conditions under which mercuric acetate reacts with the $C[B(OMe)_2]_4$, and any sort of first-order process at any stage seems most unlikely. However, the hypothesis of three-center B–C–Hg bonding in the transition state[7] is consistent with a very narrow B–C–Hg angle and small steric requirement, especially if vacant p orbitals on the neighboring mercury atoms enter into weak bonding and further delocalize the electron pair.[6b]

Our survey of the chemistry of $C(HgOAc)_4$ has so far been limited to replacement of outer ligands.[7a] Sodium nitrate precipitates a white solid after a few minutes delay, and the material is insoluble in concentrated nitric acid. A polymeric material containing linkages of the $(RHg)_3O^+$ type[8] seems the most likely structure. The BF_4^- and PF_6^- salts are similarly insoluble. The fluoride is slightly soluble in aqueous hydrofluoric acid. The yellow iodide, $C(HgI)_4$, mp >300°, is slightly soluble in concentrated sodium iodide solutions in water or diglyme, which makes it a candidate for running further reactions. Its carbon content (*Anal.* Calcd: 0.91. Found: 0.98) sets a new low for organic chemistry.

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(7) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Amer. Chem. Soc.*, 77, 3741 (1955).

(7a) NOTE ADDED IN PROOF. The precipitated bromide, presumably $C(HgBr)_4$, reacts with bromine vapor in an evacuated sealed tube at 25° to yield ~75% of carbon tetrabromide, identical with an authentic sample by infrared spectroscopy and mixture melting point.

(8) D. Grdenić and F. Zado, *J. Chem. Soc.*, 521 (1962).

(9) (a) Supported by National Science Foundation Grants GP-6069 and GP-9320; (b) Alfred P. Sloan Foundation Fellow, 1966–1968; (c) National Institutes of Health Postdoctoral Fellow, 1968–1969.

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α-Deuterium Effects in SN2 Reactions with Solvent[1]

Sir:

We wish to report α-deuterium rate effects for some well-established SN2 type solvolyses of compounds *closely related structurally* to those for which α-*d* effects have previously been established for *limiting* solvolyses.[2] These results confirm that the major determinant of the α-*d* effect in solvolysis is the nucleophilic (SN2) or limiting (SN1) character of the mechanism and that at the extremes of mechanism the variation in α-*d* effects with alkyl group structural changes are much smaller than those that can be caused by a shift in mechanism.[3] The results also allow some additional analysis of the problem of the mechanism(s) in the "borderline" region of solvolysis.

Solvolysis rates have been measured, using conductometric techniques described earlier,[2,4] for benzyl *p*-bromobenzenesulfonate (brosylate), *p*-trifluoromethylbenzyl brosylate, *p*-nitrobenzyl brosylate, and their α-d_2 analogs in a series of ethanol–water and trifluoroethanol (TFE)–water solvents.[5] The isotope effects for *p*-methylbenzyl chloride,[4] given in Table I as $k_H/k_{\alpha D}$ per D, are not strongly dependent on the water concentration in TFE solutions and are near the value for the limiting reactions of α-phenylethyl chloride (1.15, 25°).[2] We conclude that in these TFE solutions the *p*-methylbenzyl chloride solvolysis is very nearly limiting and that the limiting isotope effects for the 1-phenylethyl and benzyl compounds are very similar. In 50% ethanol, the effect for *p*-methylbenzyl chloride is much lower indicating a significant nucleophilic component.

Table I. α-Deuterium Effects (per D[a]) on Rates of Solvolysis of Some Benzyl Derivatives, 25°

	Leaving group			
	Cl	OBs[b]	OBs[b]	OBs[b]
	Substituent			
Solvents[c]	*p*-CH_3	None	*p*-CF_3	*p*-NO_2
97 *T*	1.142	1.173		1.026[d]
80 *T*		1.159	1.044[d]	
70 *T*	1.140		1.041	1.011[d]
50 *E*	1.086[d]			
70 *E*			1.019	1.006
80 *E*		1.074	1.016	1.005
90 *E*		1.060	1.014	1.002
95 *E*		1.053	1.014	
m-*E*[e]		0.415	0.304	0.279

[a] $(k_H/k_{\alpha d_2})^{1/2}$; the ratios were reproducible to within ±0.001 in most cases and ±0.002 in a few.[2,4] [b] *p*-Bromobenzenesulfonate. [c] 97 *T* indicates 97 per cent 2,2,2-trifluoroethanol–3 per cent water; 70 *E* indicates 70 vol % ethanol–30 vol % water, etc. [d] Estimated from the observed values at 45° assuming that there is no isotope effect on the Anhenius preexponential term.[4] [e] Winstein–Grunwald *m* value based on reactions in ethanol–water solvents.

As the solvent polarity is increased or as solvent nucleophilicity is decreased, the effects increase markedly for benzyl brosylate, ranging from 1.053 to 1.173. Other work indicates that the α-deuterium effect for a limiting solvolysis[3,6,7] for an arenesulfonate is approximately 1.23 while the nucleophilic extreme appears to be unity or even inverse.[8–10] Thus none of the (unsubstituted) benzyl brosylate solvolyses included in Table I appear to be following a simple nucleophilic or limiting mechanism. The isotope effects and the solvent influences on the effects are much smaller for the *p*-CF_3 derivative and still smaller for the *p*-NO_2 derivative (1.002–1.026). The solvolyses for these last two compounds must be predominately of one mechanistic type since the substituent and solvent influences on the effects are quite small. Because this reaction class is favored by lower solvent polarity and higher solvent nucleophilicity and since low isotope effects correspond to tight transition-state binding, we conclude that the reaction type is SN2. Low α-deuterium rate effects have previously been attributed to SN2 reactions.[8–10] Particularly interesting are the values of about 0.99 and 1.02 per D for the aqueous hydrolyses of CD_3OTS[9] and $CH_3–CD_2–OTS$[10] (OTS = toluenesulfonate). Although in principle one

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(1) Taken in part from the thesis submitted by M. W. Rapp to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree, 1968.

(2) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 90, 418 (1968).

(3) The effects of leaving group variations on α-D effects in limiting reactions have already been analyzed: V. J. Shiner, Jr., M. W. Rapp, M. Wolfsberg, and E. A. Halevi, *ibid.*, 90, 7171 (1968).

(4) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *ibid.*, 91, 4838 (1969).

(5) We believe that the most important solvent change effected as the amount of water in a trifluoroethanol-water solvent is increased is an increase in nucleophilicity.[4] On the other hand, an increasing concentration of water in an ethanol-water solvent mixture affects these solvolyses mainly through the increase in polarity.

(6) W. Dowd, personal communication.

(7) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

(8) V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, 74, 5285 (1952).

(9) J. A. Llewellyn, R. E. Robertson, and J. M. W. Scott, *Can. J. Chem.*, 38, 222 (1960).

(10) K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *ibid.*, 38, 1505 (1960).

expects a variation of isotope effect with structure in the SN2 reaction class,[11] it is important to note that such variations are here shown to be much smaller than those associated with the structural and solvent changes in the "intermediate region" of solvolysis.

Isotope effects in SN2 reactions will depend also on the nature of the leaving and incoming groups.[12] For different leaving groups the variations will be in the same direction as those characterized for the limiting reactions[3] but smaller. This trend is discernible in the data of Robertson and coworkers.[9,10] For different nucleophiles the variations should be in the opposite direction.

The solvolyses of substituted benzyl tosylates show plots of σ or σ^+ *vs.* log k/k_0 which are strongly curved near the point for the unsubstituted compound but which tend to linearity in regions of high positive and high negative σ.[13,14] It was suggested that this behavior might be a manifestation of a mixture of two extreme reaction types.[13] However, the simple two-reaction scheme was shown to be inconsistent with the solvent dependence of the rates[14] and the effects of added salts on some of the solvolyses.[15] The "hybrid mechanism" postulate of a transition-state structure which varied with substituent and solvent was therefore preferred.

The observed isotope effects are consistent with a two-mechanism scheme of reaction with characteristic α-*d* effects for each type (k_H/k_D of 1.23 for the limiting and 1.00 for the nucleophilic reactions) *only* if the ρ value for the limiting reaction is around -3.5; earlier results[15] indicate that this reaction should have a ρ close to -5.0 under our reaction conditions. The ρ value of -1.6 for the nucleophilic reaction, from the solvolysis rates for the *p*-CF_3 and *p*-NO_2 derivatives, is close to that obtained in the earlier work for a solvent of similar polarity.[16] The lack of agreement of the α-isotope effects with the simple assumptions based on the two-mechanism scheme may be due to: (1) the variable transition state structure for borderline solvolyses (the decrease in the isotope effect with increasing reagent nucleophilicity is in accord with the early prediction of Swain for this mechanism[17] and with the original suggestion of the Swain–Thornton Rule[18] but contrary to a more recent formulation);[19] (2) a dependence of α-isotope effects for the *nucleophilic* reaction upon substituent; or as appears more reasonable (3) the occurrence in the intermediate region of a third type of mechanism, nucleophilic attack on the tight ion pair.[20] However, we do not believe that the SN2 extreme we have here characterized can be formulated as a nucleophilic attack on the tight ion pair. The low isotope effect corresponds to a much more tightly bound transition state and the variations of isotope effect with leaving group found for reactions of the methyl derivatives[9] are too small to correspond to a large degree of leaving group ionization in the transition state.[3]

Acknowledgment. The research was supported in part by Grant No. AT(11-1)-1008 from the United States Atomic Energy Commission (Document No. COO-1008-9). Electronic computations of rate constants were performed with the facilities of the Indiana Research Computing Center.

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(21) National Science Foundation Graduate Fellow, 1964–1966, Indiana University Graduate School Fellow, 1966–1967, and Public Health Service Predoctoral Research Fellow, 1967–1968.
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Received September 22, 1969

Book Reviews

Mechanisms of Molecular Migrations. Volume 2. Edited by B. S. Thyagarajan, University of Madras, Madras, India. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. ix + 464 pp. 16 × 23.5 cm. $22.50.

This second volume in a new series on molecular rearrangements contains nine articles:

V. J. Traynelis, in "Rearrangement of *O*-Acylated Heterocyclic *N*-Oxides," summarizes current understandings of reactions converting pyridine N-oxide and various analogs to ring-substituted and deoxygenated products, and some alkyl- and alkenylpyridines to products involving changes in the side chain, upon treatment with acid anhydrides, acid chlorides, or sulfonyl chlorides. Variable blends of free-radical, cationic, and concerted electrocyclic processes may account for the numerous types of products observed. "1,3-Alkyl Migrations" from nitrogen, oxygen, or sulfur to carbon, nitrogen, or oxygen, as in the intermolecular radical mediated conversion of vinyl ethers to ketones, is handled in a unified manner by P. S. Landis. R. J. Steltenkamp and W. E. Truce give a terse account of "Oxidative Rearrangements of Vinylic Derivatives." The chapter on "Base-Catalyzed Rearrangements of Acetylenic Derivatives" by I. Iwai illustrates mechanistic studies and synthetic exploitations of reactions leading to allenes and conjugated dienes, generating new carbocyclic and heterocyclic systems, passing through carbenoid intermediates, and involving 1,2 and 1,4 migrations in carbanionic species. The examples are judiciously drawn, illustrating a few types of reactions with many classes of compounds.

In "Orbital Symmetry and Electrocyclic Rearrangements," K. Fukui and H. Fujimoto present basic principles governing molecular wave functions and molecular orbital interactions, show how these principles may govern the stereochemistry of concerted electrocyclic reactions, and discuss many specific cases where pertinent experimental facts are available. Their perspective provides a valuable alternative to the approach developed into such a powerful analytical and predictive theory by R. B. Woodward and R. Hoffmann; it merits thoughtful study. H. J. Shine summarizes evidence on and dissects mechanistic suggestions for "The Benzidine Rearrangements" with clarity and candor. The subject is noteworthy for the