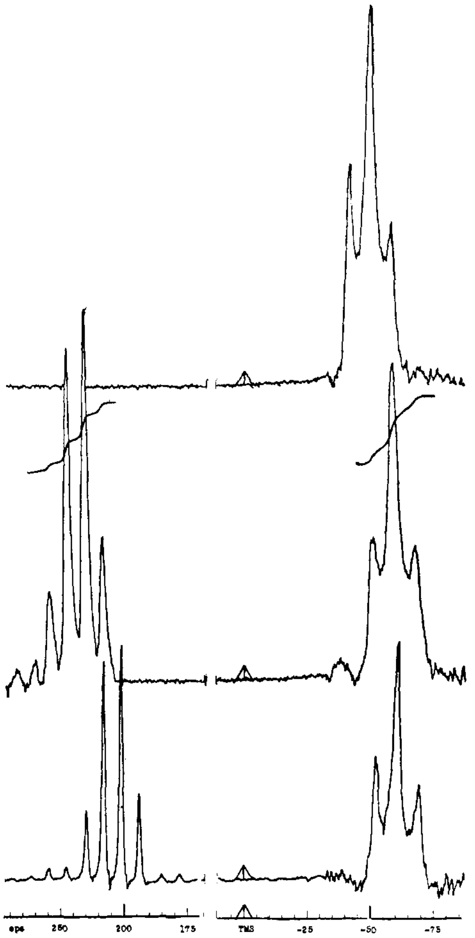

Fig. 2.—Methylene p.m.r. signals in hexane solutions. Upper curve from 1.6 mmoles of BuLi; center curve is the same, with 0.76 mmole of Et_2O; lower curve is the same, with 5.3 mmoles of ether and lower spectrum amplitude in 200-c.p.s. region.

of the BuLi methylene triplet is the properly weighted average between −50 and −59 c.p.s. Finally, and of greatest significance, *no amount of Et_2O in excess of that necessary to complex the organometallic causes any further change in the BuLi methylene signal;* the signal is −59 c.p.s. for dilute solutions of BuLi in Et_2O alone.

This fact, that the chemical shift does not change for the complexed BuLi methylene signal as the solvent changes from hexane to ether, must mean that the 1:2 complex persists in ether. This persistance is corroborated by an earlier observation that the change in BuLi chemical reactivity is slight in going from hexane solvent to Et_2O solvent, so long as sufficient Et_2O is always present to form a 1:2 complex.[1]

Freezing point depressions by Et_2O and BuLi and their mixtures were determined in cyclohexane. For example, when Et_2O and BuLi were mixed in the 1:2 mole ratio in cyclohexane to give 0.75 total stoichiometric molality, the freezing point depression was 5°, indicating only 0.25 actual molality. Ether itself causes a normal 20° molal freezing point depression of cyclohexane, while BuLi causes a depression of only one fourth that, indicating a tetramer for BuLi in the pure hydrocarbon.[3] We propose that *a symmetrical tetramer is formed by quadrapole association of two dimers, i.e.,* two $(BuLi)_2$ units from structure I, face-to-face, with the Li–Li axis of one orthogonal to that of the other. Ether unsymmetrically solvating the dimer, as in I, should result in significant dielectric character for the complex. Indeed, so great is the rise in dielectric constant of BuLi in hexane when just 0.5 mole equivalent of Et_2O is added (and so little the influence of additional ether), one can titrate butyllithium in hexane to a sharp end point with ether by simple high frequency methods.[4]

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The Hydrogen–Graphite Reaction between 360 and 800°

Sir:

The thermal reaction of hydrogen with graphite has been one of the least investigated heterogenous reactions.[1,2] This is due principally to the very low reaction rates involved. Packed column gas chromatography in conjunction with a flame ionization detector[3] has enabled us to study this reaction at temperatures as low as 360°. Although methane remained the principal product, the formation of five higher hydrocarbons below 650° provides a new insight into the reaction mechanism.

The experiment was conducted with a quartz tube reactor charged with 66 g. of spectroscopic grade graphite rods (United Carbon Products Co., ash content <10 p.p.m.). Ultrapure hydrogen (California Oxygen Co.) was further purified over a palladium catalyst and passed through a liquid nitrogen trap before entering the reactor. A Wheelco regulator controlled the furnace temperature within 3°.

After initially outgassing the graphite under vacuum for 24 hr. at 1000°, hydrogen was passed over the material an additional 6 hr. at 90 cm. pressure. This technique[4,5] has been found effective in removing any surface oxide which would interfere with the reaction. The reactor next was cooled to a predetermined temperature and, after allowing 1 hr. for thermal equilibrium, sealed off under pressure. These static runs lasted from 1 min. to 100 hr. The reaction products were analyzed on a 2-m. silica gel column, operated at 190° in series with a flame ionization detector.

Below 580° the reaction was zero order with respect to hydrogen at pressures of 90 to 180 cm. In this pressure-independent region, two distinct Arrhenius activation energies were measured. The inflection point was 515°, where the activation energy dropped from 70 to 12 kcal. per mole. Corney and Thomas,[6] working with a different grade of graphite, observed this inflection at about 600°. The reaction order gradually increased above 580° and reached 0.6 at 800°. This transition region probably extends to 1000°, where the reaction is first order[2] with an activation energy of 85.5 kcal. per mole. The rate constant for methane production varied from 2.0×10^{-16}

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[6] N. S. Corney and R. B. Thomas, United Kingdom Atomic Energy Authority Report AERE-C/R 2502 (Unclassified) Harwell, England, 1958.

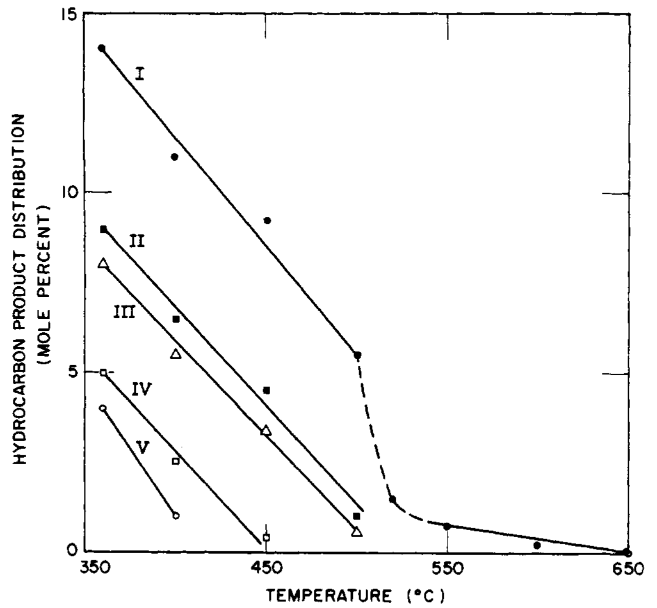

Fig. 1.—Hydrocarbon product distribution *vs.* temperature. Ethane (I), propane (II), ethylene (III), propylene (IV), butane (V), balance methane.

(360°) to 3.3 × 10^{-12} mole per g. sec. (800°). The maximum methane concentration did not exceed 0.01 mole % with no indication of an equilibrium state within this concentration range. The minimum reaction temperature appeared to be between 350 and 360°, where the rate dropped off by two orders of magnitude. The reproducibility of the rates, over a four-month period, indicated a negligible contribution from aliphatic carbon and structural defects. When powdered graphite (100 mesh) replaced the rods, the reaction rates remained the same. This revealed the absence of any mass transport effects.

Probably the most interesting result of this experiment was the increasing proportion of five higher hydrocarbons in the reaction products below 650° (Fig. 1). While the molar ratios of all hydrocarbons to hydrogen remained well below the equilibrium values,[7] the molar ratios of the higher hydrocarbons to methane gradually exceeded the equilibrium ratios as the temperature was lowered. At 360° and 1 atm. of hydrogen, less than 0.1 mole % of these higher hydrocarbons can be expected in the product; yet, they were found to account for some 40 mole % of all hydrocarbons formed.

A mechanism for the hydrogenolysis of graphite has been suggested by Zielke and Gorin.[8] The first step in the proposed reaction is the hydrogenation of exposed edges of the graphite lattice (Fig. 2). It is generally agreed that these are the active sites.[9,10] Six general bond types based on the relative saturation of the attached carbons are indicated. The rate of the first-order reaction above 1000° is probably controlled by the rate of hydrogenation of initially unsaturated "a" bonds, which are the weakest[11] and most exposed. This is supported by the close agreement between the reaction activation energy[2] and the activation energy of hydrogen chemisorption[9] above 1000°. In the transition region, between 1000 and 580°, an increasingly larger fraction of "a" bonds are probably saturated as the reaction order changes from zero to first. The implication of the zero-order reaction below 580° is that the rate-determining step is now the cleavage of saturated "a" bonds; followed by a fast "b" bond cleavage with hydrogenation to form methane.

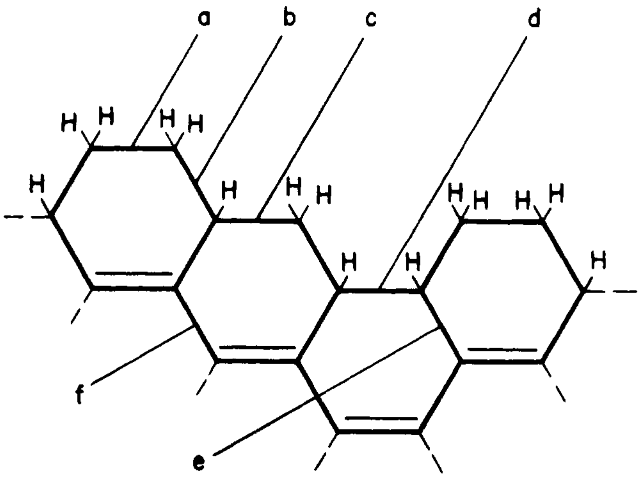

Fig. 2.—Schematic of hydrogenated graphite lattice edge.

The large buildup of ethane and higher hydrocarbons in the reaction products below 515° indicates that "b" and closely related "c" bonds are beginning to cleave at rates comparable to "a" bonds. Besides leading to methane formation, a "c" bond cleavage should promote the breaking of adjacent "a" bonds, which now would be part of a more exposed and saturated hexagon, approaching that of cyclohexane. This effect could account for the lower activation energy of methane formation below 515°.

The stepwise cleavage of alternate saturated "b" bonds with hydrogenation accounts for ethane, while the somewhat less likely simultaneous cleavage of the same bonds without hydrogenation explains the formation of ethylene. Propane formation is governed by the "b–e–d" bond cleavage sequence, while the "b–e–b" sequence accounts for butane. It is significant that no isobutane was detected, even though its equilibrium concentration should be greater than butane.[7] This is reasonable since its formation would involve two unlikely "f" bond cleavages.

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[10] R. E. Nightingale, Ed., "Nuclear Graphite," Academic Press, New York, N. Y., 1955, p. 425.

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On the Role of the Methionine-13 Sulfur in Pancreatic Ribonuclease[1]

Sir:

Hofmann, *et al.*,[2] have shown that S-protein (the subtilisin-produced 104 residue carboxyl terminal part of ribonuclease) can be 70% activated by a synthetic polypeptide containing only the first 13 of the missing amino terminal 20 residues. This synthetic peptide ends in histidine-12-methionine-13, and a peptide lacking these two residues was shown not to activate S-protein. A tridecapeptide very similar to the synthetic one can be readily obtained by cyanogen bromide

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