methyl maleate).[19] This is in accord with the cis labilization model[20] and casts some doubt on the recent interpretation of ligand dissociation from compounds *trans*-$Cr(CO)_4(PR)_3(L)$ as occurring *without* initial rearrangement to the cis isomers.[21]

Dithioacetals are important intermediates in organic syntheses.[22] The reaction sequence described in this communication amounts to a transition-metal-mediated synthesis of this class of compounds from either CS_2 or dithioformate. Not only is the organic product readily removed from the complex, but also the metal is recovered in a suitably reactive form to repeat the cycle. Work is in progress to extend this synthesis to different dithiocarboxylates as well as to nucleophiles other than hydride.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We appreciate the help of Dr. D. Scheutzow and Dr. W. Buchner with the ^{13}C and ^{31}P NMR measurements.

---

(19) Schenk, W. A.; Müller, H. *Chem. Ber.* **1982**, *115*, 3618.

(20) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

(21) (a) Wovkulich, M. J.; Feinberg, S. J.; Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2608. (b) Wovkulich, M. J.; Atwood, J. D. *Organometallics* **1982**, *1*, 1316.

(22) (a) Seebach, D.; Kolb, M. *Chem. Ind. (London)* **1974**, 687. (b) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231. (c) Gröbel, B. T.; Seebach, D. *Synthesis* **1977**, 357.

Significance of the Temperature Dependence of the Deuterium KIE Associated with the Protic Cleavage of Dialkylmercurials[1]

Dante J. Bencivengo and Joseph San Filippo, Jr.*

Department of Chemistry, Rutgers University
New Brunswick, New Jersey 08903

Received June 24, 1983

Summary: The temperature dependence of the kinetic isotope effect associated with the protic cleavage of di-*n*-octylmercury by several carboxylic acids and hydrogen chloride is reported. The results reveal that reaction is accompanied by proton tunneling which is not influenced by electronic factors but is increased by steric factors. calculations suggest a barrier width of 1.2–1.4Å. A mineral acid (anhydrous hydrogen chloride) exhibits a behavior significantly different from that of carboxylic acids. The influence of solvent and added halide on transition-state parameters is also reported.

The protic cleavage of carbon–metal σ bonds ranks among the simplest of all electrophilic substitution processes.[2] For a variety of reasons,[3] the most definitive (kinetic and stereochemical) studies of protonolyses have focused on the protic cleavage of organomercurials. In an effort to extend our understanding of the nature of such processes, we have determined the temperature dependence of the deuterium kinetic isotope effect (KIE) associated with the cleavage of a representative organomercurial by various protic acids.

$$\mathrm{RHgR} \xrightarrow{\mathrm{HA-DA}} \mathrm{RH(D)} + \mathrm{RHgA}$$

The resulting data are seen in Tables I and II and reveal several heretofore unknown aspects about the nature of such protonolyses. First, they indicate that in dioxane, protic cleavage with carboxylic acids is accompanied by appreciable proton tunneling.[4,5] Second, they show that within an homologous series, the extent of tunneling is not significantly influenced by the strength of the carboxylic acid (electronic factors) but is notably affected by steric considerations. Third, calculations based on the Bell theory[5a] of protein tunneling suggest a barrier width, a, of ca. 1.2–1.4 Å and a classical transition state which remains essentially *symmetrical* as the steric bulk of the acid increases.

Fourth, as judged by the comparatively similar rate constants, k_H, the change from polar (dioxane) to nonpolar (nonane) solvent results in only a minor (ca. a factor of 4) influence on the rate of protic cleavage of dialkylmercurials by carboxylic acids (cf. entries 1 vs. 8 and 5 vs. 9). Nevertheless, the KIE parameters for the same entries reveal that the mechanism of protonolysis is moderately influenced by the nature of the solvent. In fact, the situation in nonane is complicated by the fact that carboxylic acids are associated (dimeric) in hydrocarbon solvent but unassociated (monomeric) in dioxane at varitually all concentrations.[8,15a] Thus, the unusual solvent effect, i.e., $k_{\text{nonane}} > k_{\text{dioxane}}$, and the rate accelerating salt effect observed in dioxane (vide infra), are both consistent with the likelihood that the protic demercuration of dialkylmercurials by carboxylic acids in dioxane and nonane proceeds by different mechanisms.

Fifth, the behavior of hydrogen chloride stands in distinct contrast to that of carboxylic acids (cf. entries 1–5 and 10): the tunneling apparent with carboxylic acids is experimentally unobserved with anhydrous hydrogen chloride.

Sixth, although the calculated tunnel corrections (Table

---

(1) Supported by the NSF, Grant CHE 80-17045, and the DOE, Contract No. DE-ASO5-80Er10661.

(2) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968.

(3) Organomercurials are readily prepared in high purity, can be manipulated with facility, and are monomeric in solution.

(4) Previous studies have suggested the possibility of proton tunneling in the protic cleavage of allylmercuric halides: Kreevoy, M. M.; Steinwand, P. J.; Kayser, W. V. *J. Am. Chem. Soc.* **1966**, *88*, 124.

(5) For a discussion of the criteria which establish the participation of proton tunneling, see: (a) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman-Hall: New York, 1980. (b) Kaldor, S. B.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7594.

0276-7333/83/2302-1907$01.50/0

Table I. Kinetic and KIE Parameters Associated with the Protic Cleavage of n-$C_8H_{17}HgR$[a]

$$n\text{-}C_8H_{17}HgR \xrightarrow[\text{solvent}]{\text{HA-DA}} n\text{-}C_8H_{17}H(D) + RHgA$$

entry	R	solvent	HA	temp,[b] °C	$10^6 k_H$,[c] s^{-1}	E_H, kcal/mol	$\Delta S^{\ddagger}$, eu	k_H/k_D[d]	$[\Delta E]_H^D$, kcal/mol	A_H/A_D
1	n-C_8H_{17}	dioxane	CH_3CO_2H	61.0	7.95	19.42 ± 0.60[e]	−25.7	8.625	1.92 ± 0.1[e]	0.475
				70.9	19.3			7.705	(r = 0.994)	
				81.1	46.4			7.355		
				91.8	99.6			6.731		
				102.5	153			6.187		
2	n-C_8H_{17}	dioxane	$ClCH_2CO_2H$	40.7	35.1	19.59 ± 0.33	−18.5	9.543	1.95 ± 0.06	0.414
				50.7	103			8.448	(r = 0.998)	
				59.7	216			7.888		
				70.5	537			7.208		
				80.6	963			6.660		
3	n-C_8H_{17}	dioxane	$C_6H_5CO_2H$	69.8	5.06	20.99 ± 0.28	−23.9	8.569	2.25 ± 0.06	0.319
				80.4	12.8			7.849	(r = 0.999)	
				91.0	30.1			7.200		
				100.7	68.9			6.541		
				110.9	133			6.037		
4	n-C_8H_{17}	dioxane	$C_6H_5CO_2H$/ $(n\text{-}C_4H_9)_4N^+Br^-$	69.4	13.5	19.65 ± 0.59	−25.7	9.940	2.22 ± 0.14	0.376
				78.4	29.3				(r = 0.994)	
				87.4	53.9			8.164		
				98.7	147			7.652		
				106.5	217			7.203		
5	n-C_8H_{17}	dioxane	$(CH_3)_3CCO_2H$	69.4	6.38	23.05 ± 0.44	−16.3	9.194	2.81 ± 0.09	0.148
				79.4	16.3			8.254	(r = 0.998)	
				90.0	44.0			7.122		
				102.1	138			6.417		
				110.0	229			5.974		
6	n-C_8H_{17}	dioxane	$2\text{-}CH_3C_6H_4CO_2H$	70.4	4.72	21.18 ± 0.17	−23.7	7.241	2.07 ± 0.20	0.347
				81.1	11.7				(r = 0.990)	
				91.0	26.5			6.350		
				100.4	55.0			5.834		
				108.9	109			5.217		
7	n-C_8H_{17}	dioxane	$2,4,6\text{-}(CH_3)_3C_6H_2CO_2H$	70.9	3.13	23.46 ± 0.58	−18.0		3.06 ± 0.23	0.113
				80.9				8.753	(r = 0.991)	
				90.6	17.8			7.935		
				100.7	49.4			7.175		
				107.6	83.5			6.393		
8	n-C_8H_{17}	nonane	CH_3CO_2H	60.1	11.5	22.71 ± 0.34	−15.4	9.836	1.70 ± 0.07	0.758
				70.3	31.2			9.138	(r = 0.996)	
				80.5	75.2			8.632		
				91.0	204			7.832		
				100.5	474			7.500		
9	n-C_8H_{17}	nonane	$(CH_3)_3CCO_2H$	70.9	6.43	24.75 ± 0.28	−12.8	9.267	2.13 ± 0.11	0.406
				80.8	18.4			8.294	(r = 0.996)	
				91.4	46.9			7.779		
				101.1	122					
				107.5	212			6.806		
10	n-C_8H_{17}	dioxane	HCl	−10.0				5.176	0.843 ± 0.05	1.03
				1.0				4.765	(r = 0.994)	
				10.1				4.654		
				20.7				4.359		
				32.4				4.111		

[a] Initial composition: [n-$C_8H_{17}HgR$] = 0.07–0.1 M; [HA] = 2–8 M. All reactions exhibited rigorously pseudo-first-order kinetics for ≥3 half-lives. [b] A constant (±0.02 °C) temperature was maintained throughout each run. [c] Based on the expression rate = $k_H[n\text{-}C_8H_{17}HgR]$. At appropriate intervals, individual reaction mixtures were quenched and the concentration of n-$C_8H_{17}HgR$ was determined by HPLC (UV detector) employing unexceptional internal standard procedures for quantitation. The value of k_H was evaluated from the slope of a plot (5 points) of ln (C_0/C) vs. t (correlation coeff = 0.999). [d] The primary hydrogen–deuterium isotope effect for the competitive protonolysis–deuterolysis of n-$C_8H_{17}HgR$ can be expressed as k_H/k_D = ([RH]/[RD])([DA]/[HA]). The latter ratio was determined from high-precision, whole-molecule mass spectrometry[14] by simultaneously monitoring the 114 (M) and 115 (M + 1) ions of the n-octane-d_0/n-octane-d_1 mixture isolated after 3 half-lives. An ionizing voltage of 70 eV and a constant source pressure of 8.0×10^{-7} torr were employed. It was unnecessary to correct for an (M − 1) contribution since the parent ion cluster of n-octane exhibits no significant (<1%) (M − 1) peak. [e] All specified tolerances correspond to a deviation of ±σ.

Table II. Tunnel Corrections for the Protonolysis of Some Dialkylmercurials[a]

$$R_2Hg \xrightarrow{R'CO_2H(D)} RH(D) + RHgO_2CR'$$

R_2Hg	acid	solvent	temp, °C	$(k_H/k_D)_{calcd}$[b]	$[\Delta E_{calcd}]_H^D$,[c] kcal/mol	$[\Delta E_0]_H^D$,[d] kcal/mol	2a, Å	Q_H/Q_D
n-C_8H_{17}	CH_3CO_2H	dioxane	80	4.843	1.10	1.05	1.32	1.52
n-C_8H_{17}	$ClCH_2CO_2H$	dioxane	60	5.279	1.10	1.02	1.45	1.49
n-C_8H_{17}	$(CH_3)_3CCO_2H$	dioxane	90	3.457	0.90	1.01	1.18	2.06
n-C_8H_{17}	$C_6H_5CO_2H$	dioxane	90	4.058	1.00	1.09	1.21	1.77
n-C_8H_{17}	$C_6H_5CO_2H/(n\text{-}C_4H_9)_4N^+Br^-$	dioxane	90	5.233	1.20	*e*	1.29	1.56
n-C_8H_{17}	$2\text{-}CH_3C_6H_4CO_2H$	dioxane	90	3.593	0.90	1.05	1.22	1.77
n-C_8H_{17}	$2,4,6\text{-}(CH_3)_3C_6H_2CO_2H$	dioxane	90	3.521	0.90	1.01	1.15	2.25
n-C_8H_{17}	CH_3CO_2H	n-nonane	60	5.750[f]	1.20	1.10	1.48	1.59
n-C_8H_{17}	$(CH_3)_3CCO_2H$	n-nonane	90	4.630	1.10	1.07	1.36	1.68

[a] For a discussion of the computational methodology employed in these calculations, see ref 5b. Unless otherwise stated, these results agree to within 2% or better with values calculated from the Arrhenius parameters given in Table I. [b] Semiclassical isotope effect (i.e., that which would obtain in the absence of tunneling) as defined by $(k_H/k_D)_{obsd}/(Q_H/Q_D)$. [c] Semiclassical zero-point-energy difference. [d] Standard zero-point energy value as calculated from ambient infrared data determined on dioxane solutions made up to reaction concentrations. These values are considered accurate to ±0.05 kcal/mol. As ground-state reactants, carboxylic acids are reportedly unassociated (monomeric) at virtually all concentrations in dioxane but are associated (dimeric) in hydrocarbons such as nonane.[15a] Hydrogen chloride is also reported to be undissociated in dry dioxane.[15b] [e] Undetermined. [f] The difference between calculated and observed k_H/k_D value was 3% in this instance.

II) are modest, they are by no means negligible and account for a factor of ca. 1.5–2.3 in rate acceleration. Table II also lists the calculated semiclassical KIE parameters, most of which are essentially the value expected for a symmetrical transition state.[5,6]

Seventh, the addition of tetra-n-butylammonium bromide increases the absolute rate by a factor of ca. 2–3 (cf entries 3 and 4). The possibility[2] that this reactivity enhancement results from complex formation between the added bromide and the mercurial can probably be dismissed since such complexation is likely to increase the steric crowding in the transition state, which in turn would be reflected by an *increase* in tunneling. We conclude that in this instance the observed enhancement in absolute rate is most likely a simple salt effect that results in a lower activation barrier.

Collectively, these findings[8] illustrate the considerable information which temperature-dependent KIE studies are capable of providing about a reaction mechanism without recourse to the specific details of transition-state geometry.[9] By comparison, other common mechanistic probes rely largely on interpretation of more ambiguous extrathermodynamic properties. For example, the entropy of activation, $\Delta S^{\ddagger}$, associated with the protic cleavage of the dialkylmercurials summarized in Table I, ranges between ca. −10 to −25 eu. Traditional arguments are likely to suggest that negative values of this magnitude are resonable for a reaction that proceeds through a bimolecular transition state and that the more positive values are consistent with increased solvent motion which is coupled into the reaction coordinate,[9b] resulting in an activated complex that is less solvated than reactants. Conclusions such as these, although qualitatively reasonable, rely (either explicitly or implicitly) on the thermodynamic qualities of reactants for comparison and, as has been noted,[10,11] are frequently not justified.[12]

---

(6) Melander, L.; Saunders, W. H. Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980. See also ref 16.

(7) (a) As reinforced by a recent theoretical study,[13] it should be noted that the experimentally accessible criteria[5] employed in the present study define a sufficient but not necessary condition for proton tunneling. (b) The standard zero-point-energy difference $[\Delta E_0]_H^D$, between O–H and O–D is generally in the range of ca 1.0–1.1 kcal/mol; see Table II.

(8) The interpretation presented in this paper is subject to two reservations: (1) that the rate constants we have measured correspond to that of a *single elementary proton transfer* rather than being aggregate rate constants for various consecutive and/or competitive processes and (2) that the general shape of the apparent temperature dependence is not complex or anomalous (see ref 16).

(9) (a) Implicit in this statement is the reasonable assumption that proton transfer involves a linear or near-linear transition state. (b) Jensen, F. R.; Ouellette, R. J. *J. Am. Chem. Soc.* **1961**, *83*, 4478.

(10) Ritchie, C. D.; Van Verth, J. E.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491; *Pure Appl Chem.* **1979**, *51*, 153.

(11) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892 and references therein.

(12) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(13) Garret, B. C.; Truhlar, D. G.; Wagner, A. F.; Dunning, T. H. *J. Chem. Phys.* in press.

(14) Murphy, R. *Finnigan Spectra*, **1973**, *3*. Weissberger, A.; Rossiter, B. "Techniques of Chemistry"; Wiley: New York, 1975; Vol I, Part IV, pp 206–207. Kwart, H.; Stanulonis, J. *J. Am. Chem. Soc.* **1976**, *98*, 4009. Caprioli, R. M.; Fies, W. F.; Story, M. S. *Anal. Chem.* **1974**, *46*, 453A. Reimschüssel, W.; Paneth, P. *Org. Mass Spectrom.* **1980**, *15*, 302.

(15) (a) Sriraman, S.; Shanmugasundarum, V. *Bull, Chem. Soc. Jpn.* **1964**, *37*, 395. (b) Weith, A. J., Jr.; Hobbs, M. E.; Gross, P. M. *J. Am. Chem. Soc.* **1948**, *70*, 805.

(16) Vogel, P. C.; Stern, M. J. *J. Chem. Phys,* **1971**, *54*, 779. Stern, M. J.; Weston, R. E., Jr. *Ibid.* **1974**, *60*, 2803.