The relative reactivities shown in Table I were determined by competition reactions performed in the following manner. A mixture consisting of known amounts of two of the cycloalkanes was allowed to react with about a half of an equivalent amount of the halogenating agent. Benzene or chlorobenzene also was added in an amount equivalent to the cycloalkanes to serve as an internal standard for the gas chromatographic analysis. The reactions were performed in sealed tubes, induced with benzoyl peroxide, and allowed to proceed at the indicated temperature until about 30–70% of the halogenating reagent had been consumed. Relative reactivity ratios, that is the ratio of the reaction rate constants of the particular cycloalkanes toward attack by the hydrogen abstracting radical, were calculated in the usual manner using the equation, $\frac{k_A}{k_B} = \log (A_{\text{init}}/A_{\text{fin}})/\log (B_{\text{init}}/B_{\text{fin}})$, where the subscript, init and fin refer to the amounts of the cycloalkanes A and B before and after the reaction, respectively. The value for the amounts of the two cycloalkanes remaining after reaction were obtained by gas chromatographic analysis of the reaction mixtures.

Solubilities of Organic Salts in Hydrocarbons[1]

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It is known generally that salts of large organic ions are more soluble in organic solvents than salts of small inorganic ions. It might be imagined that this is a result of some specific attractive forces between organic molecules. However, solubilities of a wide variety of hydrocarbons in water[2,3] have been correlated by an equation whose derivation specifically assumed that energies arising from van der Waals or London forces were the same for hydrocarbon–hydrocarbon interactions as for hydrocarbon–water attractive forces.

This cancelling out of energies arising from London dispersion forces can be rationalized this way. Let us consider a molecule such as benzene immersed first in water and then in hexane. The energy arising from London forces between two small spherical molecules in the gas phase is given by this well known equation.

$$E = (-3/2)(\alpha_1\alpha_2/r^6)I_1I_2/(I_1 + I_2) \qquad (1)^4$$

The polarizability, α, and ionization potential, I, for benzene are common factors for equation 1 applied to either benzene–water or benzene–hexane. The ionization potentials for water and hexane are 12.5 and 10.5 e.v.[5] Although the absolute difference between these two numbers may seem large, the per cent difference is small when used in equation 1 so that only small energy differences arise from differences in ionization potential. The relative invariance of ionization potential is characteristic of compounds of C, H, O, and N, and these are of primary interest in organic chemistry. When elements such as sulfur, iodine, etc., are introduced, their effect is overshadowed by the mass of hydrocarbon so that, on the average, the effective ionization potential for intermolecular attractions is that of a typical hydrocarbon.

The electronic polarizabilities of water and hexane are 3.70 and 29.8 cm.³/mole.[6] These values initially seem much different, but what governs interaction energies in solution is the polarizability per unit volume of the solvents. These values are 0.21 and 0.23 for water and hexane, respectively. The London dispersion forces will nearly cancel, and this result can be generalized to most systems of interest in organic chemistry.

Table I presents data on the solubilities of a series of R_4NClO_4 salts. It is evident that the solubility in benzene (or ethanol) relative to water increases as the size of R increases. Such results cannot be rationalized by a consideration of ion–solvent electrostatic forces. Such forces must always be greater in water than benzene leading to the erroneous expectation that the salts will always be more soluble in water. Neither can such results be rationalized by a consideration of London forces since the energies arising from such forces cancel, as explained in the preceding paragraph. It is evident that any explanation based only on solute–solvent interaction energies fails.

TABLE I

RELATIVE SOLUBILITIES OF R_4N^+ SALTS (25°)[a]

Salt	Solubility in moles/l.			Relative solubility	
	Water	Ethanol	Benzene	EtOH-H_2O	C_6H_6-H_2O
$KClO_4$[b]	0.149	0.00065		0.0044	
$RbClO_4$[b]	.071	.00039		.0055	
$CsClO_4$[b]	.085	.00037		.0044	
$(CH_3)_4NClO_4$	.075	.00089	0.000165	.0119	0.0022
$(C_2H_5)_4NClO_4$	.217	.0114	.000113	.0525	.00052
$(C_3H_7)_4NClO_4$	.0204	.0149	.000075	.75	.0037
$(C_6H_5)_4NClO_4$	.000187	.00102	.000176	5.45	.94
$(C_5H_{11})_4NClO_4$	.00067	.037	.00111	56	1.67
$(C_6H_{13})_4NClO_4$	.00044	.292	.871	660	2000
$(CH_3)_4NI$[b]	0.26	0.0045		0.017	
$(C_2H_5)_4NI$[b]	1.4	.38		.27	
$(C_3H_7)_4NI$[b]	0.60	.64		1.1	

[a] The solid phase in equilibrium with the saturated ethanol solution was analyzed in each case and shown to be the simple R_4NClO_4 salt (Table II). Data on $(C_4H_9)_4NClO_4$ is omitted because Ralph Seward of Pennsylvania State University found that the phase in equilibrium with the saturated solution in benzene contained benzene in the crystal lattice. The alkyl groups are the straight chain *n*-alkyl groups except for C_6H_5, which is phenyl. [b] Data from A. Seidell, "Solubilities," D. Van Nostrand Co., New York, N. Y., 1960.

The answer lies in solvent–solvent forces and the principle of volume energies.[2,3,7,8] Briefly, it costs energy to make a hole in the solvent to place a solute molecule or ion. This energy is the product of the volume of the hole times the internal pressure of solvent. This energy will be greater for a solvent such as water with its high internal pressure arising from intermolecular hydrogen bonding. In contrast, this energy will be much smaller for most organic liquids in which the intermolecular forces are predominantly London forces.[4] In the series listed in Table I, as the size of R increases,

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(3) N. Deno and H. E. Berkheimer, *J. Chem. Eng. Data*, **4**, 1 (1960).

(4) F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

(5) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, pp. 116 and 122.

(6) Calculated by the familiar relation, $(n^2 - 1)(n^2 - 2)/(M/e)$.

(7) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

(8) H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960); F. H. Stillinger, Jr., "Equilibrium Theory of Pure Fused Salts," a chapter in "Selected Topics in the Physical Chemistry of Molten Salts," Milton Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

the volume energy increasingly favors greater solubility in benzene relative to water. At $(C_4H_9)_4NClO_4$, the volume energy effect equals the effect of the ion–solvent electrostatic energy and the salt is equally soluble in water and benzene. As the size of R increases beyond butyl, the ratio of solubility in benzene to solubility in water appears to increase without limit. The overshadowing of the electrostatic effect by the volume energy is, of course, aided by a decrease in the electrostatic effect with increasing size of R as well as the clustering of ions in the benzene phase.

TABLE II

NITROGEN ANALYSES AND MELTING POINTS FOR TETRAALKYL AMMONIUM PERCHLORATES

$R_4N^+ClO^-$ R	Nitrogen, % Calcd.	 Found a	 b	M.p., °C.
Methyl	8.07	8.15	8.14	
Ethyl	6.10	6.17	6.20	
Propyl	4.90	4.87	5.12	237–239
Butyl	4.10	4.49	4.67	207–209
Pentyl	3.52	3.90	3.89	110–116
Hexyl	3.09	3.15	3.04	105–106

[a] Prepared as described in the Experimental. [b] Precipitated from ethanol.

Two practical results are suggested. If it is desired to conduct a reaction in a hydrocarbon solvent using a small inorganic ion, solubility can be achieved by using a salt of a large counter ion of the size of C_{20} or larger, preferably spherical to minimize micelle formation. Fortunately, such large salts generally have low lattice energies so that the absolute solubility will not be reduced to insignificance by high lattice energies.

The second practical result is that large salts will be extracted from water by organic solvents and may be recrystallized from the organic solvent. These possibilities must be recognized in purification. Lest a misunderstanding arise, proteins, although large salts, will still be more soluble in water than benzene because each hydrogen bond between the protein and water changes the distribution coefficient by about 10^2.[3]

Experimental

The $R_4N^+ClO_4^-$ salts, (R = methyl, ethyl, propyl, and phenyl) were prepared by treating a water solution of $R_4N^+Br^-$ or $R_4N^+I^-$ (commercially available) with perchloric acid and washing with cold water with or without added alcohol to decrease solubility.

For R = butyl, pentyl, and hexyl, the $R_4N^+I^-$ salts were prepared by treating R_3N with RI using procedures patterned after those of Smith and Frank.[9] To prepare the perchlorate, a warm solution of silver perchlorate in ethanol was added to a warm solution of the $R_4N^+I^-$ salt in 95% ethanol. The silver iodide was removed by filtration. Cold water was added to the filtrate and much of the ethanol allowed to evaporate. The precipitated $R_4N^+ClO_4^-$ was filtered, washed with water, recrystallized from ethyl acetate, and washed with ether in that order.

The method used for R = methyl was not applicable for R = C_4–C_6 because the $R_4N^+I^-$ salts were too insoluble in water. The tetraphenylammonium perchlorate is a well known insoluble salt.[10]

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Kinetics of Reaction of Lithium Aluminum Hydride with Terminal Acetylenes in the Presence of Lithium Aluminum Amides[1]

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It has been reported[3] that lithium aluminum amides produced by the reaction of excess lithium aluminum hydride in ethyl ether with primary and secondary amines and amine N-oxides are catalysts for the reaction for lithium aluminum hydride with 1-hexyne in ethyl ether.

$$LiAlH_4 + 4HC{\equiv}C{-}C_4H_9 \longrightarrow LiAl(C{\equiv}C{-}C_4H_9)_4 + 4H_2 \quad (1)$$

With carefully purified 1-hexyne and the initial concentrations of 1-hexyne and lithium aluminum hydride 1 M and 0.25 M, respectively, and at 36°, the half-life of reaction 1 is about twelve hours when a catalyst is not present. The presence of a catalyst can so increase the rate that it has been described as "instantaneous."[3] The reaction of phenylacetylene is similar to that of 1-hexyne except that the phenylacetylene reacts faster than hexyne in the absence of catalyst (half-life about one hour).

The purpose of this note is to report the results of some kinetic studies of the catalyzed reaction with 1-hexyne. Experiments were carried out to determine the dependence of the reaction rate upon the catalyst concentration, the 1-hexyne and lithium aluminum hydride concentrations, and the temperature. The kinetics was found to be complex, but susceptible to an approximate description that permits a comparison of the different catalysts. It was found that, except for the case of the lithium aluminum dicyclohexylamide, the kinetics might be described approximately as first order in 1-hexyne in the following sense: the logarithm of the hexyne concentration is a linear function of the time for at least 70% of the reaction, even when the hexyne was in excess. Analogous plots of the logarithm of the lithium aluminum hydride concentration are not linear for cases in which the hydride was in excess. First-order rate constants were calculated from the slopes of the linear plots. The dependence of the rate constant on the catalyst concentration was found to be approximately linear, *i.e.*

$$k \simeq \alpha M + 2 \times 10^{-5} \text{ (sec.}^{-1}\text{)}$$

where α is a constant, and M is the molar concentration of the catalyst (in terms of amine added). Values of the constants α for all the catalysts studied are given in Table I. A value is given for dicyclohexylamine for comparison purposes, although the reaction in the presence of that catalyst is better described as second order (first order in hexyne and first order in hydride). However, even in this case, when the hydride was in excess plots of the logarithm of the hexyne concentration as a function of the time were sufficiently close to

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(2) To whom inquiries should be sent.

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