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

$R_4N^+ClO^-$	Nitrogen, %			
		Found		
R	Calcd.	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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[9] P. A. S. Smith and S. Frank, *J. Am. Chem. Soc.*, **74**, 509 (1952).

[10] H. Willard and L. Perkins, *Anal. Chem.*, **25**, 1634 (1953).

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.*

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

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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[1] This work was sponsored by the U. S. Army Research Office (Durham).

[2] To whom inquiries should be sent.

[3] G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **82**, 3560 (1960).

linearity to permit one to calculate approximate first-order constants, from which a value of α was calculated.

Activation energies were determined by obtaining rate constants at three different temperatures between 15° and 40°. Since the reaction with no catalyst is very slow at 15° (and also follows no simple rate law, even approximately) it was necessary to use initial rates to determine the activation energy in that case. The activation energies decrease with increasing catalyst concentration and then level off to a constant value. These limiting constant values of E_a are given in Table I for four different catalysts. It is probable that the lower effectiveness (smaller α) of the catalysts from diphenylamine and the dicyclohexylamine is not the result of higher activation energies, but rather of lower frequency factors.

TABLE I

CATALYTIC EFFECTS OF DIFFERENT CATALYSTS

Source of catalyst	α ($\times 10^3$)[a]	E_a (kcal.)
Diethylamine	70 (±10%)	13 (±1)
Di-*n*-propylamine	60	..
Di-*n*-butylamine	55	12
Diisobutylamine	6.5	..
Di-*sec*-butylamine	4.0	..
Diphenylamine	1.0	10
Diisopropylamine	0.8	..
Dicyclohexylamine	0.6	12
No catalyst	..	17

[a] These values are for 36.5° and the units are l. $\times$ mole^{-1} sec.$^{-1}$ The initial concentrations of lithium aluminum hydride and 1-hexyne ranged from 0.33 to 0.41 M and from 1.00 to 1.33 M, respectively.

Experimental

Materials.—1-Hexyne (Farchan) was found to contain traces of catalytic impurities after distillation. In order to remove these, most of the hexyne was treated with 2% hydrochloric acid solution, 2% sodium carbonate solution, washed with distilled water, dried with anhydrous calcium chloride, passed through an alumina column, and then distilled, b.p. 68° (745 mm.). Further treatment had no observable effect. In one case the hexyne was passed over alumina and distilled without the pretreatment with acid, and the results were not noticeably different from those obtained with the hexyne which had been washed with acid.

Phenylacetylene was passed over alumina and distilled, b.p. 140° (730 mm.).

The liquid amines were freshly distilled; diphenylamine was Fisher Certified. Dilute ether solutions were made and then stored under refrigeration.

The preparation of the lithium aluminum hydride solution has been described elsewhere.[3]

Apparatus.—The apparatus and method used to determine the reaction rates by following the hydrogen evolution previously has been described.[3] The reacting mixture was maintained under reflux and the temperature was varied by adding the appropriate amount of butane or hexane, or a mixture of these, to the ether solution. The total volume of hydrocarbon added never exceeded 21% of the total volume and no significant solvent effect other than the temperature effect was observed.

Error Estimates.—The estimated error of ±1 kcal. for the activation energies is based on the maximum scatter that was observed. Most points were within ±0.5 kcal. of the values given in Table I.

It was impossible to obtain a good estimate of the error in the values of α. The most rapid reactions were less reproducible than the slower ones. With some of the catalysts there was a definite decrease in the value of the rate constant with increasing initial lithium aluminum hydride concentration. This effect was not studied in detail and causes an increase in the uncertainty in the values of α. However, it is not likely that the error is great enough to cause the true relative order of the catalysts to be different from that shown in Table I.

A Convenient Preparation of Allyllithium[1]

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The recently reported preparation of allyllithium by the metal–metal exchange reaction between allyltin derivatives and organolithium compounds[3] has made accessible pure samples of this reactive organolithium compound. The chemical versatility of allyllithium has been exploited for the preparation of allyl derivatives of both metal and organic substrates in high yields.[3,4] However, the necessity of employing allyltin and organolithium starting materials detracts from the convenience of the method. On the other hand, alternate approaches to allyllithium, such as the interaction of allylsodium with lithium chloride,[5] the treatment of allyl Grignard reagents with metallic lithium,[6] and the cleavage of allyl halides by lithium,[3,7] are less advantageous and often low-yielding processes. Wurtz coupling, leading to biallyl, is a prominent side reaction when allyl halides are exposed to lithium metal.[3,7]

As a sequel to the observation that anisole could be cleaved by lithium–biphenyl adducts in refluxing tetrahydrofuran (THF) solution,[1c,8] the analogous cleavage reaction of allyl phenyl ether was investigated. Indeed, the cleavage of the allyl ether by the 2:1 lithium–biphenyl adduct proceeded rapidly even below 0°. Subsequently, it was found that lithium metal alone in tetrahydrofuran readily cleaved allyl phenyl ether at −15° to form allyllithium and lithium phenoxide[9] (equation 1).

$$\mathrm{CH_2{=}CH{-}CH_2{-}O{-}C_6H_5 + 2Li \xrightarrow[-15^\circ]{THF} CH_2{=}CH{-}CH_2Li + C_6H_5{-}O{-}Li} \quad (1)$$

The yields of allyllithium, as determined by the double titration method of Gilman and Haubein,[10] ranged from 45%, in runs using stoichiometric quantities of lithium metal, up to 65%, when a sixfold excess of lithium was employed. Yet in instances where the yields of allyllithium also were determined by formation of chemical derivatives and subsequent isolation of the pure product (*cf. infra*), the resultant figures were ap-

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[1] Paper IV in the series, Chemistry of Alkali Metal–Unsaturated Hydrocarbon Adducts. Previous papers are (a) J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, **27**, 3745 (1962); (b) J. J. Eisch and R. M. Thompson, *ibid.*, **27**, 4171 (1962); and (c) J. J. Eisch, *ibid.*, **28**, 707 (1963).

[2] Undergraduate Research Participant, National Science Foundation, 1962.

[3] D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959); **26**, 4797 (1961).

[4] D. Seyferth and M. A. Weiner, *Org. Syn.*, **41**, 30 (1961).

[5] E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).

[6] T. E. Londergan, U. S. Patent 2,734,091 (February 7, 1956).

[7] W. Kawai and S. Tsutsumi, *J. Chem. Soc. Japan, Pure Chem. Sect.* **81**, 109 (1960), report the preparation of allyllithium from allyl halides and lithium metal in ethyl ether solution. However, subsequent workers (ref. 3) were unable to achieve satisfactory results with this approach.

[8] J. J. Eisch and W. C. Kaska, *Chem. Ind.* (London), 470 (1961).

[9] Although the presence of biphenyl had little discernible effect upon the yields of allyllithium obtained from allyl phenyl ether and lithium metal, small amounts of biphenyl served as an excellent initiator for the cleavage. (*Cf.* Paper III of this series, *J. Org. Chem.*, **28**, 707 (1963), for the role of lithium–biphenyl adducts in such cleavage reactions).

[10] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).