 74–75°) and a 39 kcal/mol decomposition exotherm peaking at 120°. Pmr (100 MHz, CCl_4) showed a methyl triplet (J = 7) at δ 1.02 and overlapping quartets (J = 7 Hz) for the diastereotopic methylene protons at 2.09 and 2.12.

Thermolysis of ACP without solvent for 5 min at 120–150° gave a product mixture with just enough (<5%) of the (*Z*)- and (*E*)-3-cyano-2-pentenes to be identified (not distinguished) by the vinyl quartets (J = 7.0 Hz) of triplets (J = 1.4 Hz) 1.31 and 1.69 ppm upfield from benzene solvent with the upfield pattern *ca.* three times as intense as the downfield. The predominant constituent of the mixture was tetraethylsuccinodinitrile (TESN), which was recrystallized twice from methanol and gave a pmr spectrum (100 MHz, CCl_4) with a methyl triplet at δ 1.16 and a methylene quartet at ~1.88. Both patterns were distorted by inequivalence of δ and J for the diastereotopic methylene protons.

Photolysis of ACP in a degassed benzene solution at 25–35° for 4.5 hr gave complete decomposition with <5% of olefins as shown by pmr. In the aliphatic region of the spectrum other signals overlapped the methyl and methylene patterns of TESN and a new methylene quartet constituting 14.7% of the total aliphatic integral appeared 0.33 ppm downfield of that for TESN. On the assumptions that this signal is due to the allylic methylene protons of diethyl-*N*-(3-cyano-3-pentyl)ketenimine and that no third compound contributed to the signals, one may calculate a yield of 25% for the ketenimine. Photolysis of the crystalline solid at −24° for 5.5 hr with light from an Osram HBO 200-W arc filtered through copper sulfate solution gave complete decompostion and liquifaction. Again only traces of olefin were present. The partitioning between TESN and ketenimine was 1:2.

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[33] Nearest neighbors 5.51 Å in monoclinic modification, 5.55 Å in triclinic.

[34] The authors thank Professors S. D. Colson and M. D. Cohen for helpful discussions of this point.

[35] H. Morawetz, "Physics and Chemistry of the Organic Solid State," D. Fox, M. M. Labes, and A. Weissberger, Ed., Vol. I, Interscience, New York, N. Y., 1963, Chapter 4.

[36] As explained above this may be due to light scattering by the crystals.

[37] See for example: W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970); N. A. Porter, M. E. Landis, and L. J. Marnett, *ibid.*, **93**, 795 (1971); M. J. Goldstein and H. A. Judson, *ibid.*, **92**, 4119 (1970); and J. C. Martin and S. A. Dombchik, *Advan. Chem. Ser.*, No. **75**, 269 (1968).

[38] A. W. Dox, *J. Amer. Chem. Soc.*, 47, 1471 (1925).

[39] We thank Prof. H. H. Wasserman for making this instrument available to us.

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Solvent Steric Effects. III. Molecular and Crystal Structures of Azobisisobutyronitrile and Azobis-3-cyano-3-pentane. A Structural Deuterium Isotope Effect[1]

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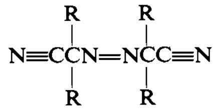
Abstract: Lattice parameters were determined for normal and perdeuterated azobisisobutyronitrile (AIBN) in $P\bar{1}$ and $P2_1/c$ modifications and showed significant variation with isotopic substitution. Three dimensional intensity data were collected by diffractometer for three of these crystals and for a crystal of azobis-3-cyano-3-pentane (ACP) and all were refined to conventional *R*'s of 0.05–0.09. The refinement of ACP was in space group *Cmca* ($Z = 4$) and gave a long C–C bond, a wide C–C–C angle, and unrealistic thermal parameters suggesting disorder with respect to the mirror plane which was confirmed by the observation of diffuse scattering. Otherwise bond lengths and angles are consistent among the determinations and with those of other azoalkanes. The nitrile and azo groups are nearly eclipsed to give planar, S-shaped N≡CCN=NCC≡N backbones for molecules in these crystals. The backbones are arranged into sheets containing a herringbone pattern of nitrile groups. The photochemistry of crystalline AIBN and ACP is discussed in terms of these packings, and it is concluded that dipolar forces are probably predominant in product determination. An approach to computer simulation of radical reactions in crystalline matrices is mentioned. The thermal transformation of $P2_1/c$ AIBN to $P\bar{1}$ AIBN is not consistently topotactic.

Azobisisobutyronitrile (AIBN) crystallizes from methanol in two modifications.[1a] Photolysis of either generates pairs of cyanoisopropyl radicals which collapse to give abnormally high yields of the disproportionation products isobutyronitrile (IBN) and methacrylonitrile (MAN), low yields of the symmetrical coupling product tetramethylsuccinodinitrile (TMSN), and little or none of the unsymmetrical coupling product dimethyl-*N*-(2-cyano-2-propyl)ketenimine (KI), which predominates in the solution reaction.[1a] To interpret this reactivity pattern and to analyze the epr spectrum of the metastable intermediate triplet-state radical pairs[3] it is necessary to know the geometry of the lattice in which reaction occurs.

Since we have studied deuterated as well as unlabeled AIBN in our other work, we decided to investigate isotope effects on the crystal structures in addition to determining the crystal structures themselves. Such isotope effect studies of organic molecules seem previously to have been confined to methane[4] and certain hydrogen bonded systems.[5]

The solution photochemistry of azobis-3-cyano-3-pentane (ACP), the analog of AIBN in which methyl groups are replaced by ethyl, is quite similar to that of AIBN. However in contrast to AIBN, solid-state photolysis of ACP yields a product distribution similar to that found in solution, giving substantial amounts of tetraethylsuccinodinitrile and ketenimine and negligible amounts of disproportionation products.[1a] We also undertook the determination of an approximate molecular structure and crystal packing for disordered crystals of this compound.



$$\mathrm{N{\equiv}C\overset{R}{\underset{R}{C}}N{=}N\overset{R}{\underset{R}{C}}C{\equiv}N}$$

AIBN $\quad$ $R = CH_3$
AIBN-d_{12} $\quad$ $R = CD_3$
ACP $\quad$ $R = C_2H_5$

The success of others in using empirical atom–atom potentials to calculate crystal packing energies[6] suggested the possibility of simulating reaction paths in the crystalline environment of AIBN by analogous calculations. For these calculations a set of realistic values of the pairwise potentials must be available, and at the end of this paper we touch on some first steps toward defining such a set of potentials for our system.

Experimental Section

AIBN. AIBN crystals grown from methanol solution at room temperature[1a,7] were mounted among red cotton fibers in 0.5-mm

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[1] (a) Part II: A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Amer. Chem. Soc.*, **94**, 8510 (1972); (b) presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-118, and at the Second International Symposium on Organic Solid-State Chemistry, Rehovot, Sept 1970, Abstract Ic.

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[3] (a) Ya. S. Lebedev, *Dokl. Akad. Nauk SSSR*, **171**, 378 (1966); (b) A. B. Jaffe and J. M. McBride, to be submitted for publication.

[4] S. C. Greer and L. Meyer, *J. Chem. Phys.*, **52**, 468 (1970).

[5] K. J. Gallagher, "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, New York, N. Y., 1959, p 45.

[6] See for example, (a) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966); **47**, 460 (1967); (b) E. Giglio and A. M. Liquori, *Acta Crystallogr.*, **22**, 437 (1967); (c) A. I. Kitaigorodskii, *ibid.*, **18**, 585 (1965); (d) R. Mason, *Mol. Cryst. Liquid Cryst.*, **9**, 1 (1969).