J. Am. Chem. Soc. **1984**, *106*, 2917-2923

not give sufficiently intense CH_2 or CH_3 resonances for interpretation even after 5000 scans even in the presence of $Cr(acac)_3$.

NMR Studies. Reactions with allylbenzene and 1-phenyl-3-butene were run in an NMR tube (**1**, 30 mg; 180 K; olefin 10 mol equiv/Ir; CD_2Cl_2 0.5 mL). The changes described in the text were observed on warming the solution to room temperature for allylbenzene. 1-Phenyl-3-butene isomerized to the corresponding 2- and then 1-butenes below 250 K. Only at 290 K did the resonances of $[Ir(BuPh)(PPh_3)_2]BF_4$ (see Table I) appear. Allyl phenyl ether isomerized to allyl propenyl ether below 215 K, the lowest temperature studied. The rhodium complex $[Rh(PhEt)(PPh_3)_2]BF_4$ was observed at 290 K in the reaction of styrene with $[RhH_2(EtOH)_2(PPh_3)_2]BF_4$ but was too unstable to be isolated in a pure state.

Dihydrido(η^3(Cl,C,C)-2,6-dichlorostyrene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate. The title complex was formed when 2,6-dichlorostyrene was used in the synthesis described above. Spectral and other data are given in Table I. Analogous species were obtained with $2\text{-}XC_6H_5CH{=}CH_2$ (X = Cl, Br, and I), but these were only observed by ^1H NMR. Their thermal instability precluded their isolation in the pure state.

Acknowledgment. We thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Department of Defense, Army Research Office for support. R.H.C thanks the Henry and Camille Dreyfus Foundation for a Fellowship, Professors O. Eisenstein and K. Jordan for helpful discussions, Dr. C. A. Tolman for communicating some of his results prior to publication, and Johnson Matthey Inc. for a loan of iridium.

Phase-Transfer Reactions Catalyzed by Lipophilic [2.2.2]Cryptands and Dicyclohexano-18-crown-6: Dehydrating Effect of Concentrated Aqueous Alkaline Solutions

Dario Landini,* Angelamaria Maia,* and Fernando Montanari

*Contribution from Centro CNR and Istituto di Chimica Industriale dell'Universita',
Via Golgi 19, I-20133 Milano, Italy.* *Received September 8, 1983*

Abstract: A study of how the concentration of aqueous KOH affects the hydration and hence the reactivity of anions (Cl^-, Br^-, I^-, SCN^-, N_3^-) in aliphatic nucleophilic substitutions catalyzed by lipophilic [2.2.2,C_{10}]cryptand (**1a**) and dicyclohexano-18-crown-6 (DCH 18C6) (**2**) under phase-transfer conditions is reported. A comparison with the same reactions performed in classical liquid–liquid PTC and homogeneous anhydrous conditions is also included. Unlike quaternary onium salts, even at the highest KOH concentrations (53%; i.e., conditions in which $a_{H_2O} \sim 0$), water in the presence of **1a** is not completely removed. Residual hydration depends on the nature of the anion and is the highest for anions with localized and/or less polarizable charge, such as Cl^-, Br^-, and N_3^-. As a consequence, rate constants noticeably increase in comparison with those found under conventional PTC conditions but do not reach those of anhydrous solutions. The different behavior of cryptates and quaternary salts is discussed on the basis of the different topology of the two systems. Behavior of crown ethers is in between that of quaternary salts and cryptates, since residual hydration in the presence of 53% aqueous KOH is lower than that of cryptates, whereas anionic reactivity becomes practically identical with that found under anhydrous conditions.

The presence of a limited number of water molecules in the organic phase greatly influences reactions performed under liquid–liquid phase transfer catalysis (PTC) conditions.[1-3] In particular the specific hydration of the anions strongly decreases the reaction rates[4-8] and may also influence the outcome of reactions.[9]

Highly concentrated aqueous solutions of KOH or NaOH were found to be an effective system for ensuring an anhydrous organic phase under liquid–liquid PTC conditions in the presence of quaternary onium salts.[10,11] In this way, unhydrated anions are transferred from the aqueous to the organic phase by quaternary cation Q^+; hence, the anionic reactivity becomes identical with that found under anhydrous homogeneous conditions.[10] The main disadvantage of this system is that quaternary onium salts are easily decomposed by the strongly alkaline solution, in some cases even at room temperature.[10,12,13]

Lipophilic cryptands or crown ethers are effective phase-transfer agents;[1-3,7,8] moreover, they are chemically stable even in the presence of strongly alkaline aqueous solutions. Therefore, it was of interest to determine whether the dehydrating effect of these alkaline solutions also works for cryptands and crown ethers.

Here we report a study of how the concentration of aqueous KOH affects the hydration and hence the reactivity of anions (Cl^-, Br^-, I^-, SCN^-, N_3^-) in aliphatic nucleophilic substitutions, catalyzed by [2.2.2,C_{10}]cryptand (**1a**) or by dicyclohexano-18-crown-6

---

[1] Starks, C. M.; Liotta, C. "Phase-Transfer Catalysis: Principles and Techniques"; Academic Press: New York, 1978.

[2] Dehmlow, E. V.; Dehmlow, S. S. "Phase-Transfer Catalysis"; Verlag-Chemie: Weinheim/Bergstr., Germany, 1980.

[3] Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147-200 and references therein.

[4] Starks, C. M.; Owens, R. *J. Am. Chem. Soc.* **1973**, *95*, 3613-3617.

[5] Landini, D.; Maia, A.; Montanari, F.; Pirisi, F. M. *J. Chem. Soc., Chem. Commun.* **1975**, 950-951.

[6] Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796-2801.

[7] Landini, D.; Maia, A.; Montanari, F.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 2526-2530.

[8] Landini, D.; Maia, A.; Montanari, F.; Pirisi, F. M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 46-51.

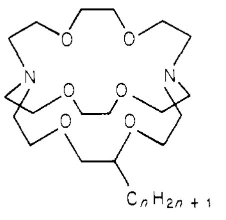
[9] See, inter alia: (a) McIntosh, J. M.; Khalil, H.; Pillon, D. W. *J. Org. Chem.* **1980**, *45*, 3436-3439. (b) Halpern, M.; Yonowich-Weiss, M.; Sasson, Y.; Rabinovitz, M. *Tetrahedron Lett.* **1981**, *22*, 703-704. (c) Halpern, M.; Sasson, Y.; Willner, I.; Rabinovitz, M. *Ibid.* **1981**, *22*, 1719-1722. (d) Lopez, A.; Maurette, M. T.; Martino, R.; Lattes, A. *Ibid.* **1978**, 2013-2014. (e) Kem, K. M.; Nguyen, N. V.; Cross, D. J. *J. Org. Chem.* **1981**, *46*, 5188-5192. (f) D'Incan, E. *Tetrahedron* **1977**, *33*, 951-954. (g) D'Incan, E.; Loupy, A. *Ibid.* **1979**, *37*, 1171-1179.

[10] Landini, D.; Maia, A.; Podda, G. *J. Org. Chem.* **1982**, *47*, 2264-2268.

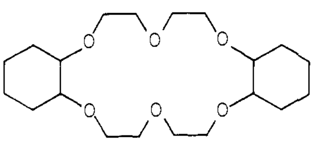
[11] (a) Antoiue, J. P.; De Aguirre, I.; Janssens, F.; Thyrion, F. *Bull. Soc. Chim. Fr.* **1980**, *2*, 207-232. (b) Makosza, M.; Bialeka, E. *Synth. Commun.* **1976**, *6*, 313-318.

[12] Landini, D.; Maia, A., unpublished results from this laboratory.

[13] Dehmlow, E. V.; Slopianka, M.; Heider, J. *Tetrahedron Lett.* **1977**, 2361-2364.



1a, $n = 10$
b, $n = 14$



2

(DCH 18C6) (**2**), under PTC conditions. A comparison with the same reactions performed under classical liquid–liquid PTC and homogeneous anhydrous conditions is also included.

Results

Rates of displacement of the methanesulphonate group in *n*-octyl methanesulphonate (**3**) by anionic nucleophiles (Cl^-, Br^-, I^-, N_3^-, SCN^-) were measured in a 53% aqueous KOH–chlorobenzene two-phase system in the presence of catalytic amounts of lipophilic cryptand **1a** or of crown ether **2** (reaction 1). In

$$\underset{\mathbf{3}}{n\text{-}C_8H_{17}OSO_2Me} + KY \xrightarrow[\text{PhCl–53\% aq KOH}]{\text{catalyst}} n\text{-}C_8H_{17}Y + MeSO_3K \quad (1)$$

4a, Y = Cl
4b, Y = Br
4c, Y = I
4d, Y = SCN
4e, Y = N_3

catalyst = **1a**, **2**

the case of **2** reaction with Cl^- was not studied due to the low complexation percent under the reaction conditions.[8]

Reactions were carried out at 60 °C with a 5:1 molar ratio of KY/substrate, the inorganic salt being added to the 53% KOH aqueous solution. Under these conditions the inorganic salt remained partially undissolved. Reaction rates were measured by ^1H NMR analysis, monitoring the disappearance of **3**, with phenyl benzyl ether as internal standard. A study of the partition coefficients, carried out as previously reported,[7,8] showed that in the system PhCl–53% aqueous KOH, catalysts **1a** and **2** are entirely in the organic phase, as free or complexed ligands. The percents of ligands complexed to cations were determined by potentiometric titration of the anion in the organic phase.[7,8] Except for KCl they remained constant during the reaction and were found to be in the ranges 53–100% and 17–98% for **1a** and **2**, respectively (Tables I and II). Moreover, titrimetric measurements indicated that, in the case of Br^-, I^-, SCN^-, and N_3^-, the mesylate ion formed in the course of the reaction is quantitatively transferred into the aqueous phase, so that equilibrium 2 is fully shifted to the right.

$$([K^+\subset\text{ligand}]MeSO_3^-)_{org} + (Y^-)_{aq} \rightleftharpoons ([K^+\subset\text{ligand}]Y^-)_{org} + (MeSO_3^-)_{aq} \quad (2)$$

Under these conditions reactions follow pseudo-first-order kinetics (eq 3) up to at least 80% conversion. Second-order rate

$$\text{rate} = k_{obsd}[\text{substrate}] \quad (3)$$

constants, $k_{obsd}/([K^+\subset\text{ligand}]Y^-)_{org}$, are reported in Tables I and II.

In the case of the reaction with Cl^- catalyzed by **1a**, as already found for tetraalkylammonium chloride,[10] the mesylate ion remains in the organic phase associated with the complexed cation $[K^+\subset(2.2.2,C_{10})]$ (see Experimental Section) to reach a 4:1 ($([K^+\subset(2.2.2,C_{10})]MeSO_3^-)_{org}/([K^+\subset(2.2.2,C_{10})]Cl^-)_{org}$ ratio after about 30% conversion. This ratio is constant throughout the reaction up to 100% conversion (Figure 1). Second-order rate constants were evaluated taking into account the actual $[K^+\subset(2.2.2,C_{10})]Cl^-$ concentration present at different times in the organic phase (Table I). Moreover, as shown by titrimetric measurements, an appreciable amount of OH^- (~9%) is present in the organic phase as $[K^+\subset(2.2.2,C_{10})]OH^-$. This amount slightly increased (up to ~11%) in the absence of any other anion, whereas no appreciable amount of OH^- was found in the presence of the anions Br^-, I^-, SCN^-, and N_3^-.[14] The same behavior was found for crown ether **2**, the amount of OH^- in the organic phase being ~2% in the absence of any other salt. Reactions with Br^- and SCN^-, catalyzed by **1a** and **2**, respectively, were also studied at various KOH aqueous concentrations (8.6–53%) (Tables III and IV).

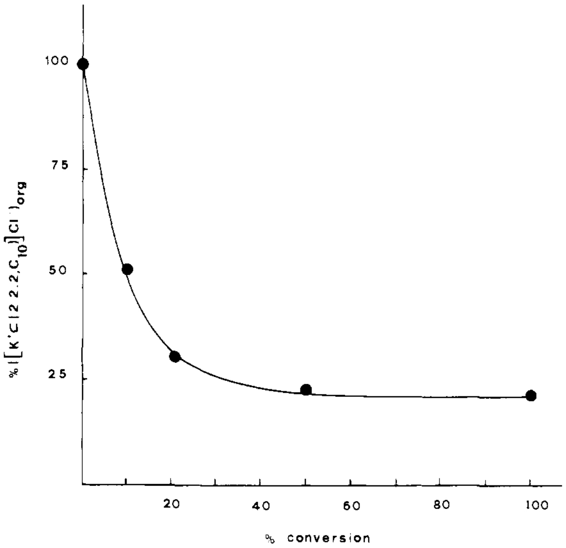


Figure 1. Dependence of the amount of Cl^- associated with $[K^+\subset(2.2.2,C_{10})]$ cation in the organic phase on the percent conversion for the displacement of the methanesulfonate group with chloride ion in the PhCl–53% aqueous KOH two-phase system, at 60 °C. For reaction conditions see ref *c*, Table I.

Kinetic measurements were extended to classical liquid–liquid PTC conditions and to anhydrous chlorobenzene solutions. In the latter case, comparable amounts of substrate ($(2–4) \times 10^{-2}$ M) and the preformed complex $[K^+\subset(\text{DCH 18C6})Y^-$ ($(0.5–4) \times 10^{-2}$ M) were used (Table II). In the reactions catalyzed by **1a**, rate constants were compared with those already measured[7] under liquid–liquid PTC and homogeneous anhydrous conditions by using ligand $[2.2.2,C_{14}]$, **1b** (Table I). Repeat measurements with both cryptands **1a** and **1b** gave rate constant values identical within experimental error (Table I). The hydration state of complexed ligands **1a** and **2**, $[K^+\subset\text{ligand}]Y^-$, in the organic phase was determined for all the two-phase systems by Karl Fisher titration, as previously described (Tables I–IV).[7,8]

Reactions Products

Reactions were also performed on a preparative scale in the presence of 53% aqueous KOH, under conditions similar to those followed for kinetic measurements. For catalysts **1a**,**b** and for all the anions examined the mass balance was ≥95% except for the reactions with SCN^- for which it was ≥81%. The product distribution depended on the nature of nucleophile. For I^-, Br^-, and N_3^- at 98–100% conversion the reaction mixture consisted essentially of substitution products **4b**,**c**,**e** (91–99%), together with minor amounts of di-*n*-octyl ether (**5**) (0.5–4%) and octenes **6** (0,1–1%). In the case of Cl^- the reaction mixture at 99% conversion consisted of ether **5** (64%), chloride **4a** (33%), and traces (≤1%) of octenes **6** (Table V).

Thiocyanate ion afforded a more complex mixture, the main constituents being the substitution product **4d** (46%), di-*n*-octyl disulfide (**7**) (33%), and di-*n*-octyl ether (**5**) (2%) (Table V). Disulfide **7** is a product of alkaline decomposition of thiocyanate **4d** by an already known reaction.[15] Ether **5** clearly derives from

---

[14] A similar behavior was found also in the case of lipophilic quaternary ammonium chlorides, which, under analogous conditions in the absence of KCl, transfer a small amount of OH^- (~11%) into the organic phase.[12,13] A more rigorous search showed, indeed, the presence of dioctyl ether (**5**) among the reaction products.[10]

[15] Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Company, Inc.: New York, 1965; Vol. VI, p 45.

Table I. Second-Order Rate Constants for Nucleophilic Substitutions of Methanesulfonate by Anions (Y^-)[a] in *n*-Octyl Methanesulfonate in the Presence of [2.2.2,C_{10}]- or [2.2.2,C_{14}]Cryptands (**1a** and **1b**), at 60 °C

	phase-transfer conditions						homogeneous conditions anhydrous PhCl[b]	
	$PhCl-H_2O$[b]			PhCl–53% aqueous KOH[c]				
Y^-	10^3k, $M^{-1}\ s^{-1}$ [d]	hydration state *n* of $[K^+\subset(2.2.2,C_{14})]Y^-\cdot nH_2O$[d]	% complexation[d]	10^3k, $M^{-1}\ s^{-1}$ [e,f]	hydration state *n* of $[K^+\subset(2.2.2,C_{10})]Y^-\cdot nH_2O$[g]	% complexation	10^3k, $M^{-1}\ s^{-1}$ [d]	% complexation[d]
N_3^-	28.6	4.8 ± 0.2	95	130	1.4 ± 0.1	93	150	90
Cl^-	3.5	5.3 ± 0.2	95	38	2.5 ± 0.1[h]	56	50.8	43
Br^-	5.6[i]	4.3 ± 0.2	97	24.6	0.88 ± 0.1	98	36.6[j]	97
I^-	4.7	3.2 ± 0.1	100	9.2	0.39 ± 0.1	100	8.7	100
SCN^-	1.1	2.8 ± 0.2	100	1.5	0.61 ± 0.1	100	1.5	100

[a] From $[K^+\subset(2.2.2,C_n)]Y^-$, $n = 10, 14$. [b] For reaction conditions see ref 7. [c] A chlorobenzene solution (20 mL) of substrate (6×10^{-1} M) and of $[K^+\subset(2.2.2,C_{10})]Y^-$ ($(1-4) \times 10^{-2}$ M) and 53% aqueous KOH (15 mL) in the presence of KY (63 mmol), partially as solid phase. [d] From data previously reported, see ref 7. [e] k is defined as $k = k_{obsd}/[\text{cryptate}]$. [f] Average of at least two runs. [g] Average of at least four determinations. [h] This hydration value is likely due in part to 9% of $[K^+\subset(2.2.2,C_{10})]OH^-$ cryptate present in the organic phase together with $[K^+\subset(2.2.2,C_{10})]Cl^-$; indeed for $[K^+\subset(2.2.2,C_{10})]OH^-$ a hydration state *n* of 5.5 was found in the system PhCl–53% aqueous KOH in the absence of KY. [i] $k = 5.5 \times 10^{-3}\ M^{-1}\ s^{-1}$, by using [2.2.2,$C_{10}$]cryptand (**1a**), instead of [2.2.2,C_{14}]cryptand (**1b**). [j] $k = 36.9 \times 10^{-3}\ M^{-1}\ s^{-1}$, by using [2.2.2,$C_{10}$]cryptand (**1a**) instead of [2.2.2,C_{14}]cryptand (**1b**).

Table II. Second-Order Rate Constants for Nucleophilic Substitutions of Methanesulfonate by Anions (Y^-)[a] in *n*-Octyl Methanesulfonate in the Presence of Dicyclohexano-18-crown-6 (DCH 18C6) (**2**), at 60 °C

	phase-transfer conditions						homogeneous conditions anhydrous PhCl[d]	
	$PhCl-H_2O$[b]			PhCl–53% aqueous KOH[c]				
Y^-	10^2k, $M^{-1}\ s^{-1}$ [e,f]	hydration state *n* of $[K^+\subset(\text{DCH 18C6})]Y^-\cdot nH_2O$[g]	% complexation	10^2k, $M^{-1}\ s^{-1}$ [e,f]	hydration state *n* of $[K^+\subset(\text{DCH 18C6})]Y^-\cdot nH_2O$[g]	% complexation	10^2k, $M^{-1}\ s^{-1}$ [f]	% complexation
N_3^-	3.6	4.5 ± 0.2	19	8.8	0.34 ± 0.1	18	8.9	18
Br^-	0.82	3.5 ± 0.2	18	1.3	0.54 ± 0.15	17	1.3	18
I^-	0.59	3.0 ± 0.2	87	0.94	0.55 ± 0.15	95	0.92	94
SCN^-	0.10	4.3 ± 0.2	93	0.12	0.37 ± 0.1	98	0.11	99

[a] From $[K^+\subset(\text{DCH 18C6})]Y^-$. [b] A chlorobenzene solution (20 mL) of substrate (6×10^{-1} M) and of $[K^+\subset(\text{DCH 18C6})]Y^-$ ($(0.5-4) \times 10^{-2}$ M) and an aqueous solution (15 mL) of KY (4.2 M). [c] Same amounts of PhCl, substrate $[K^+\subset(\text{DCH 18C6})]Y^-$ as in *b*, with 53% aqueous KOH (15 mL) in the presence of KY (63 mmol), partially as solid phase. [d] [Substrate] = $(2-4) \times 10^{-2}$ M, preformed complex [DCH 18C6,KY] = $(0.5-4) \times 10^{-2}$ M. [e] k is defined as $k = k_{obsd}/[\text{complexed DCH 18C6}]$. [f] Average of at least two runs. [g] Average of at least four determinations.

Table III. Effect of the KOH Concentration in the Aqueous Phase on the Second-Order Rate Constants of the Reaction of *n*-Octyl Methanesulfonate with Bromide Ion[a] under PTC Conditions[b] Catalyzed by (2.2.2,C_{10})Cryptand (**1a**), at 60 °C

[KOH], M	KOH, %	hydration state *n* of $[K^+\subset(2.2.2,C_{10})]Br^-\cdot nH_2O$[c]	10^3k, $M^{-1}\ s^{-1}$ [d,e]
		4.3 ± 0.2[f]	5.6
1.7	8.6	3.7 ± 0.2	6.4
3.5	17.0	3.2 ± 0.2	6.9
5.9	26.3	2.9 ± 0.2	9.7
8.3	34.9	2.3 ± 0.2	11.4
11.2	43.7	2.1 ± 0.2	15.7
14.4	53.0	0.88 ± 0.1	24.6

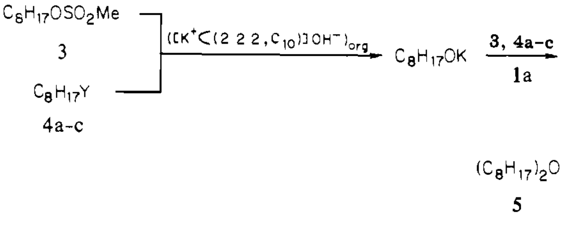
[a] From $[K^+\subset(2.2.2,C_{10})]Br^-$. [b] In the system PhCl–aqueous KOH; for the reaction conditions, see ref *c* of Table I. [c] Average of at least four determinations. [d] k is defined as $k = k_{obsd}/[\text{cryptate}]$. [e] Average of at least two runs. [f] Hydration state *n* in the absence of KOH, see ref 7.

Table IV. Effect of the KOH Concentration in the Aqueous Phase on the Second-Order Rate Constants of the Reaction of *n*-Octyl Methanesulfonate with SCN^- Ion[a] under PTC Conditions[b] in the Presence of DCH 18C6 (**2**), at 60 °C

[KOH], M	KOH, %	hydration state *n* of $[K^+\subset(\text{DCH 18C6})]SCN^-\cdot nH_2O$[c]	10^2k, $M^{-1}\ s^{-1}$ [d,e]
		4.3 ± 0.2[f]	0.107
3.5	17.0	2.6 ± 0.1	0.113
8.3	34.9	1.4 ± 0.1	0.115
14.4	53.0	0.37 ± 0.1	0.122

[a] From $[K^+\subset(\text{DCH 18C6})]SCN^-$. [b] In the system PhCl–aqueous KOH; for reaction conditions see ref *c* of Table II. [c] Average of at least four determinations. [d] k is defined as $k = k_{obsd}/[\text{complexed DCH 18C6}]$. [e] Average of at least two runs. [f] Hydration state *n* in the absence of KOH, see Table II.

reaction of substrate and/or products **4a–c** with potassium octylate, in turn deriving from attack of OH^- on **3** and/or **4a–c** (reaction 4).



$$\left.\begin{array}{c} C_8H_{17}OSO_2Me \\ \mathbf{3} \\ C_8H_{17}Y \\ \mathbf{4a\text{-}c} \end{array}\right] \xrightarrow{([K^+\subset(2.2.2,C_{10})]OH^-)_{org}} C_8H_{17}OK \xrightarrow[\mathbf{1a}]{\mathbf{3,\ 4a\text{-}c}} \underset{\mathbf{5}}{(C_8H_{17})_2O} \qquad (4)$$

In the absence of the inorganic salt, ether **5** was practically the only product (≥95%). Without **1a** and for times comparable with those of the slowest reaction, only traces (≤3%) of ether **5** were formed, which excludes the possibility of competitive reactions at the interface. Reactions catalyzed by crown ether **2** gave essentially the substitution products **4b,c,e**, in the case of Br^-, I^-, and N_3^-, together with traces (<1–3%) of ether **5**, whereas in the case of SCN^- a 4:1 mixture of thiocyanate **4e** and disulfide **7** was obtained (Table V).

Discussion

Anion-promoted nucleophilic substitutions are generally carried out in highly polar media, namely protic or dipolar aprotic solvents. In any case, solvation totally obscures intrinsic reactivities of

Table V. Distribution of Reaction Products for Nucleophilic Substitutions on *n*-Octyl Methanesulfonate with Various Nucleophiles Y^-, Catalyzed by **1a** or **2** in PhCl–53% Aqueous KOH Two-Phase System, at 60 °C

	catalyst **1a**				catalyst **2**			
Y^-	conversion,[b] %	R-Y(**4**),[b] %	R_2O(**5**),[b] %	$(RS)_2$(**7**),[b] %	conversion,[b] %	R-Y(**4**),[b] %	R_2O(**5**),[b] %	$(RS)_2$(**7**),[b] %
Cl^-	99	32[c]	64					
Br^-	99	93[c]	2.5		98	94.4[c]	3	
I^-	100	94[c]	1		100	99[c]	<1	
N_3^-	99	91[c]	4		99	94[c]	2	
SCN^-	98	46[c]	2	33	99	63[c]		17

[a] For reaction conditions see Experimental Section. [b] By GLC analysis; in all cases the authenticity of compounds was checked via ^1H NMR and GLC analyses by comparison with pure samples prepared independently. [c] Together with traces (≤1%) of octenes **6**.

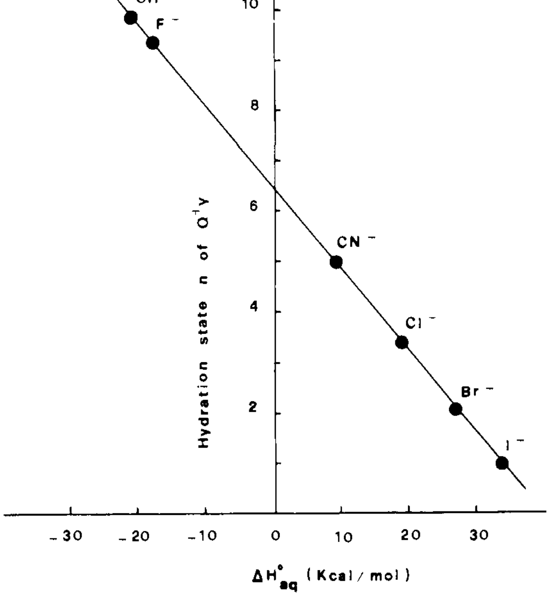


Figure 2. Correlation between hydration state *n* of quaternary onium salts, Q^+Y^-, measured under liquid–liquid PTC conditions (data from ref 6) and the enthalpies of aquation (ΔH°_{aq}, kcal/mol) (data from ref 18) of the corresponding gas-phase anions, Y^-. The hydration states of OH^-, and F^- are extrapolated values.

nucleophiles and substrates, which are typically shown in the gas phase.[16,17] By use of quaternary onium salts or lipophilic polyethereal ligands (crown ethers, cryptands, podands), it is possible to transfer anions into solvents of low polarity and/or polarizability, such as aliphatic and aromatic hydrocarbons. In this way, due to the reduced cation–anion interaction and to very limited solvation, anionic reactivity approaches that found in the gas phase.[17]

The simplest way of transferring the anion into a low polarity solvent is liquid–liquid phase-transfer catalysis.[1-3] However, as reported above, water that under these conditions is associated with the anion in the organic phase counteracts its high destabilization, partially reducing its reactivity,[3] The hydration number depends on the anion and, for halides and pseudohalides associated with quaternary cations in aromatic solvents such as chlorobenzene, ranges from 1 to 5.[3]

When the specific hydration of the anion is eliminated by working in homogeneous anhydrous solution, the reactivity of the anion also noticeably increases, with the most significant increase for anions with localized and/or less polarizable charge. For example, in reaction 1 substitution rates of mesylate by I^-, Br^-, and Cl^- associated with the $C_{16}H_{33}P^+Bu_3$ cation increase 1.1-, 2.5-, and 11-fold, respectively, in going from PTC to anhydrous conditions,[6] Increases are even more significant if cation–anion interaction is lowered. Thus, under anhydrous conditions, an additional rate increase of 3–5-fold is found when the bulkier $[K^+\subset(2.2.2,C_{14})]$ is used instead of the quaternary cation,[7]

As pointed out by Benson,[18] the heats of solvation in the gas phase of negative ions seem to be monotonically related to their diameter. We have found a good linear correlation between hydration entalpies in the gas phase of few relevant anions tabulated be Benson[18] and the hydration numbers of the same anions associated with quaternary cations in the organic phase under PTC conditions (Figure 2), Since the two sets of values have been obtained in completely independent ways, the linearity of correlation is a clear proof of their correctness. This same correlation allows evaluation of one of the two parameters, when the other one is known: e.g., the hydration state of OH^- and F^-. But it is especially significant as direct evidence that gas-phase condition can be approached if progressive anion desolvation is obtained in nonpolar organic solvents.

Complete anion dehydration in aqueous–organic two-phase systems, such as those of phase-transfer catalysis, requires a decrease of water activity (a_{H_2O}) in order to balance hydration enthalpies of the same anions.

As shown in Figure 3, in which a_{H_2O} is reported as a function of solute concentration, even saturated solutions of highly soluble salts, like NaBr and NaI, give rise to limited a_{H_2O} decreases. On the contrary, solutes like KOH or NaOH may afford aqueous solutions whose activity is practically null,[19] They are therefore the solutes of choice. Indeed, about 50% NaOH or KOH aqueous solutions completely dehydrate anions associated with quaternary onium cations under PTC conditions, and as a consequence, anionic reactivity becomes identical with that found under homogeneous anhydrous conditions.[10]

Behavior of cryptand **1a** under these same reaction conditions is in some aspects similar to, but in other ones quite different from, that of quaternary salts. We observed in previous papers[7,8] that under aqueous–organic two-phase conditions anions associated with lipophilic cryptates and complexed crown ethers in the organic phase retain a primary hydration sphere, depending on the anion, identical with that found for lipophilic quaternary salts. Furthermore, independently of the anion, two molecules of water always accompany cryptands **1** and crown ether **2**, both as free or complexed ligands, in the organic base.[7,8] The exact location of these molecules of water inside the complexed ligand compared with that of molecules that accompany the anions is still unknown (see below).

As found for quaternary salts, the hydration shell of cryptates in the organic phase is progressively removed by increasing concentration of KOH or NaOH in the aqueous phase (Table III). However, even in the presence of 53% aqueous KOH, water removal is incomplete (Tables I and III). Thus a still significant

---

(16) (a) Taft, R. W. *NATO Adv. Study Inst. Ser., Ser. B* **1979**, *40*, 271–293. (b) Bohme, D. K.; Mackay, G. I.; Payzant, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 4027–4028. (c) Bohme, D. K.; Rakshit, A. B.; Mackay, D. I. *Ibid* **1982**, *104*, 1100–1101.

(17) The possibility of dramatically increasing reactivity of anions with localized charge under conditions of low interaction with the solvent and the counterion has been authoritatively shown by Taft.[16] Moreover, under these condensed-phase conditions, acid–base chemistry in solution may be conditioned in such a way to force equilibria toward conditions miming those realized in gas phase.

(18) Benson, S. W.; Nangia, P. S. *J. Am. Chem. Soc.* **1980**, *102*, 2843–2844. We are indebted to Professor Saul Wolfe, Kingston University, Ontario, for allowing us to become acquainted with this paper.

(19) Kraceck, F. C. "International Critical Tables"; McGraw-Hill: New York, 1928; p 351.

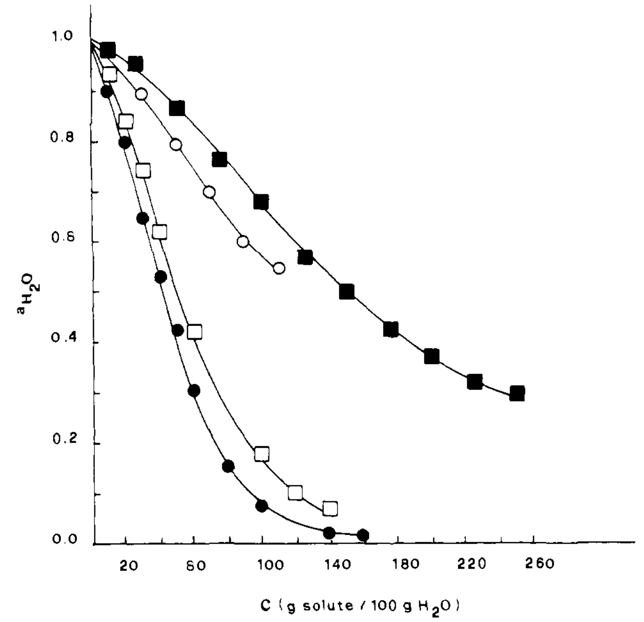


Figure 3. Concentration effect on the activity of water (a_{H_2O}) in solution for a series of inorganic solutes: NaI (■), NaBr (○), KOH (●), and NaOH (□), at 60 °C. a_{H_2O} was calculated from vapor pressure data (ref 19).

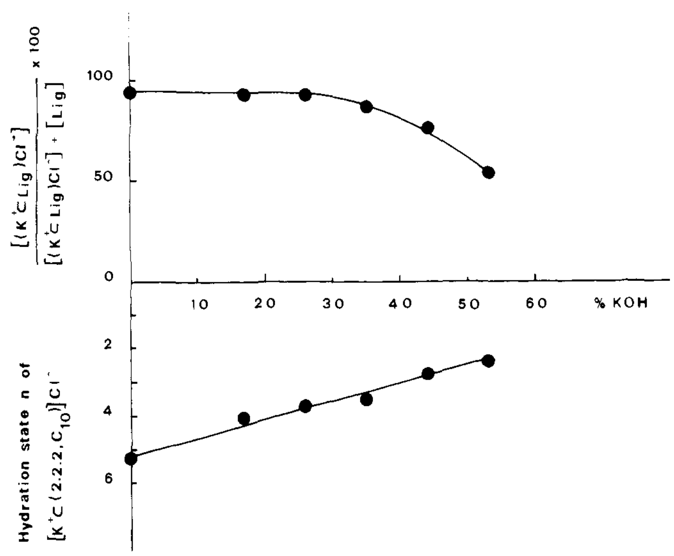


Figure 4. Dependence of the percent complexation of $[2.2.2,C_{10}]$ ligand **1a** with KCl and hydration state *n* of $[K^+\subset(2.2.2,C_{10})Cl^-$ on the aqueous concentration of KOH in the PhCl–aqueous KOH two-phase system, at 60 °C.

residual hydration is present. Again it depends on the nature of the anion and is related to its electronegativity. Anions with dispersed and/or polarizable charge like I^- and SCN^- are almost completely dehydrated, and their reactivity becomes, as expected, identical with that found in homogeneous anhydrous solution (Table I). For anions with localized and/or less polarizable charge, such as Cl^-, Br^- and N_3^-, the residual hydration is more significant, though less than under PTC conditions (2.5, 0.9, and 1.4 mol of water per mol of Cl^-, Br^-, and N_3^-, respectively).[20] As a consequence, rate constants observed under these conditions noticeably increase in comparison with those found in PTC conditions but without reaching those of anhydrous solutions. Enhancements are 10.8, 4.4, and 4.5 times for Cl^-, Br^-, and N_3^-, respectively, compared with 14.5, 6.5, and 5.2 times,[7] respectively, in anhydrous media (Table I).

The different behavior of cryptates and quaternary salts evidently lies in the different topology of the two systems. In low-polarity solvents quaternary salts exist as ion pairs in which cation and anion can still slightly interact.[7] On the other hand in [2.2.2]cryptates, the ligand forms a stable inclusion complex with the cation, replacing its solvation sphere. Thus more complete cation–anion separation is possible, practically giving rise to a sort of solvent-separated ion pair.[7]

X-ray measurements, for example for $[K^+\subset(2.2.2)]I^-$ cryptate have shown that the anion lies outside of the 10-Å diameter spheroidal ligand surrounding the cation.[21,22] The $[K^+\subset(2.2.2,C_{10})]F^-$ cryptate can be easily prepared in chloroform solution, but not in benzene. However, it retains its stability even in the latter solvent, provided that F^- is selectively solvated by one molecule of $CHCl_3$.[25]

Therefore, in cryptates the lower energy of interaction between anion and complexed cation must be balanced by a higher interction of the anion with solvent, thus, in the aqueous–organic two-phase system, by its higher hydration energy. In anhydrous homogeneous conditions the unsolvated anion shows maximum reactivity, probably the highest[26] that can actually be obtained in solution.

As shown in Table I, percentages of complexed ligand are always higher under two-phase conditions compared to anhydrous conditions, in the case of anions with localized and/or less polarizable charge, as Cl^- and N_3^-. A particularly interesting example is given by $[K^+\subset(2.2.2,C_{10})]Cl^-$ cryptate. The stability of this complex (Figure 4) is independent of aqueous KOH concentration up to about 25%, whereas at high concentrations the stability of the complex progressively decreases down to 56% complexation at the highest KOH concentration. This complexation percent is close to that found in anhydrous chlorobenzene (43%).

A plot of hydration number of the complex in the organic phase against concentration of aqueous alkaline solution reveals a linear relationship (Figure 4 and Table III). A comparison with the behavior of quaternary salts[10] shows that the hydration sphere of cryptate diminishes even at low KOH concentrations, while in quaternary salts hydration remains constant up to 25% aqueous KOH. Afterward, hydration progressively decreases on increasing the aqueous base concentration.[10,27] The first two molecules of water, specific to the ligand, are lost relatively easily, whereas the remaining waters, associated with the anion, are not so easily removed. Extrapolation shows that total dehydration can be achieved only for a hypothetical 70% aqueous KOH concentration.

The behavior of quaternary salts parallels that of $[K^+\subset(2.2.2,C_{10})]Cl^-$ (see above), whose decomplexation only begins at KOH concentrations above 25%. This seems to confirm the hypothesis that there is a limit of water activity above which anions are insensitive to dehydration, and the two molecules of water

---

(20) In the system KCl–53% KOH, KOH competes, although limitedely (~9%), with KCl to form $[K^+\subset(2.2.2,C_{10})]OH^-$ cryptate. The 2.5 mol equiv of H_2O found in this case are likely to be attributed in part to the latter cryptate.

(21) Moras, D.; Weiss, R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 396–399.

(22) X-Ray analysis of [2.2.2]cryptates with some lanthanoid nitrates and perchlorates showed that anions are positioned in a gap between two bridging chains, two oxygens being directed toward the metal cation. Thus, in this case, a direct interaction between the opposite ions is allowed.[23] Spectroscopic measurements on sodium 9-fluorenone ketyl in the presence of [2.2.2]cryptand have been interpreted[24] on the basis of two different kinds of cryptates: one cryptand separated, the other one a contact-type cryptate, in which the carbonyl oxygen atom penetrates the molecular framework of cryptand and contacts the metal cation. Possibly, these results might be interpreted on the basis of coexistence at the equilibrium of two species of sodium ketyl, cryptated and free, respectively; the latter evidently with the typical properties of intimate ion pairs.

(23) (a) Hart, F. A.; Hursthouse, M. B.; Malik, K. M. A.; Moorhouse, S. *J. Chem. Soc., Chem. Commun.* **1978**, 549–550. (b) Ciampolini, M.; Dapporto, P.; Nardi, N. *Ibid.* **1978**, 788–789.

(24) Nakamura, K. *J. Am. Chem. Soc.* **1980**, *102*, 7846–7848.

(25) Clement, D.; Damm, F.; Lehn, J. M. *Heterocycles* **1976**, *5*, 477–484.

(26) Landini, D.; Maia, A.; Montanari, F.; Rolla F. *J. Chem. Soc., Perkin Trans. 2* **1981**, 821–824.

(27) This corresponds to a 30% value, reported in the preceeding paper,[10] corrected for the title of KOH used.

initially withdrawn from the cryptate are not part of the specific hydration sphere of the anion.

The behavior of crown ethers in the presence of alkaline solutions is different from both that of quaternary salts and cryptates. As for cryptates, the hydration of complexed polyether under two-phase conditions is substantially equal to the sum of the specific hydration of the anion in quaternary salts and the two molecules of water that, also in this case, accompany the uncomplexed ligand (Table II).[28] Increased aqueous KOH concentration is accompanied by a progressive decrease of specific hydration of the complex in the organic phase, the two parameters being linearly related from the lowest KOH concentrations up (Table IV).

Unfortunately, the relatively low complexation of KBr with crown ether **2** (Table II) makes errors in measuring the complex hydration as a function of KOH concentration unacceptably high, so that we preferred to perform these measurements for SCN^- ion (Table IV). In this case, percent of complexation is very high, but the difference of reactivity among the hydrated species is quite small (Table II). It may be observed that the residual hydration sphere at maximum KOH concentration (0.37 mol of H_2O) is higher than that found in quaternary salts (≤ 0.2), but lower than the residual hydration found in cryptate **1a** (0.61).

This seems to confirm the possibility that direct cation–anion interaction contributes to stabilizing the complexed anion, therefore lowering the extent of anion specific hydration down to a value close to that found for quaternary salts. Accordingly, the reactivity of ions complexed with the crown ether becomes almost identical with that found in homogeneous anhydrous media. It should be noted that the direct cation–anion interaction in crown ethers eliminates the significant differences in anionic reactivity found in quaternary salts and cryptates on passing from two-phase to homogeneous anhydrous conditions. Indeed, as we have already discussed,[8] removal of an anion's hydration sphere leads to rather small variation of its reactivity.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian EM-390 90-MHz spectrometer with tetramethylsilane as internal standard. Potentiometric titrations were performed with a Metrohm Titroprocessor E636; silver or glass and calomel electrodes, the latter isolated with a potassium sulfate bridge, were used. GC data were obtained on a Varian 3700 gas chromatograph equipped with a 50 cm × 1/8 in. OV-101 5% on chromosorb GHP 100–120 mesh column and were evaluated with a Varian Model 401 data system by the internal standard method.

Materials and Solvents. All inorganic salts were Analar grade commercial products; potassium azide was obtained according to the literature.[30] They were used without further purification, except for runs carried on in anhydrous conditions in which they were carefully dried and stored in a desiccator.

n-Octyl methanesulfonate (**3**), bp 112–114 °C (2 mm), n^{20}_D 1.4398, was prepared according to the literature [lit.[31] bp 110–114 °C (2 mm), n^{20}_D 1.4392]. The [2.2.2,C_{10}]cryptand (**1a**) was an Analar grade commercial product, purchased in toluene solution. It was used after solvent evaporation under vacuum without further purification. The synthesis of [2.2.2,C_{14}]cryptand (**1b**) was previously described.[7,32] Dicyclohexano-18-crown-6 (**2**) was an Analar grade commercial product used without further purification. Chlorobenzene and benzene were Analar grade commercial solvents, used without further purification in the experiments carried out under PTC conditions. For the reactions performed under anhydrous conditions, they were carefully purified and dried as previously reported.[33] They were stored over molecular sieves. Karl Fischer analyses showed a water content of ≤40 ppm.

Extent of Complexation and Distribution Coefficients. The extent of complexation of cryptands **1a,b** and crown ether **2** under phase-transfer conditions was determined by stirring 20 mL of a standardized chlorobenzene solution of **1a**, **1b**, or **2** ($(2-8) \times 10^{-2}$ M) with 15 mL of an aqueous solution of 53% KOH (~14.5 M) and 63 mmol of the corresponding inorganic salt KY in a flask thermostated at 60 °C; under these conditions the potassium salt is largely present as solid phase. The system was stirred for 60 min, then kept without stirring for an additional 30–60 min to allow good separation of the two phases. Aliquots of the organic phase were withdrawn and titrated with 0.01 N silver nitrate (potentiometric titration). Ancillary experiments showed that in all cases a stirring time of about 60 min was sufficient to obtain a constant value of complexation.

Distribution coefficients under classical PTC conditions and the extent of complexation both under PTC and anhydrous conditions were determined as previously described.[7,8] Equilibrium 2 was studied under the same conditions as for kinetic measurements, adding to the system 12 mmol of potassium methanesulfonate corresponding to the amount formed in the reaction 1 at 100% conversion. For Cl^- equilibrium 2 was studied at the following percents of reaction: 10, 20, 50, 100% (Figure 1).

Hydration State of Cryptates and Complexed Crown. The hydration state of complex **1a**, **1b**, and **2** was determined by stirring for 60 min 20 mL of a standardized organic solution of $[K^+ \subset \text{ligand}]Y^-$ ($(0.5-4) \times 10^{-2}$ M) with 15 mL of an aqueous solution of 53% KOH (14.5 M) and 63 mmol of the corresponding inorganic salt KY in a flask thermostated at 60 °C. Stirring was stopped, and aliquots (3–5 mL of organic phase were withdrawn at intervals until a constant content of water was measured (Karl Fischer analysis, 1–3 h). Concentration of complexed KY in the organic layer was measured in parallel by potentiometric titration. The hydration state of free ligands **1a,b** and **2** under classical PTC conditions were determined as previously reported.[7,8]

Extractability of KOH in the Organic Phase. The extractability of KOH in the system PHCl–53% aqueous KOH by ligands **1a** and **2** was determined by stirring for 60 min 20 mL of a standardized chlorobenzene solution of **1a** or **2** ($(2-6) \times 10^{-2}$ M) with 15 mL of an aqueous solution of 53% KOH both in the absence and in the presence of 63 mmol of the appropriate inorganic salts KY (Y = Cl, Br, I, N_3, SCN) in a flask thermostated at 60 °C. Stirring was stopped and after 1–3 h aliquots (3–5 mL) of the organic phase were withdrawn and titrated with 0.01 N HCl. In the case of ligand **1a** acid–base titrations were performed in the presence of excess of potassium nitrate to ensure that all **1a** is complexed. Indeed acid–base titration must be carried on in the absence of free ligand **1a**, since the latter is also titrated by HCl. In the presence of inorganic salts, the concentration of complexed KY in the organic phase was measured in parallel by potentiometric titration of the anion.

Kinetic Measurements. The apparatus used for kinetic measurements under phase-transfer conditions has been previously described.[6] In a typical procedure, the reaction flask was thermostated at 60 ±0.1 °C and charged with 15 mL of an aqueous solution of potassium salt (4.2 M) and 20 mL of a standardized chlorobenzene solution of ligand **1a**, **1b**, or **2** ($(4-16) \times 10^{-2}$ M). The mixture was stirred for 60 min, then two portions (5 mL) of the organic phase were withdrawn, and the extent of complexation of ligands was determined by potentiometric titration. A chlorobenzene solution (10 mL) of substrate **3** (1.2 M) and benzyl phenyl ether (0.8 M) as internal standard, already at 60 ±0.1 °C, was added to the flask, and stirring and timing were started. Portions of the organic phase were withdrawn at intervals by stopping the stirrer for 40–60 s to allow adequate separation. These were quenched by cooling in an ice bath and analyzed by ^{1}H NMR. Reaction rates were determined by following the disappearance of the triplet (CH_2OSO_2Me) centered at δ 4.05 and using the singlet at δ 4.80 (OCH_2Ph) as standard. The pseudo-first-order rate constants (k_{obsd}) were obtained by plotting log [substrate] vs. time and determining the slope of the straight lines. The second-order rate constants, k, were evaluated by dividing k_{obsd} by the complexed ligand concentration in the organic phase. In the kinetic experiments carried out in the presence of KOH, aqueous solutions (8.6–53%) of the base (15 mL) were added with 63 mmol of KY in the reaction flask thermostated at 60 ±0.1 °C. Under these conditions KY was not completely soluble: e.g., for KBr, at 8.6%, 25%, and 53% aqueous KOH, a 3.9, 2.6, and 0.5 M KBr concentration, respectively, was found instead of the expected 4.2 M concentration. The kinetic measurements under homogeneous conditions by using the ligands **1a**, **1b**, or **2** were performed as previously reported.[7,8] The second-order rate constants were evaluated using a least-squares computer program from the

---

[28] The exact location of 1–2 molecules of water that specifically solvate crown ethers inside their cavity has been recently demonstrated by X-ray analysis.[29]

[29] Newkome, G. R.; Taylor, H. C. R.; Franczek, F. R.; Delord, T. J.; Kohli, D. K. *J. Am. Chem. Soc.* **1981**, *103*, 7376–7378.

[30] Miller, M. W.; Audrieth, L. F. *Inorg. Synth.* **1946**, *2*, 140–143.

[31] Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 2984–2987.

[32] Cinquini, M.; Montanari, F.; Tundo, P. *Gazz. Chim. Ital.* **1977**, *107*, 11–14.

[33] Riddick, A.; Bunger, W. B. "Organic Solvents, 2", 3rd ed.; A. Weissberger: New York, 1970; pp 767–768.

equation $1/[([B_0] - [A_0])\ln([BA_0]/[AB_0])] = kt$, where [A] = [substrate] and [B] = [complexed ligand] or vice versa. All rates involved at least 10 samplings and gave correlation coefficients of 0.996 or better.

Reaction Products. In a typical procedure the flask used for kinetic runs termostated at 60 °C was charged with 63 mmol of the appropriate inorganic salt KY, with 15 mL of a 53% aqueous solution of KOH, and with 10 mL of a benzene (or chlorobenzene) solution of substrate **3** (1.2 M), of catalyst **1a** (0.025 M) or **2** (0.05 M), and of *n*-decane (0.4 M) (as GLC internal standard). The heterogeneous mixture was stirred for 1–11 h. The progress of the reaction was monitored by GLC analysis (50 cm × 1/8 in. in OV-101-5% on Chromosorb GHP 100–120 mesh column, in a program temperature from 50 to 150 °C). At 98–100% conversion the mass balance was ≥95%, except for the reactions with SCN^-, for which it was ≥81%, the remainder being tars. The distribution of reaction products for various nucleophilic substitutions is reported in Table V.

Reaction of Organotin Hydrides with Acid Chlorides. Mechanism of Aldehyde and Ester Formation[1]

J. Lusztyk,[2] E. Lusztyk, B. Maillard,[3] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and Laboratoire de Chimie Appliquée, Université de Bordeaux I, 33405 Talence, France. *Received September 23, 1983*

Abstract: Tri-*n*-butyltin hydride reacts with acid chloride, RCOCl, spontaneously at ambient temperatures to form $n\text{-Bu}_3SnCl$, RCHO, $RC(O)OCH_2R$, and a number of minor products. The reaction is not a radical chain process, nor are radicals involved as intermediates. The initial products are $n\text{-Bu}_3SnCl$ and RCHO; it is not known whether these are formed in a direct reaction between $n\text{-Bu}_3SnH$ and RCOCl or via an unstable chloroalkoxytin species, $n\text{-Bu}_3SnOCHClR$. The remaining products are formed by subsequent reactions of the aldehyde. Thus, the alkoxytin species, $n\text{-Bu}_3SnOCH_2R$, is formed from aldehyde and tin hydride. This can react further with RCOCl to form the ester $RC(O)OCH_2R$, with RCHO to form $n\text{-Bu}_3SnOCH(R)OCH_2R$, and with $n\text{-Bu}_3SnH$ to form RCH_2OH. The aldehyde can also react with RCOCl to form the α′-chloro ester, RC(O)OCHClR.

Triorganotin hydrides react spontaneously at ambient temperatures with many acid chlorides to form the corresponding triorganotin chloride, aldehyde, and ester as the major products.[4–11]

$$R'_3SnH + RCOCl \rightarrow R'_3SnCl + RCHO + RC(O)OCH_2R \tag{1}$$

Surprisingly, the relative yields of aldehyde and ester have been found to depend not only on the structure of the acid chloride but also on the experimental conditions, e.g., whether or not a solvent is employed.

A rather detailed mechanistic study of the tri-*n*-butyltin hydride/acid chloride reaction has been carried out by Kuivila and Walsh.[9,10] It was concluded that both aldehyde and ester were produced by free-radical chain processes involving acyl radicals as intermediates. The formation of aldehyde was suggested to be mechanistically analogous to the formation of alkane in the tin hydride/alkyl halide reaction,[12]

$$n\text{-Bu}_3Sn\cdot + RCOCl \rightarrow n\text{-Bu}_3SnCl + R\dot{C}{=}O \tag{2}$$

$$R\dot{C}{=}O + n\text{-Bu}_3SnH \rightarrow RCHO + n\text{-Bu}_3Sn\cdot \tag{3}$$

Four pathways for the formation of ester were considered,[10] and it was concluded that the most probable involved acyl radical addition to the aldehyde formed in reaction 3.

$$R\dot{C}{=}O + RCHO \rightarrow RC(O)O\dot{C}HR \tag{4}$$

$$RC(O)O\dot{C}HR + n\text{-Bu}_3SnH \rightarrow RC(O)OCH_2R + n\text{-Bu}_3Sn\cdot \tag{5}$$

In a preliminary communication[13] we presented evidence that free radicals are not involved in the spontaneous reaction of tri-*n*-butyltin hydride with at least some acid chlorides and that if free radicals are deliberately generated in the system, the nature of the products may be changed. For example, in the $n\text{-Bu}_3SnH$/pivaloyl chloride reaction, the main product of the spontaneous reaction was pivalaldehyde and the main product of the radical initiated reaction was isobutane.

$$\begin{aligned} n\text{-Bu}_3SnH + Me_3CCOCl &\xrightarrow{\text{spontaneous}} n\text{-Bu}_3SnCl + Me_3CCHO \\ &\xrightarrow{\text{initiated}} n\text{-Bu}_3SnCl + Me_3CH + CO \end{aligned} \tag{6}$$

In the present paper we amplify our earlier report.[13] Additional data on the spontaneous reaction serves to confirm the nonradical mechanism of aldehyde formation. Ester is also shown to be produced by a nonradical process.

Results

To distinguish between radical and nonradical processes we have studied the products and kinetics of the spontaneous and of the

---

(1) Issued as NRCC No. 23216.

(2) NRCC Research Associate 1982–84.

(3) NRCC Summer Visitor, Bordeaux, 1982.

(4) For brief reviews, see: (a) Kupchik, E. J. In "Organotin Compounds"; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; Vol. 1, pp 28–33. (b) Kuivila, H. G. *Synthesis* **1970**, 499–509.

(5) Van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 356–365.

(6) Kuivila, H. G. *J. Org. Chem.* **1960**, *25*, 284–285.

(7) Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47–87.

(8) Kupchik, E. J.; Kiesel, R. J. *J. Org. Chem.* **1964**, *29*, 3690–3691; **1966**, *31*, 456–461.

(9) Kuivila, H. G.; Walsh, E. J., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 571–576.

(10) Walsh, E. J., Jr.; Kuivila, H. G. *J. Am. Chem. Soc.* **1966**, *88*, 576–581.

(11) Walsh, E. J., Jr.; Stoneberg, R. L.; Yorke, M.; Kuivila, H. G. *J. Org. Chem.* **1969**, *34*, 1156–1157.

(12) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047–3051.

(13) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 4475–4477.