The equilibrium constant for cyclization depends on the molecular weight, e.g., at 25° it is found to be about 5 for D.P. $\sim$ 25, and less for higher D.P. values.

Steric reasons make it obvious that the cyclization caused by the anthracene addition cannot take place with the living α-methylstyrene dimer, and consequently this two-living-ended oligomer reacts quantitatively with anthracene, adding 2A per $^-\alpha\alpha^-$ in the course of the very fast reaction.

In the reaction of one-ended living polystyrene the dilution makes the association of $\sim$S,$^-$A,Na$^+$ with $\sim$S$^-$,Na$^+$ relatively slow, and consequently anthracene competes favorably for $\sim$S$^-$,Na$^+$. Thus virtually 100% of conversion is achieved in fast reaction, although more accurate experiments show that in this step the conversion is always slightly lower than 100%.

The described phenomenon should be kept in mind when studying the reactions of two-living-ended low molecular weight polymers. For example, the carboxylation may give cyclic ketones instead of dicarboxylic acids, since after the addition of the first molecule of CO_2 to one end the other may react with the formed carboxylate and eventually give the ketone derivative. Such processes may account for synthetic difficulties experienced by some workers in this field.

The detailed kinetic studies of the fast and slow stages of the anthracene addition are now in progress and the results will be reported later.

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Nuclear Magnetic Resonance Study of Weak Acids in Liquid Ammonia

Sir:

Because liquid ammonia is a basic solvent with a very low self-ionization constant (2 × 10^{-28} at 25°),[1] it can serve as a solvent for comparing the acidities of weak acids over an enormous span of pK values. We have found that n.m.r. spectroscopy in ammonia is a useful tool for determining relative acidities and for measuring rates of proton exchange between acids and ammonia.

Acids can be roughly divided into three categories based on their behavior in liquid ammonia. (1) Relatively strong acids (aqueous pK less than $\sim$15) exchange their acidic protons rapidly with ammonia. Malononitrile (aqueous pK = 11.14)[2] is an example of this type; ammonia solutions of this acid show only one proton resonance, which is a time-averaged signal of the solvent and acid protons. (2) Acids of intermediate strength (aqueous pK $\sim$ 15-42) exchange their acidic protons slowly with ammonia and yield appreciable amounts of their corresponding anions only upon the addition of amide ion. We have studied several examples of this type; the results are discussed below.

(1) L. V. Coulter, J. R. Sinclair, A. G. Cole, and G. C. Roper, *J. Am. Chem. Soc.*, **81**, 2986 (1959).
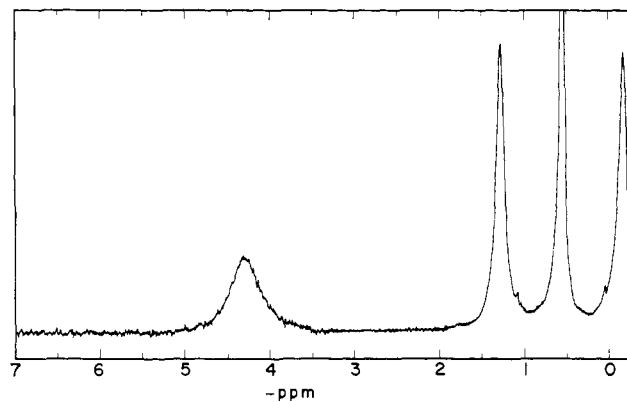(2) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

Figure 1. Proton n.m.r. spectrum of a solution of 0.86 M water in liquid ammonia saturated with sodium hydroxide.

(3) Very weak acids (aqueous pK greater than $\sim$42) exchange their protons slowly and do not react appreciably with the amide ion. Toluene (aqueous pK $\sim$ 59)[3] is an example of this type.

A solution of an acid of the second category together with its anion generally shows distinct n.m.r. signals for both the acid and the anion. The spectrum of the solvent ammonia is observed as a sharp multiplet ($J_{N^{14}-H}$ = 43.5 c.p.s.; $J_{N^{15}-H}$ = 61 c.p.s.) or in various states of collapse, depending on the acid and the acid-to-anion ratio. Thus acetophenone (aqueous pK $\sim$ 19)[3] and indene (aqueous pK $\sim$ 21),[3] in the presence of their anions, give spectra in which the ammonia triplet is sharp and in which the N^{15} satellite peaks are easily seen. This indicates that proton exchange is negligible in these solutions. However, in solutions of cyclopentadiene (aqueous pK $\sim$ 15)[3] and sodium cyclopentadienide, the triplet can be made to collapse by increasing the acid-to-anion ratio. This result suggests that the collapse of the triplet is due to the exchange reaction

$$NH_4^+ + NH_3 \rightleftharpoons NH_3 + NH_4^+$$
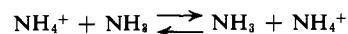
The ammonium ion concentration, and hence the rate of the exchange reaction, would be expected to increase with decreasing pK of the acid and increasing acid-to-anion ratio. We have usually found collapse of the acidic proton signal and the ammonia signal to a single sharp line in plain solutions of acids stronger than cyclopentadiene (o-nitroacetanilide, malononitrile, and diethyl malonate). Nitromethane (aqueous pK $\sim$ 10)[3] is an exception; separate sharp lines are observed for the nitromethane and the ammonia. This result is consistent with the slowness of the reactions of nitromethane in aqueous systems.[4]

We have also examined the behavior of some acids of the type ROH, where R = hydrogen, methyl, isopropyl. The n.m.r. spectra of solutions of these acids, in the presence of their anions, show the ammonia triplet, the shape of which depends upon the acid and the acid-to-anion ratio. Separate peaks characteristic of the acid and anion are not observed but only an averaged spectrum: the acidic proton exchanging between the acid and anion sites. The

(3) D. J. Cram, *Chem. Eng. News*, **93**, 92 (Aug. 19, 1963).
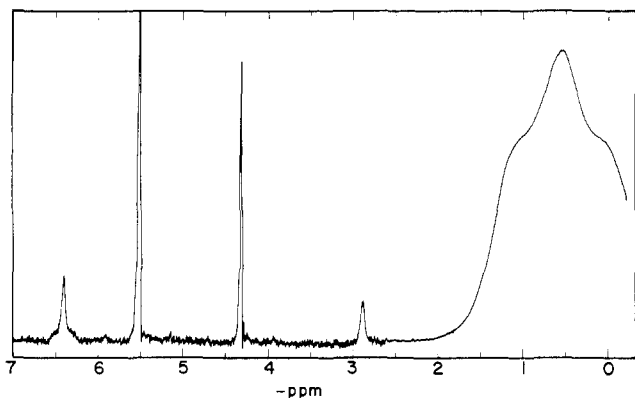(4) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

Figure 2. Proton n.m.r. spectrum of a solution of water in liquid ammonia buffered with cyclopentadiene and its anion.

spectrum of a solution of 0.86 M water in liquid ammonia saturated with sodium hydroxide is shown in Figure 1. The peak at -4.32 p.p.m. from external tetramethylsilane, corresponding to the water protons, is broadened because of exchange with hydroxide. The solvent signal is a sharp triplet, indicating that the ammonia is not taking part in the exchange process to any appreciable extent. A solution 6 M in water and 0.02 M in sodium hydroxide gives a partially collapsed ammonia triplet.

Figure 2 shows the n.m.r. spectrum of a solution of water in ammonia buffered with cyclopentadiene and its anion. The peaks at -6.43 and -2.91 p.p.m. are due to cyclopentadiene, that at -5.56 p.p.m. is due to the cyclopentadienide ion, and the sharp resonance at -4.32 p.p.m. is due to water. No precipitation of sodium hydroxide is observed. These observations indicate that water is a weaker acid than cyclopentadiene and that it does not exchange rapidly with ammonia. Ogg[5] has suggested a rate constant of approximately 4.6×10^8 l. mole^{-1} sec.$^{-1}$ for the reaction

$$H_2O + NH_3 = OH^- + NH_4^+$$
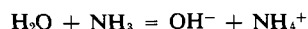
but a rate constant closer to that found for the analogous reaction of ethyl alcohol with ammonia (0.0303 sec.$^{-1}$) would seem more appropriate.[6] The exchange of water in unbuffered liquid ammonia solutions may be explained by a mechanism involving ammonium ion

$$NH_4^+ + \overset{H}{\underset{|}{O}}-H + NH_3 \rightleftharpoons NH_3 + H-\overset{H}{\underset{|}{O}} + NH_4^+$$
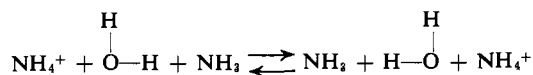
A similar mechanism has been shown to operate in aqueous solutions of ammonium ion.[7]

(5) R. A. Ogg, Discussions Faraday Soc., 17, 215 (1954).
(6) W. L. Jolly and C. J. Hallada, in "Non-aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965.
(7) S. Meiboom, A. Loewenstein, and S. Alexander, J. Chem. Phys., 29, 969 (1958).

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Reaction of Thermal Carbon Atoms in Solids. Relation to Properties of Vapor-Deposited Carbon

Sir:

In recent years extensive investigations have been made of the properties of free carbon atoms[1] in the form of C[11] (20 min.) as produced by nuclear reaction. With hydrocarbons the most common primary reactions have been shown to be addition to the C—H and C=C bonds.[2] The resulting adducts undergo secondary processes, the nature of which depend on (1) the internal excitation and spin state of the adduct[2] and (2) the character and phase of the surrounding molecules.[2,3]

The effect of the first factor has been investigated making use of the fact that C[11], as produced by nuclear recoil, has excess kinetic energy. It has been shown that in pure hydrocarbons carbon atoms will usually react while still moderately "hot."[2,4,5] The adducts formed are therefore highly excited and unless rapidly deactivated by collision are likely to undergo extensive decomposition. Thus the reaction of recoil C[11] with pure gaseous hydrocarbons usually leads to a large yield of acetylene.[6] On the other hand, if the carbon atoms are thermalized prior to reaction by diluting the system with a large excess of inert noble gas moderator, the adducts are less excited and less likely to fragment to form products such as acetylene. (However, they are still sufficiently excited by the energy released on binding the carbon atom that in excess neon, a poor deactivator, there is still substantial acetylene yield.) This competition is shown in outline form in Figure 1.
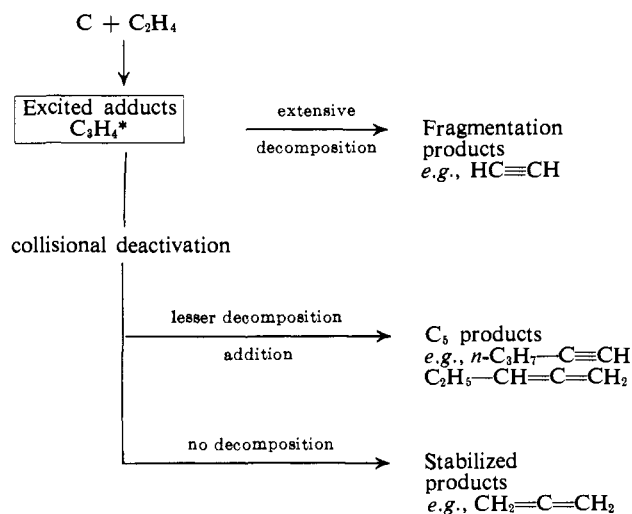

Figure 1. Outline of competing modes of reaction of adducts formed by carbon atom insertion into C—H and C=C bonds (see ref. 2).

(1) For recent reviews see A. P. Wolf, Advan. Phys. Org. Chem., 2, 201 (1964); R. L. Wolfgang, Progr. Reaction Kinetics, in press; C. MacKay and R. Wolfgang, Science, 148, 899 (1965).
(2) (a) M. Marshall, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc., 86, 4741 (1964); (b) J. Dubrin, C. MacKay, and R. Wolfgang, ibid., 86, 4747 (1964).
(3) G. Stocklin and A. P. Wolf, ibid., 85, 229 (1963).
(4) C. MacKay, P. Polak, H. E. Rosenberg, and R. Wolfgang, ibid., 84, 308 (1962).
(5) J. Dubrin, H. E. Rosenberg, R. Wolfgang, and C. MacKay, Proceedings of the Symposium on Chemical Effects Associated with Nuclear Reactions, I.A.E.A., Vienna, 1964.
(6) C. MacKay and R. Wolfgang, J. Am. Chem. Soc., 84, 2399 (1962).