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
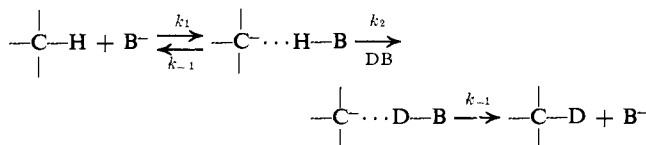New Haven, Connecticut 06520*

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.

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

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

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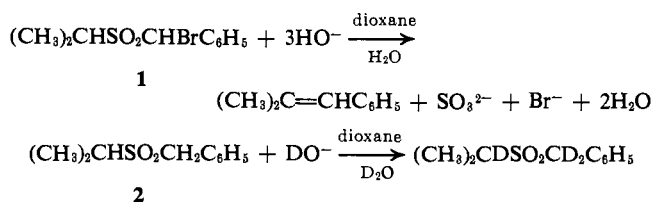
(3) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962).

(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).
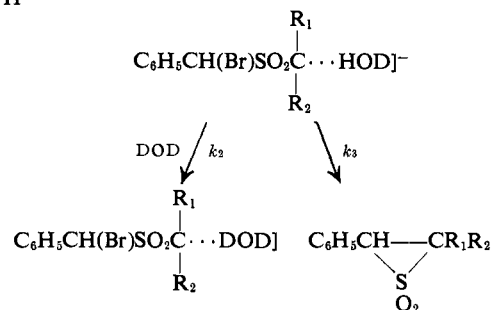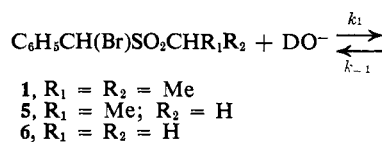
hydroxide ion initiated 1,3 elimination of HBr in 40% aqueous dioxane from isopropyl α-bromobenzyl sulfone (1) in the Ramberg-Bäcklund reaction is 560 times faster than deuterium exchange of the tertiary α hydrogen of the analogous isopropyl benzyl sulfone (2) under these conditions. (Exchange of the benzylic hydrogen atoms in 2 precedes, of course, the exchange of the tertiary hydrogen atom.)

$$(CH_3)_2CHSO_2CHBrC_6H_5 + 3HO^- \xrightarrow[H_2O]{dioxane}$$

1

$$(CH_3)_2C{=\!=}CHC_6H_5 + SO_3{}^{2-} + Br^- + 2H_2O$$

$$(CH_3)_2CHSO_2CH_2C_6H_5 + DO^- \xrightarrow[D_2O]{dioxane} (CH_3)_2CDSO_2CD_2C_6H_5$$

2

We estimate that only *ca.* fivefold of the 560-fold increase in rate for **1**, relative to **2**, can be accounted for by the inductive effect of the bromine atom.[7] Furthermore, there is good reason to believe that the additional acceleration is not caused by concerted breaking of the HC and CBr bonds of **1** in the Ramberg-Bäcklund reaction.[10] Additional information as to the cause of the rate difference was derived from the observation that the rate of exchange was affected dramatically by alkyl substitution, whereas the rate of Ramberg-Bäcklund reaction was not. In the series $C_6H_5CH_2SO_2$-$CHMe_2$ (**2**), $C_6H_5CH_2SO_2CH_2Me$ (**3**), $C_6H_5CH_2SO_2CH_3$ (**4**), the rate of exchange at the nonbenzylic α position was in the order $1.0:10^2:10^4.$[11] In contrast, the rates of the Ramberg-Bäcklund reaction, under comparable conditions, for $Me_2CHSO_2CHBrC_6H_4$ (**1**), $MeCH_2SO_2$-$CHBrC_6H_5$ (**5**), and $CH_3SO_2CHBrC_6H_5$ (**6**) were in the order $1.0:1.7:0.62.$

The rates of internal return (k_{-1}), solvent exchange (k_2), and ring closure in the Ramberg-Bäcklund reaction (k_3) will all be affected somewhat by methyl substitution. Methyl groups should be effective in excluding solvent molecules from the vicinity of the carbanion, suggesting that the rate of solvent exchange could be decreased markedly with methyl substitution. This would account for at least part of the 10^4 decrease in k_{obsd} for deuterium exchange of **2** relative to **4**.[12] On the other hand, methyl substitution may have relatively little effect on the rate of internal return or the rate of ring closure in the Ramberg-Bäcklund reaction. This would explain why k_{obsd} for the Ramberg-Bäcklund reaction of **1** is much *faster* than deuterium exchange of the methinyl proton (as judged by comparison with

2) whereas k_{obsd} for the Ramberg-Bäcklund reaction of **6** is much *slower* than deuterium exchange of the methyl protons (recovered **6** showed complete exchange of methyl protons).

$$C_6H_5CH(Br)SO_2CHR_1R_2 + DO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

1, $R_1 = R_2 = Me$
5, $R_1 = Me; R_2 = H$
6, $R_1 = R_2 = H$

$$[C_6H_5CH(Br)SO_2\overset{R_1}{\underset{R_2}{C}}\cdots HOD]^-$$

$$DOD \swarrow k_2 \qquad \searrow k_3$$

$$[C_6H_5CH(Br)SO_2\overset{R_1}{\underset{R_2}{C}}\cdots DOD] \qquad C_6H_5CH\!-\!\!-\!CR_1R_2 \underset{O_2}{\overset{S}{\diagdown\!\diagup}}$$

One would expect elimination of bromide ion, or the like, from a carbon atom adjacent to a carbanion center (carbanoid 1,2 elimination) to be much more successful than carbanoid 1,3 elimination in competing with solvent exchange. The fact that syn and anti 1,2 eliminations from 2-*p*-tolylsulfonylcyclohexyl and 2-*p*-tolylsulfonylcyclopentyl tosylates are *ca.* 10^5–10^7 times faster than deuterium exchange in the corresponding sulfones,[15] can be interpreted as support for this view. (Here, we estimate that the inductive effect of the OTs group might cause *ca.* 10^3 acceleration.[7,15,16]) It is possible that the faster rates for the elimination reactions are due to their concerted nature,[15] but it now appears more likely that the difference in rates, after correction for inductive effects, is a measure of the relative ability of (intramolecular) elimination *vs.* (intermolecular) solvent exchange to compete with internal return from a carbanion intermediate.[16]

(15) J. Weinstock, J. L. Bernardi, and R. G. Pearson, *J. Amer. Chem. Soc.*, **80**, 4961 (1958).
(16) A more complete discussion is given by F. G. Bordwell, J. Weinstock, and T. F. Sullivan, *ibid.*, **93**, 4728 (1971).

F. G. Bordwell,* **Mark D. Wolfinger**
Department of Chemistry, Northwestern University
Evanston, Illinois 60201
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(7) This assumes a ρ^* value of *ca.* 2 for the deprotonation reaction (by analogy with $\rho^* = 1.59$ for the acetate ion catalyzed bromination of ketones[8] and $\rho^* = 1.78$ for the methoxide ion catalyzed deuterium exchange of the α hydrogen atoms in esters[9]) and a transmission coefficient of 2.8.[8]
(8) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. Newman, Ed., Wiley, New York, N. Y., 1956, p 608.
(9) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967).
(10) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).
(11) Comparable differences in rates of tritium exchange in NaOMe–MeOH have been observed by J. R. Jones (private communication) in the series p-ClC$_6$H$_4$SO$_2$CHMe$_2$, p-ClC$_6$H$_4$SO$_2$CH$_2$Me, p-ClC$_6$H$_4$SO$_2$CH$_3$.
(12) Judging from hydroxide deprotonation rates for CH$_3$NO$_2$ *vs.* Me$_2$CHNO$_2$ (89:1.0[13], where internal return is not a factor, and for (CH$_3$)$_2$C=O *vs.* (Me$_2$CH)$_2$C=O (119:1.0[14]), where internal return is probably minimal, substitution of two methyl groups α to the sulfone group should cause a *ca.* 10^2 decrease in k_1. On this basis as much as 10^2 of the 10^4 decrease in k_{obsd} could have its origin in a decrease in k_2.
(13) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, *Ser. A*, **294**, 273 (1966).
(14) R. P. Bell and H. C. Longuet-Higgens, *J. Chem. Soc.*, 636 (1946).

Flash Thermolysis. The Reactivity and Infrared Spectrum of Sulfene[1]

Sir:

We have recently reported[2] that flash thermolysis of chlorosulfonylacetic acid ($ClSO_2CH_2COOH$) at 650° gives at least a small amount of sulfene ($CH_2{=}SO_2$) as a volatile intermediate. The transient, formed in the hot zone, reacts with methanol on the cold finger to give methyl methanesulfonate. We now report further

(1) Flash Thermolysis. VII. Organic Sulfur Mechanisms. XI.
(2) J. F. King, P. de Mayo, and D. L. Verdun, *Can. J. Chem.*, **47**, 4509 (1969).