Table III. Force Constants Calculated for HBO

Fundamentals and frequencies, cm⁻¹	Force constants × 10⁵ —dyn/cm—		
	k_1	k_2	$k_\sigma/l_1 l_2$
ν_3 (H¹¹BO), ν_3 (D¹¹BO) (1817, 1648)	4.27	13.86	
ν_3 (H¹¹BO), ν_3 (H¹⁰BO) (1817, 1855)	4.45	13.83	
ν_1 (D¹¹BO), ν_3 (D¹¹BO) (2259, 1648)	4.10	14.32	
ν_2 H¹¹BO (754)			0.233
ν_2 D¹¹BO (606)			0.233

HBO with H—B and B—O bond distances of 1.18[10] and 1.20 Å,[11] respectively, are summarized in Table III. Values of the B—O stretching force constants (Table III) are close to that found in B_2O_2 (13.86 × 10⁵ dyn/cm).[8] The ¹¹B–H stretching frequency in HBO, which was too weak for detection, is calculated from the DBO force constants to be 2849 cm⁻¹ and is probably reliable to within ±10 cm⁻¹. This is higher than any B–H stretching frequency known and is close to that reported for BH_3.[5]

The photodecomposition of $H_2B_2O_3$ in an argon matrix must involve at least one reaction path in addition to those leading to HBO and B_2O_3. The band of a photolysis product at 3367 cm⁻¹ is interesting because it can most reasonably be assigned to a hydrogen-bonded OH stretching vibration. This band, the weaker bands in the normal OH stretching regions, and the bands between 1380 and 1440 cm⁻¹ may be associated with a hydrogen-bonded complex formed by intramolecular transfer of H atoms from boron to oxygen sites.

(10) W. V. Brooks, C. C. Costain, and R. F. Porter, *J. Chem. Phys.*, 47, 4186 (1967).

(11) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950, p 512. (Value assumed is that found for BO.)

Earl R. Lory, Richard F. Porter*
Department of Chemistry
Cornell University, Ithaca, New York 14850

Rotational Diffusion Control of Radical Disproportionation in the Solid-State Photolysis of Azobisisobutyronitrile

Sir:

For some time we have been studying the chemistry of the cyanoisopropyl radical pair and the nitrogen molecule generated in crystalline azobisisobutyronitrile (AIBN) by photolysis.[1] Disproportionation to methacrylonitrile (MAN) and isobutyronitrile (IBN) accounts for only 5% of the radical–radical reactions in fluid solution but for 95% in the crystal.[2] From epr studies and dynamic computer simulations we suspected that disproportionation of the nitrogen-separated

(1) A. B. Jaffe, D. S. Malament, K. J. Skinner, and J. M. McBride, papers presented at the Second International Symposium on Organic Solid-State Chemistry, Rehovot, Israel, Sept 1970, Abstract Ic, and at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-118.

(2) Previous work[1] leaves no doubt that this is a true solid-state reaction under the conditions used here.

radical pair was limited in rate by rotational diffusion about a C—C≡N axis which brings a methyl group into the position formerly occupied by the nitrogen
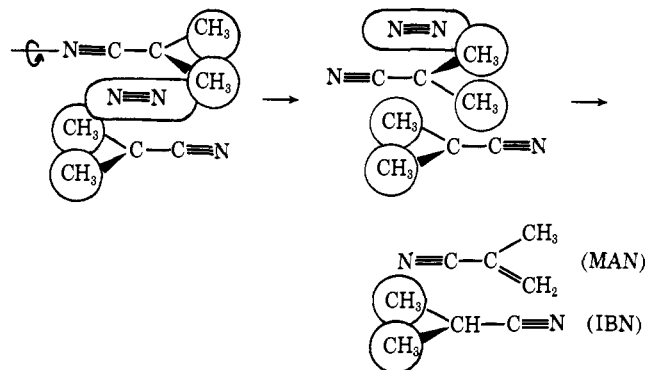
molecule. We show below that the rate of disproportionation is limited not by atom transfer but, presumably, by this diffusion.[3]

Two deuterated samples of AIBN were prepared. One from exchanged acetone 2-cyano-2-propylhydrazone was 75 mol % AIBN-d_6 with one pair of geminal methyls labeled and 25 mol % of roughly equal parts of AIBN-d_0 and AIBN-d_{12}.[4] In deuterated positions labeling was 94% complete.[4] The other from partially exchanged acetone contained 73 atom % deuterium randomly distributed.[4]

Samples recrystallized three times from methanol were sealed in nmr tubes at 10⁻³ Torr and photolyzed in a Dry Ice–acetone bath for 10–15 hr with a Pyrex-filtered Hanovia L mercury arc. Products were analyzed by nmr after opening the tube, adding solvent, and resealing. The AIBN-d_6 sample was 79% decomposed to give 94% disproportionation and 6% tetramethylsuccinodinitrile (TMSN). The randomly labeled AIBN was about 72% decomposed to give a ratio of disproportionation to TMSN of about 9.

Integrals for AIBN-d_6 products based on 3 for MAN methyl were: MAN vinyls, 1.06 and 1.05; IBN methyl, 6.64.[5] Crude calculation of an apparent k_H/k_D from the excess of IBN-d_0 + IBN-d_1 over MAN-d_0 gives 0.85 or 0.92 based on MAN methyl and MAN vinyl, respectively.[6] These values are nearly within experimental error of unity. Neglecting isotopic differences, pathways for atom donation by the two radicals are equivalent by symmetry in the centrosymmetric reaction

(3) Product determination during an initial photolytic holocaust, bypassing the vibrationally equilibrated, centrosymmetric, nitrogen-separated radical pair, seems unlikely from our epr studies.[1]

(4) Analysis was from m/e 119 to 131 in the mass spectrum of TMSN from thiol-scavenged thermolysis. The presence of equal amounts of AIBN-d_0 and AIBN-d_{12} suggests reversible HCN elimination and hydrolysis to acetone hydrazone during addition of cyanide to the exchanged compound. A synthesis through α-chloro-α'-cyanoazoisopropane may avoid this complication.

(5) As expected from the isotopic impurity of the starting material 36% of the IBN methyl signal was in a doublet (J = 7 Hz, methine proton) and 64% in a triplet (J = 1 Hz, methine deuteron). The 5% excess in the vinyl positions of MAN is probably due to experimental error.

(6) AIBN-h_{12} runs have shown that polymerization of MAN does not occur under these conditions. The observations are consistent with a detailed calculation assuming that the d_0 radical moves 0.85 or 0.94 times as fast as the d_6 radical. The sense of this difference is reasonable.[7,8]

(7) The unit cell sides of AIBN-d_{12} are uniformly 0.1% shorter than for AIBN-h_{12}; A. B. Jaffe, to be published.

(8) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, 86, 1733 (1964).

site.[9] Since there is an intrinsic isotope effect for the disproportionation (see below), the apparent absence of an isotope effect in this case implies that the degenerate pathways do not compete and that the *disproportionation is diffusion limited.*[10] These results do not preclude competition between geminal methyls.

Careful integration of the spectrum of purified products from the randomly labeled sample showed 1.32 for the methine signal of IBN *vs.* 6 for its methyl signal and 1.60 for the vinyl region of MAN *vs.* 3 for its methyl signal.[11] Within experimental error (± 0.08) the excess in IBN methine balances the deficit in MAN vinyl showing that MAN methyl had not been depleted in protium and thus had not competed in the atom transfer step with the methyl group which served as atom donor.[10,12] If the per atom kinetic isotope effect in atom transfer is $k_H/k_D \equiv R$, then, since competition in the atom transfer step occurs among hydrogens of a single methyl group but not between methyl groups, a sample of deuterated AIBN with a fraction f of randomly distributed protium will give MAN having a vinyl integral which is a fraction F of the "expected" two-thirds of its methyl signal where $F = f^2 + [3f(1-f) \cdot (R+1)/(2R+1)] + 3(1-f)^2/(R+2)$. The observed $0.72 < F < 0.88$ is consistent with $1.8 < R < 2.3$.[13]

Taken together these three observations—(1) that no kinetic isotope effect is observed when only one of two geminate radicals is deuterated, (2) that such an effect is operative when protium and deuterium are available within the same methyl group, and (3) that with random labeling protium is depleted from the vinyl positions of MAN but not from its methyl group— imply that in the crystal lattice methyl rotation is rapid on the time scale of the atom transfer step while motion of the radical pair which brings a methyl group into position for the atom transfer is slow.

(9) We assume that the initial radical pair is or can easily become centrosymmetric, as seems certain from a computer analysis of the crystal packing; to be published.

(10) The reasoning behind this conclusion and the generality of this technique for detailed studies of diffusion-limited reactions will be elaborated in the full paper.

(11) Accurate analysis of this sample required purification of MAN and IBN by bulb-to-bulb distillation because of peak width and consequent overlapping with the TMSN signal.

(12) Geminal methyls would not have been equivalent by symmetry.

(13) Professor M. Gibian (personal communication) has found $R = 1.87$ for α-phenylethyl radicals in solution.

(14) Alfred P. Sloan Research Fellow.

J. Michael McBride[14]

*Department of Chemistry, Yale University
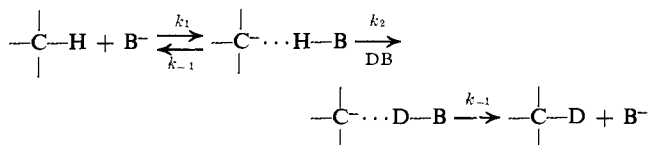New Haven, Connecticut 06520*

Intramolecular *vs.* Intermolecular Capture of Carbanions

Sir:

Deuterium exchange of protons in carbon acids as catalyzed by lyate ion, B^- (or other bases), can occur by either of two carbanion mechanisms.[1] In one

(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter I.

mechanism the rate of internal return (k_{-1}) is much greater than the rate of solvent exchange with the solvated carbanion (k_2), leading to a prerate equilibrium, with k_2 rate limiting, whereas in the other k_{-1} is much smaller than k_2, making k_1 rate limiting.

$$-\overset{|}{\underset{|}{C}}-H + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} -\overset{|}{\underset{|}{C}}^- \cdots H-B \overset{k_2}{\longrightarrow}$$

$$-\overset{|}{\underset{|}{C}}^- \cdots D-B \overset{k_{-1}}{\longrightarrow} -\overset{|}{\underset{|}{C}}-D + B^-$$

The low k^H/k^D isotope effects (some less than 1.0) observed under some conditions for certain carbon acids, including $C_6H_5CH(Me)Et$,[2a] $C_6H_5CH(Me)OEt$,[2a] $HexCH(Me)SO_2C_6H_5$,[2b] toluene,[2c] 2,2-diphenylcyclopropanecarbonitrile,[2d] and N-methylpyridinium iodide,[2e] appear to be best interpreted in terms of the prerate equilibrium mechanism.[2] This interpretation gains strong support from the demonstration that for 2,2-diphenylcyclopropanecarbonitrile the k^H/k^D ratio shows but little temperature dependence.[2d] This mechanism also accounts best for the linear relationship found between log k for the methoxide-catalyzed racemization of 2-methyl-3-phenylpropionitrile in DMSO–MeOH mixtures and the H_- function.[1,3] It is particularly noteworthy in connection with the present work that exchange α to a sulfone group is included in this category,[2b] and that even for a disulfone, $(CH_3SO_2)_2CH_2$, where the acidity has been increased by *ca.* 15 pK_a units over $HexCH(Me)SO_2C_6H_5$, it is estimated that between one-tenth and one-half of the ion pairs formed by water deprotonation undergo internal return.[4]

Despite the rapidity of internal return for very weak carbon acids, there is at least one instance where another process appears to be competitive in rate with internal return. This process is also faster than solvent exchange. Thus, it has been observed that k^H/k^D is *ca.* 5 for alkene isomerization catalyzed by *tert*-BuOK in DMSO under conditions where k^H/k^D is *ca.* 1 for toluene.[2c,5] Here, intramolecular movement of the "singly hydrogen-bonded conjugate acid molecule"[6] from one site on the allylic carbanion to another apparently competes with internal return (leading to a sizable k^H/k^D ratio), and is 16 times faster than exchange with the internal solvent.[5]

In this paper we present evidence to show that intramolecular capture of a carbanion by an electrophilic center, namely, a carbon atom bonded to bromine, may also occur much more rapidly than exchange with solvent molecules. This can cause k_{obsd} for base-initiated 1,3 eliminations of HBr, or like reactions, to be considerably faster than k_{obsd} for comparable deuterium exchange reactions. The experimental basis for this statement is the observation that the rate of

(2) (a) D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Amer. Chem. Soc.*, **83**, 3688 (1961); (b) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961); (c) J. E. Hoffman, A. Schriesheim, and R. E. Nickols, *Tetrahedron Lett.*, 1745 (1965); (d) H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, **92**, 2445 (1970); (e) J. A. Zoltewicz and L. S. Helmick, *ibid.*, **92**, 7547 (1970).

(3) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962).

(4) J. Hine, J. C. Philips, and J. I. Maxwell, *J. Org. Chem.*, **35**, 3943 (1970).

(5) S. Bank, C. A. Rowe, Jr., and A. Schriescheim, *J. Amer. Chem. Soc.*, **85**, 2115 (1963).

(6) W. T. Ford, E. W. Graham, and D. J. Cram, *ibid.*, **89**, 4661 (1967).