acetylene, δ 2.0 ± 0.1 (1 H, t, J = 2.5 Hz), and none absorbed in the allene region.

Preparation of 1-Aryl-3-buten-1-ols. These alcohols were prepared from the reaction of the allyl Grignard reagent with the appropriately substituted benzaldehyde, following essentially the procedure of Smith and Voorhees.[7] All arylbutenols utilized are fully described in the above reference, with the sole exception of the following compound.

1-*m*-Chlorophenyl-3-buten-1-ol. This compound was isolated, in 38% yield, by distillation of the crude material resulting from the above procedure,[7] bp 99° (0.2 mm), $n^{22}\text{D}$ 1.543.

Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.75; H, 6.07. Found: C, 65.88; H, 6.12.

Kinetic Procedures. The method used for following the thermolysis rates of the 1-aryl-3-butyn-1-ols and 1-aryl-3-buten-1-ols was exactly as previously described, method A, ref 2. Tetralin was used as the internal standard for all the alcohols with the exception of 1-(*m*-methoxyphenyl)-3-butyn-1-ol, for which *p*-*tert*-butyltoluene was used. A run with 1-phenyl-3-butyn-1-ol using *p*-*tert*-butyltoluene as an internal standard gave a rate of 4.44×10^{-4} sec^{-1} at 270° compared with 4.53×10^{-4} sec^{-1} using tetralin as an internal standard.

The reaction was shown to be independent of starting concentration. For example, 1-phenyl-3-buten-1-ol was thermolyzed at 270° in xylene solution at 1, 4, and 10% (v/v) to give rate constants of 3.04, 2.97, and 3.06×10^{-4}, respectively. Reaction homogeneity was established by packing a tube with thin capillaries such that the surface area was increased by a factor of at least five. Under such conditions the above alcohol afforded a rate constant of 2.9×10^{-4}. The rate constants obtained are listed in Table VI.

Phase-Transfer Catalysis. II. Kinetic Details of Cyanide Displacement on 1-Halooctanes

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Abstract: Displacement reactions of alkyl halides in an organic phase with anions in an aqueous phase that are inhibited because of phase separation may often be strongly catalyzed by addition of small amounts of tetraalkylammonium or tetraalkylphosphonium salts. This ability of organic-soluble cations to function as *phase-transfer* catalysts was further explored to determine kinetics and characteristics of the system. Evidence is presented to show that catalysis is directly proportional to the amount of quaternary salt present in the organic phase, that the rate is first order in 1-haloalkane concentration, and that the rate is not dependent on stirring speed beyond just enough to obtain moderate mixing (*ca.* 250 rpm). Displacement depends strongly on the aqueous-phase cyanide ion/chloride ion ratio, since this affects the equilibrium position for transfer of cyanide into organic phase by quaternary salt. The anion transfer equilibrium constant is sensitive to the amount of water present, the relative concentrations of NaCN and NaCl, and the polarity of the organic phase, probably because cyanide ion tends to be more highly hydrated than chloride. The quaternary salts used as catalysts aggregate only to a low degree (1.5–3 at 0.1 *M*) in anhydrous nonpolar solvents. These data are consistent with the proposed ability of the organic-soluble cations to repeatedly bring anions into the organic phase where displacement occurs, probably without participation of micelles.

Phase-transfer catalysis, introduced and qualitatively described in a previous report,[1] is further described here relative to the kinetics of cyanide displacement on 1-chloro- and 1-bromooctane. Phase-transfer catalysis is applicable to reactions which are inhibited because of the inability of the reagents to physically come together. For example, in the reaction between aqueous sodium cyanide and 1-chlorooctane, addition of an organic-soluble quaternary ammonium or phosphonium salt catalyzes cyanide displacement on RCl. As illustrated by eq 1, the function of the quaternary salt, QX, is to bring cyanide ion into the organic phase in a form suitable for reaction with RCl and return the displaced chloride ion to the aqueous phase where QCN can be regenerated. The previous paper[1] and other reports[2] show a number of applications using quaternary ammonium or phosphonium salts as phase-transfer catalysts. An important assumption in systems described by eq 1 is that the rate-determining step of the reaction takes place in the organic phase of the reaction mixture rather than in the aqueous phase, at the interface, or in micelles. Experimental evidence to support this assumption and kinetics and general physical details of the Q^+-catalyzed NaCN(aq)/RCl(org) reaction are presented here.

$$\begin{tikzcd} \mathrm{RCl + QCN} \arrow[r] & \mathrm{RCN + QCl}\ \text{(organic phase)} \arrow[d] \\ \mathrm{NaCl + QCN} \arrow[u] \arrow[r, shift left] & \mathrm{NaCN + QCl}\ \text{(aqueous phase)} \arrow[l, shift left] \end{tikzcd} \qquad (1)$$

Results and Discussion

1. Evidence That Displacement Occurs in the Organic Phase. Much work has been reported[3,4] showing that cationic surfactants substantially catalyze reactions between certain anions and organic substrates with close correlation between rate enhancement and micelle formation. Since the quaternary salts used in phase-transfer catalysis are similar to those used in micelle-catalyzed reactions, it is necessary to determine whether the cyanide attack on RCl takes place in the organic phase, in the aqueous phase, in micelles, or at the interface.

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(1) C. M. Starks, *J. Amer. Chem. Soc.*, **93**, 195 (1971).

(2) (a) M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, 4659 (1969); (b) A. Brändström and U. Junggren, *ibid.*, 473 (1972), and references contained therein; (c) W. P. Weber and G. W. Gokel, *ibid.*, 1637 (1972); (d) E. V. Dehmlow, *Tetrahedron*, **27**, 4071 (1971); (e) A. W. Herriott and D. Picker, presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., 1972; (f) M. S. Newman and S. J. Gromelski, *J. Org. Chem.*, **37**, 3220 (1972).

(3) E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, **2**, 329 (1969).

(4) E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

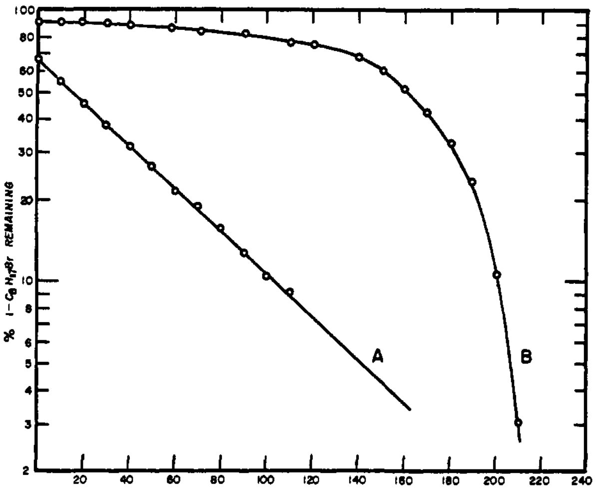

Figure 1. Disappearance of 1-bromooctane in reaction with aqueous sodium cyanide: curve A, catalyzed with 0.02 *M* $(C_{16}H_{33})PBu_3{}^+Br^-$; curve B, catalyzed with 0.04 *M* Bu_4PBr.

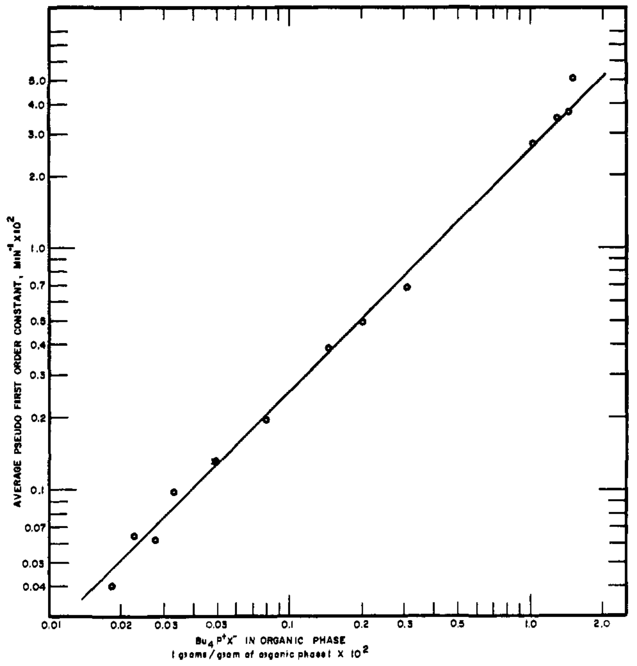

Figure 2. Average rate coefficients for 1-bromooctane reaction with aqueous sodium cyanide at 90°, catalyzed by 0.04 *M* Bu_4PBr as a function of the amount of $Bu_4P^+X^-$ in the organic phase.

Several lines of evidence suggest that the displacement reaction between QCN and RCl takes place in the organic phase as illustrated by eq 1. Highly effective catalysis by poor surfactants such as tetra(dodecyl)-ammonium salts, the first-order dependence of rate on the concentration of such organic-soluble quaternary salts (see below), and the known ability of these salts to participate in displacement reactions at high rates even in nonpolar media[5] support eq 1, as opposed to micelle-centered reactions. The effects of stirring rate and salt concentration in the aqueous phase, as described below, indicate that rates are not highly dependent on interfacial area or RCl solubility in the aqueous phase.

The strongest evidence that the reaction occurs in the organic phase was obtained from tetrabutylphosphonium bromide catalyzed cyanide displacement on 1-bromooctane, as compared to the same reaction catalyzed by tributylhexadecylphosphonium bromide. Salts of $C_{16}H_{33}PBu_3{}^+$ are essentially completely soluble in 1-bromo- and 1-cyanooctane and insoluble in water and aqueous sodium cyanide solutions. Salts of tetrabutylphosphonium bromide, on the other hand, are relatively insoluble in 1-bromooctane but are highly soluble in 1-cyanooctane. In a 1-bromooctane–aqueous sodium cyanide system, $Bu_4P^+X^-$ is mostly partitioned into the aqueous phase, but in 1-cyanooctane–aqueous sodium cyanide, $Bu_4P^+X^-$ salts are partitioned mostly into the organic phase. If displacement occurs only in the organic phase, the reaction catalyzed by $C_{16}H_{33}PBu_3{}^+X^-$ will start rapidly and continue until all RBr is consumed, whereas the reaction catalyzed by $Bu_4P^+X^-$ will start slowly and will proceed more rapidly as RBr is converted to RCN. This behavior was indeed observed experimentally as shown in Figure 1.

To verify that the tetrabutylphosphonium salt concentration in the organic phase increased with increasing RBr conversion, this experiment was repeated using ^{14}C-labeled $Bu_4P^+Br^-$. Samples of the organic phase taken during reaction were analyzed for 1-bromooctane and 1-cyanooctane by gas chromatography and were assayed for ^{14}C. From these data, point-to-point, first-order rate constants and the concentrations of quaternary salt in the organic phase were calculated and compared as shown in Figure 2. The linear log–log plot with slope equal to unity clearly shows that the rate is proportional to the organic-phase solubility of the catalyst.

2. Kinetics of Quaternary-Salt Catalyzed Reaction between Aqueous Sodium Cyanide and 1-Chlorooctane. It is helpful to consider phase-transfer catalysis in terms of the two functions served by the phase-transfer agent. Anion transfer into the organic phase may be viewed as an equilibrium in which two different ions in the aqueous phase associate with a quaternary cation in the organic phase

$$(\mathrm{QCl})_{\mathrm{org}} + (\mathrm{CN}^-)_{\mathrm{aq}} \overset{K}{\rightleftharpoons} (\mathrm{QCN})_{\mathrm{org}} + (\mathrm{Cl}^-)_{\mathrm{aq}} \qquad (2)$$

from which it may be shown that

$$(\mathrm{QCN})_{\mathrm{org}} = \frac{KQ_0(\mathrm{CN}^-)_{\mathrm{aq}}}{(\mathrm{Cl}^-)_{\mathrm{aq}} + K(\mathrm{CN}^-)_{\mathrm{aq}}} \qquad (3)$$

If it is assumed that the displacement reaction itself is the slow step in the sequence, then the rate of alkyl halide consumption is

$$-\mathrm{d}(\mathrm{RCl})/\mathrm{d}t = k(\mathrm{RCl})(\mathrm{QCN}) \qquad (4)$$

By substitution of eq 3 into eq 4 and integration, it may be shown that

$$\frac{\alpha}{\beta}\ln\left[\frac{\chi(\alpha+\beta\chi_0)}{\chi_0(\alpha+\beta\chi)}\right] - (1-K)\ln\left[\frac{(\alpha+\beta\chi)}{(\alpha+\beta\chi_0)}\right] = -kKQ_0t \qquad (5)$$

where χ = fraction of charged RCl that remains unreacted at time t, $\chi_0 = \chi$ at $t = 0$; $\alpha = N - R$, where N = moles of CN^- and R = moles of RCl in

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[5] J. Uglestad, T. Ellingsen, and A. Berge, *Acta Chem. Scand.*, 20, 1593 (1966).

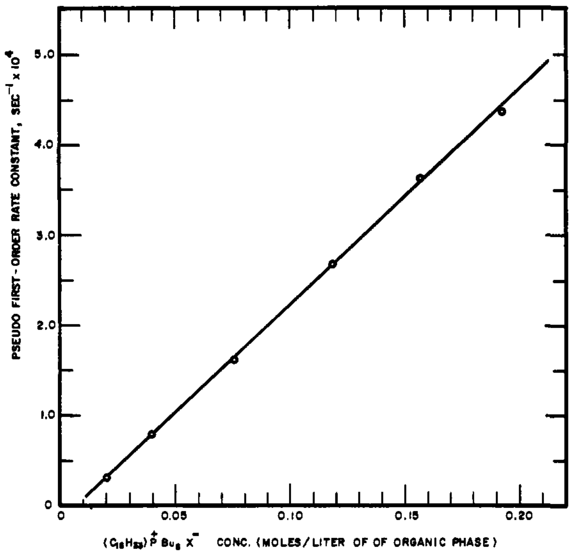

Figure 3. Rate coefficients for 1-chlorooctane reaction with aqueous NaCN at 90°, with various concentrations of $(C_{16}H_{33})PBu_3^+Br^-$.

the original mixture ($R \neq N$); $\beta = A + R + \alpha K$, where A = g-atoms of Cl^- present at $t = 0$. If it is assumed that the Cl^-/CN^- ratio is essentially constant throughout the period when kinetic data are taken, then the rate equation can be derived in a greatly simplified form, eq 6, where r = average Cl^-/CN^- ratio. The

$$\ln\left[\frac{RCl}{RCl_0}\right] = -\left[\frac{kK}{r + K}\right]Q_0t = -k_1Q_0t \qquad (6)$$

rate of alkyl halide consumption should be first order in RCl and pseudo-first order in quaternary salt concentration (assuming essentially all of Q_0 to be in the organic phase). The reaction rate by eq 6 will also be sensitive to the values of K and r.

The pseudo-first-order kinetic behavior of $C_{16}H_{33}PBu_3^+Br^-$ catalyzed cyanide displacement on 1-bromooctane is illustrated by curve A of Figure 1. Very similar kinetic behavior was observed with 1-chlorooctane, used as a model alkyl chloride in most of the experiments described below to examine the general kinetic aspects of phase transfer catalysis.

a. The Anion Partitioning Equilibrium. The equilibrium represented by eq 2 was measured by using either $Na^{14}CN$ or $Na^{36}Cl$ to determine the relative amounts of these two anions associated with the quaternary salt in two organic liquids, toluene and 1-cyanooctane. The results of these measurements, listed in Table I, show that the value of K increases with increasing total salt concentration and is dependent on the NaCN/NaCl ratio but approaches a value of 1.3 when the aqueous phase is saturated with either NaCN or NaCl. The value of K is also dependent on whether the solvent is toluene or 1-cyanooctane.

b. Dependence on Catalyst Concentration. The data plotted in Figure 3 show that the rate of RCl consumption is directly proportional to the concentration of catalyst added, as expected on the basis of eq 5 or 6. A disturbing feature of this plot, however, is that the line does not extrapolate through the origin or even through a positive displacement on the ordinate. Rather, at a catalyst concentration of zero, it extrapolates to an apparent negative value. If these results are real, then it would appear that a small amount of some impurity is present in the reaction system which can behave as a catalyst poison.

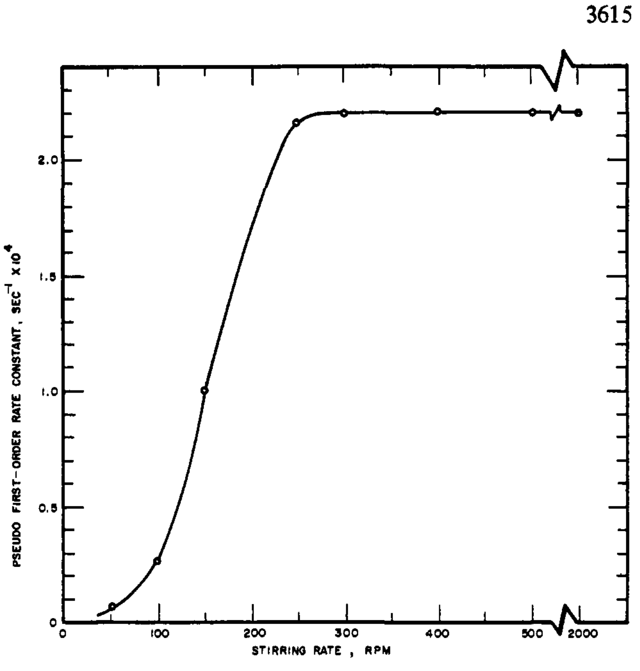

Figure 4. Effect of stirring rate on rate coefficients for 1-chlorooctane reaction with aqueous sodium cyanide at 90°, catalyzed by $(C_{16}H_{33})PBu_3^+Br^-$.

Table I. Apparent Equilibrium Constants, K, for Chloride and Cyanide Association with Hexadecyltributylphosphonium Cation in Toluene and 1-Cyanooctane

Mol of salt in 2.78 mol of water			K in	K in 1-
NaCN	NaCl	Total	Toluene	Cyanooctane
		($Na^{14}CN$ + NaCl)		
0.204	0.086	0.290	0.32	0.46
0.204	0.128	0.332	0.38	0.59
0.204	0.171	0.375	0.42	0.66
0.204	0.257	0.460	0.54	0.98
0.204	0.342	0.546^a	0.73	1.29
		(NaCN + $Na^{36}Cl$)		
0.204	0.086	0.290	0.31	0.46
0.408	0.086	0.494	0.40	0.53
0.612	0.086	0.698	0.40	0.55
1.020	0.086	1.106^b	0.71	1.25

^{a} All NaCl not soluble. ^{b} All NaCN not soluble.

c. Dependence on Stirring Rate. The kinetic eq 5 and 6 were derived on the assumption that the anion exchange equilibrium between the anions in the aqueous phase and those associated with quaternary salt in the organic phase was very fast relative to the organic-phase displacement reaction. This assumption will not be correct if mass transfer across the interface is retarded, for example, as evidently occurs at low stirring rates, as shown in Figure 4. At sufficiently high agitation levels, stirring rate >*ca.* 250 rpm and using a simple flat-blade stirrer in a three-necked flask, anion exchange equilibrium is very fast relative to the organic-phase displacement reaction and the RCl consumption rate becomes independent of the stirring rate. This behavior is in sharp contrast to reactions taking place at a water–organic phase boundary, where the reaction rate is directly proportional to stirring rate.[6]

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[6] F. M. Menger, *J. Amer. Chem. Soc.*, 92, 5965 (1970).

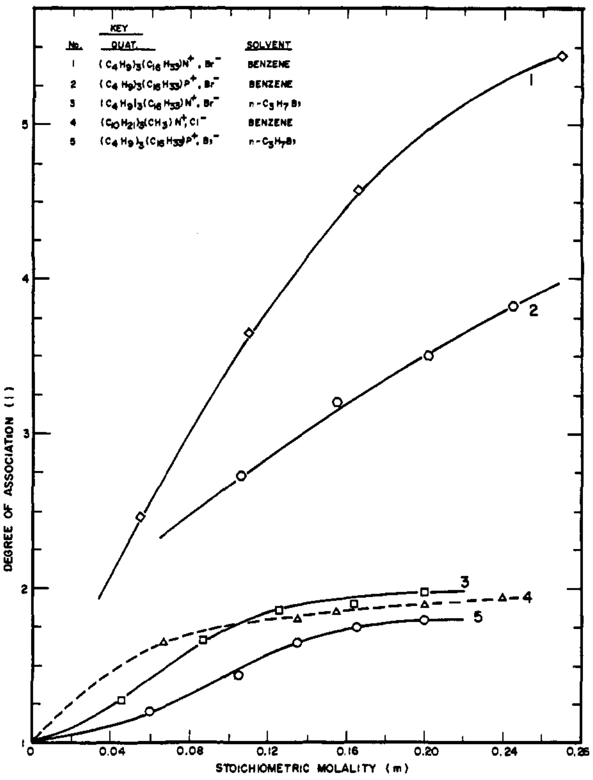

Figure 5. Aggregation of quaternary salts in benzene and 1-bromopropane.

d. Effect of the Amount of Water Employed. The data in Table II show that a little water is required for operation of the phase-transfer catalyzed displacement system, but that as the amount of water is increased past the NaCN saturation level, the rate declines. That some water is required indicates the quaternary salt cannot exchange anions with crystalline sodium cyanide. Decline in rate with increasing water beyond the amount required to dissolve all NaCN is qualitatively consistent with decreasing values of K on dilution of the aqueous phase. Additional data for K values are required for a quantitative correlation but directionally, and in the order of magnitude (*ca.* twofold), these changes correlate well. This conclusion is in agreement with the basic assumption that the amount of water present should have no effect on the reaction rate except as it may change the relative thermodynamic properties of Cl^- and CN^- (and therefore the value of K), and if additional water does not extract catalyst from the organic phase or hinder anion transfer across the interface. Data presented below indicate that cyanide ions tend to be more highly hydrated than chloride. Increasing water concentration would therefore be expected to hydrate cyanide ions more strongly, and therefore reduce their tendency to be taken into the organic phase by the quaternary cation.

Table II. Effect of Amount of Water Employed on the Rate of Cyanide Displacement on 1-Chlorooctane, as Catalyzed by $C_{16}H_{32}PBu_3{}^+Br^{-a}$

Mol of water added	Rate constant, k,[c] l./(mol sec)	Mol of water added	Rate constant, k,[c] l./(mol sec)
0	0	3.34	0.076
0.555[b]	0.088	5.56	0.054
0.833[b]	0.099	8.35	0.044
1.67[b]	0.076	27.8	0.037

[a] Reaction of 0.337 mol of 1-$C_8H_{17}Cl$, 1.02 mol of NaCN, and 0.005 mol of $C_{16}H_{33}PBu_3{}^+Br^-$, at 90°; 500 rpm stirring rate. [b] Aqueous phase saturated with NaCN. [c] Corrected by factor $K/(r + K)$ as per eq 6, where K was assumed to have an average value of 0.8, and $r = Cl^-/CN^-$ ratio at 50% reaction.

e. Effect of Changing the NaCN/RCl Ratio. The effect on displacement reaction rate of increasing the sodium cyanide concentration while all other ingredients are held constant is shown by the data in Table III.

Table III. Effect of Changing the NaCN/1-$C_8H_{17}Cl$ Ratio on the Rate of Cyanide Displacement on 1-Chlorooctane, as Catalyzed by $C_{16}H_{33}PBu_3{}^+Br^{-a}$

Mol of NaCN charged to reaction	Rate constant, k,[c] l./(mol sec)	Mol of NaCN charged to reaction	Rate constant, k,[c] l./(mol sec)
0.336	0.041	0.816	0.044
0.408	0.038	1.020	0.054
0.510	0.043	1.530[b]	0.071
0.611	0.045		

[a] Reaction of 0.337 mol of 1-$C_8H_{17}Cl$, 5.56 mol of water, and 0.005 mol of $C_{16}H_{33}PBu_3{}^+Br^-$, plus the amount of NaCN listed, at 90°; 500 rpm stirring rate. [b] Aqueous phase saturated with NaCN. [c] Corrected by the factor $K/(r + K)$, as per eq 6, where K was assumed to have an average value of 0.8 and $r = Cl^-/CN^-$ ratio at 50% conversion of RCl.

The rather abrupt increase in reaction rate as the aqueous phase becomes saturated with NaCN is evidently due to changes in K which show a similar increase as the aqueous phase becomes saturated with NaCN.

3. State of the Organic Phase Quaternary Salt. Other aspects of interest in sorting out the nature of quaternary ammonium and phosphonium salts as phase-transfer catalysts are their states of aggregation and hydration while in the organic phase. If micelles are formed in the organic phase then one would expect the quaternary salts to be highly aggregated, and that perhaps these reverse micelles would bring small amounts of aqueous sodium cyanide into the organic phase in a form suitable for displacement reaction. To test this possibility the degree of aggregation of several quaternary salts was measured by the method of Walker and Ashby.[7] The results, illustrated in Figure 5, show the quaternary salts to be somewhat aggregated, particularly in benzene solution and at relatively high quaternary salt concentrations. Clearly, the degree of aggregation is not to the extent normally thought to comprise micellization, particularly in bromopropane solutions. However, molecular aggregates of 3–10 for alkylammonium surfactants in nonpolar media have been referred to as "micelles."[8] To say that the quaternary ammonium and phosphonium salts acted as "micellar" catalysts would then imply that a species comprised of an aggregate of 3–10 quaternary salt molecules is required for reaction to proceed in nonpolar media. Comparison of data in Figures 3 and 5 argues against the "micellar catalyst" concept, in that a linear variation of the cyanide displacement rate is observed

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(7) F. W. Walker and E. C. Ashby, *J. Chem. Educ.*, **45**, 654 (1968).

(8) F. M. Fowkes in "Solvent Properties of Surfactant Solutions," K. Shinoda, Ed., Marcel Dekker, New York, N. Y., 1967, p 65; A. Kitahara in "Cationic Surfactants," E. Jungerman, Ed., Marcel Dekker, New York, N. Y., 1970, p 289.

over the quaternary salt concentration range where greatest change in aggregation number is expected. Rather than aggregates, it is believed that single quaternary salt molecules are themselves capable of undergoing facile displacement. Thus the initial 5–10% reaction in cyanide displacements on 1-chlorooctane has often been observed to be about half as fast as the remainder of the reaction. One explanation for this behavior is that quaternary salts change from an average aggregate size of two in pure 1-chlorooctane to one after a small amount of 1-cyanooctane has been formed. The possibility of having NaCN brought into the organic phase by the quaternary salt was checked by analysis of the organic phase for sodium. These analyses showed the sodium content of the organic phase to be less than 10^{-5} mol/l. at quaternary salt concentrations of 0.01–0.1 mol/l., using 1-chlorooctane as the organic phase with $(C_{10}H_{21})_3N^+CH_3Cl^-$ or $(C_{18}H_{37})_2N^+(CH_3)_2Cl^-$ as quaternary salt.

The state of hydration of the quaternary salt was measured by shaking the salt solutions containing tritiated water with solutions of $C_{16}H_{33}PBu_3^+X^-$, where $X^- = Cl^-, CN^-$, and NO_3^-. These measurements were made at various concentrations of quaternary salt in toluene and in 1-cyanooctane. Plots of the tritium assay of the organic phase *vs.* quaternary salt concentration gave straight lines whose slopes were used to calculate the number of gram-atoms of hydrogen associated with each mole of quaternary salt. Assuming that these hydrogens are present in the form of water, the results (as shown in Table IV) are presented in terms of moles of water associated with each mole of quaternary salt. These results demonstrate that the water of hydration is primarily associated with the anion X^-, rather than the quaternary cation. The higher hydration numbers observed with CN^- indicate that the CN^- is more heavily hydrated than Cl^-, and explains why the value of K (*cf.* Table I) decreases as aqueous solutions of NaCl and NaCN are diluted. These data also show that the unusually high displacement rates observed with quaternary salts are not necessarily due to the absence of water of hydration.

Table IV. Hydration State[a] of $C_{16}H_{33}PBu_3^+X^- \cdot nH_2O$

X^-	n
NO_3^-	0.4 ± 0.05
Cl^-	4 ± 0.2
CN^-	5 ± 0.5

[a] At 90° with aqueous solutions saturated with NaX.

In catalyzed, heterogeneous reactions the actual site of the rate-limiting step depends on the nature of the reaction and the catalyst. In the present work, for example, the slow step is an organic-phase displacement, although at low stirring speeds mass transfer across the phase boundary may also restrict rates. Other workers have suggested rate-limiting steps of similar reactions to occur at the interface and in the organic phase,[2a] in the aqueous phase,[9] in normal[3,4] and invert[10] micelles, in liquid crystalline phases,[11] and at phase boundaries.[12,13]

Quaternary salts in nonpolar media are largely in the form of ion pairs, which are normally considered to be relatively unreactive in displacement reactions. However, the remarkable ability of anions associated with quaternary cations in nonpolar media to undergo rapid displacement with alkyl halides was demonstrated by Uglestad, Ellingsen, and Berge.[5] This result may be due to a relatively large separation between cation and anion, such that displacement is readily accommodated, but never so great a separation that electrodes can discern the presence of ions.

Experimental Section

The kinetic experiments were run in an ordinary smooth-wall, three-necked flask, fitted with a flat-bladed stirring paddle, reflux condenser, and sampling port. The stirrer was driven by a "SERVODYNE" laboratory stirrer (Cole-Parmer Instrument Co., Chicago, Ill.) and the temperature was controlled at 90 ± 0.5° by a "THERM-O-WATCH" Electronic Controller (I^2R Co., Cheltenhan, Pa.) attached to narrow-range thermometer. All ingredients were placed in the flask; the mixture was heated rapidly to 90° (*ca.* 5–10 min required). Samples of the organic phase were withdrawn at 5–30-min intervals by stopping the stirrer for 15–30 sec such that the organic phase had separated well enough to get a good sample. Analyses were performed by gas chromatography (12 ft × $^3/_{16}$ in. SE-30 on Chromosorb W at 150°) with the aid of an electronic integrator. The results, when plotted on semilogarithmic paper, gave straight lines from the slope of which could be calculated the pseudo-first-order rate constant, k_1, from which second-order rate constants, k, could be calculated by dividing the catalyst concentration and the correction factor of eq 6.

Hexadecyltributylphosphonium bromide and tetrabutylphosphonium bromide were prepared by the method previously reported.[1] 1-Chlorooctane, 1-bromooctane, sodium cyanide, and other chemicals were used as obtained from commercial suppliers. The rates observed were independent of the source.

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(9) J. Solodar, *Tetrahedron Lett.*, 287 (1971).

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(11) S. I. Ahmad and S. Friberg, *J. Amer. Chem. Soc.*, **94**, 5196 (1972).

(12) F. M. Menger, *Chem. Soc. Rev.*, 1, 229 (1972).

(13) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York, N. Y., Chapter 6.