$$\bigcirc \rightarrow \bigoplus + e \quad I_\text{p} \quad \text{(ionization potential)} \tag{2}$$

$$\bigoplus \rightarrow \bigoplus \cdot sp^2 \; L\cdot \quad \text{(localization energy)} \tag{3}$$

$$\bigoplus \cdot sp^2 \rightarrow \bigoplus \cdot sp^3 \; -E_\text{h} \quad \text{(rehybridization energy)} \tag{4}$$

$$Y^+ + e \rightarrow Y\cdot \quad -E_\text{a} \quad \text{(electron affinity of } Y^+) \tag{5}$$

$$Y\cdot + \bigoplus \cdot sp^3 \rightarrow \bigoplus \diagdown \begin{matrix} Y \\ H \end{matrix} \; -E_\sigma \quad (\sigma\text{-bond energy}) \tag{6}$$

$$\bigcirc + Y^+ \rightarrow \bigoplus \diagdown \begin{matrix} Y \\ H \end{matrix} \; \Delta E \tag{7}$$

$$\Delta E = I_\text{p} + L\cdot - E_\text{h} - E_\text{a} - E_\sigma \tag{8}$$

The more conventional localization energy L, where M and M^+ are the total π-energies of the aromatic hydrocarbon and the carbonium ion I, is given by eq. 9 in units of the resonance integral β.

$$L = M - M^+ \tag{9}$$

where $L\cdot$ is related by

$$L\cdot = (M - m) - M^+ = L - m \tag{10}$$

and m is the energy of the highest filled molecular orbital.

$$\Delta E = Ip + L - m + \text{constant} \tag{11}$$

If L and m are self-consistent field energies then the energy of the highest filled molecular orbital, m, is equal to the ionization potential and E is simply a
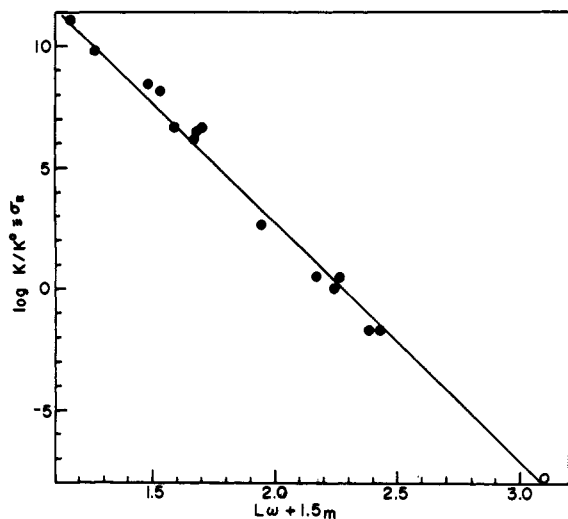

Figure 1. Logarithm of relative equilibrium constants for protonation in HF as a function of $L^\omega + 1.5m$, taken from ref. 1.

function of the SCF localization energy L. In the Hückel approximation, however, m is not equal to Ip; it is, however, linearly related, and from

$$Ip = km\beta + \text{constant} \tag{12}$$

$$\Delta E = L + m(k - 1) + \text{constant} \tag{13}$$

where L may be L^+ or L^ω and k may be evaluated from the slope of a plot of ionization po-
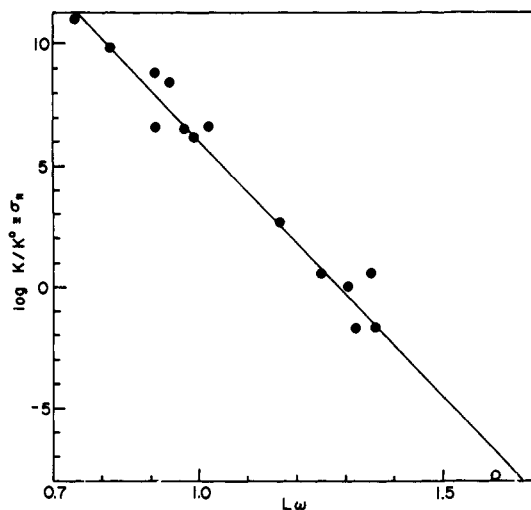

Figure 2. Logarithm of relative equilibrium constants for protonation in HF as function of L^ω, taken from ref. 1.

tentials[1] as a function of m, the highest filled Hückel molecular orbital energies. At the moment a certain arbitrariness is necessary in the value of k since it depends on the choice of ionization potentials of the hydrocarbons and the value of the resonance integral. The particular value of $k = 2.5$ results from the ionization potentials of Wacks and Diebler[5] and empirical resonance energies for the hydrocarbons of $\beta = 0.9$ to 1.0 e.v.

A plot of the log of the equilibrium constant,[1] divided by that for naphthalene, for protonation in hydrogen fluoride of 11 condensed aromatic hydrocarbons, including pyrene and perylene, as a function of $L^\omega + 1.5m$[6] has a standard deviation of 0.4 σ_r unit (Figure 1). The σ_r value 7.8 of benzene is supplied in Figure 1 as the missing protonation equilibrium constant. A reference plot is given in Figure 2 for basicity as a function of L^ω alone; here the standard deviation is 0.8 σ_r unit. The $L^\omega + 1.5m$ function is thus a considerable improvement over other functions. Similarly, the $L^+ + 1.5m$ function with a standard deviation of 0.8 σ_r is an improvement, although not as large, over the L^+ function, standard deviation 1.0 σ_r. Furthermore, pyrene and perylene no longer deviate significantly from the $L^+ + 1.5m$ regression.

(5) M. E. Wacks and V. H. Diebler, J. Chem. Phys., 31, 1557 (1959).
(6) Values of m taken from E. Heilbronner and J. W. Murrel, J. Chem. Soc., 2611 (1962).

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Ionic Strength as a Factor in a Thiocyanate-Induced Reduction of Acidified Trivalent Gallium on Mercury. A Doublet Admittance Peak in Salicylate Media[1]

Sir:

One result of a prior study[2] dealing with the dropping gallium amalgam electrode was the unanticipated find-
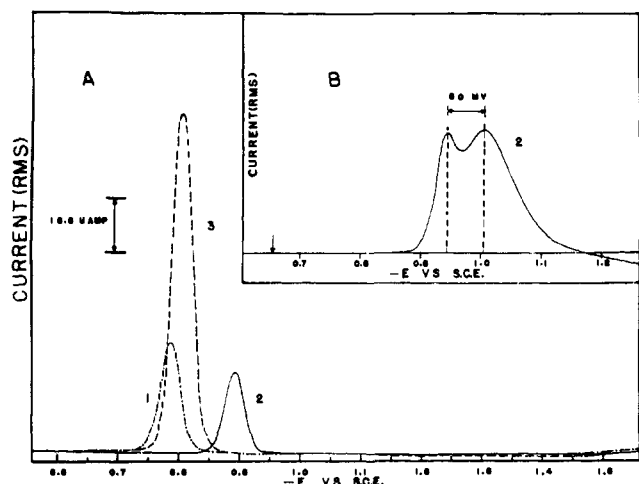
Figure 1. (A) Thiocyanate-induced Ga(III) admittance peak for different 5 *M* base electrolytes (pH 2, signal frequency-locked): curve 1, 5 *M* LiCl, 0.1 *M* in KSCN; curve 2, 5 *M* KSCN; curve 3, 5 *M* NaClO₄, 0.5 *M* in NaSCN. (B) Ga(III) admittance curve for a solution (pH 4, signal phase-locked at the potential indicated by the arrow) 0.1 *M* in salicylate, 1 *M* in KSCN. For A and B, Ga(III) concentration, 1.8 m*M*; 50 c.p.s., 10 mv., r.m.s., 30°.

ing that the Ga(III)–Ga(0) couple is rendered polarographically reversible in acidified solutions concentrated in thiocyanate (>5 *M*), despite reports[3] which picture the slow, over-all gallium reduction rate at the dropping microelectrode ($E_{1/2}$ = −1.05 to −1.1 v. *vs.* s.c.e., a figure 0.3 v. more negative than the corresponding $E°_{Ga(s)}$) to be virtually immune to acceleration by halides, even of high concentration, or to the presence of such complexing organic substances as, *e.g.*, salicylate[3d,e] or catechol.[3c]

This paper describes several preliminary results recently obtained from low-frequency (<100 c.p.s.) alternating current studies of gallium at the d.m.e. which (1) indicate that Ga(III) reduction at pH 4 in salicylate or salicylate–KSCN base electrolytes, heretofore depicted as a single irreversible d.c. step,[3c,d,e] is actually comprised of two overlapping processes separated in potential by 60 mv.; and (2) reveal that, though a rapid or reversible rate of Ga(III) reduction seems indeed dependent upon the presence in solution of thiocyanate, the extent of this effect appears conjunctively determined by the ionic strength of the solution.[4]

Alternating current polarograms of Ga(III) solutions either (a) 5 *M* in LiCl, (b) 5 *M* (saturated) in KBr, (c) 0.5 *M* in KBr, 5 *M* in NaClO₄, (d) 1 *M* in NaI, (e) 0.1 *M* in KSCN, or (f) 5 *M* in NaNO₃ or NaClO₄, yielded entirely "flat" base-line currents, except for a

shallow convexity centered at −1.7 v. which, from separate studies,[5] was ascribed to slow proton reduction.

In sharp contrast to the catalytic influence of halides and pseudo-halides on the irreversible reduction of In(III)[6] and other tightly aquated cations, the absence of Ga(III) current (admittance) peaks for solutions a through e above substantiates the more or less "totally" irreversible nature of Ga(III) reduction in these media.[7] As anticipated from d.c. studies,[2] gallium solutions 7.5 *M* in KSCN afforded a clearly defined, first-harmonic peak (39 μa., E_p = −0.90 v. *vs.* s.c.e.) which, nonetheless, exhibited asymmetry as revealed by the depressed forward lobe of the second harmonic polarogram.

It was therefore surprising, in view of these facts, to discover a much larger peak produced on adding thiocyanate in small concentration to a gallium solution 5 *M* in NaNO₃. Extensive measurements made among different electrolytes at ionic strengths of 5 to 5.5 (pH 2) were more revealing and gave results several of which are summarized in Figure 1A. Curves 2 and 3 show that on simply switching from 5 *M* KSCN to 5 *M* NaClO₄, 0.5 *M* in KSCN, there resulted a faradaic peak (124 μa.) which was larger than previous by a factor of 4.1 and less reducing by 100 mv., although thiocyanate was present a decade lower in concentration; such might be expected of a process dependent upon an intermediate Ga–SCN complex ion. A 40-μa. peak slightly more positive than curve 3 and larger in size than curve 2 (30 μa.) was found for gallium in 5 *M* LiCl, 0.1 *M* in KSCN (curve 1). No peak was found in 0.1 *M* KSCN alone, and since a Ga(III) reduction had not been observed previously in 5 *M* LiCl, it was concluded that the thiocyanate-dependent reduction of Ga(III) is functionally dependent for its occurrence upon conditions of high solution ionic strength.[8] Notwithstanding the chloride concentration at which curve 1 was obtained, its position relative to curve 3, coupled with the absence of any peak activity in other concentrated halides, affords good evidence that the reaction in this case does not occur *via* a Ga(III)–chloro species or ion pairing involving chloride, despite anion-exchange and solvent-extraction data[9] which underscore the formation of such entities under similar solution conditions. It is believed that this is the first reported instance where the rate of reduction of a metal cation has been observed to be specifically influenced by a conjunctive action of thiocyanate and ionic strength. Results gained thus far point to a unique action of thiocyanate and may intimate an ion-pair mechanism involving this anion, though this could only prove conjectural in the absence of more definitive information. Experiments are under way to ascertain generally the effects of other linear isoelectronic anions.

(3) (a) See ref. 2 for citations to potentiometric and voltammetric studies reported prior to 1959; (b) N. Crabb, Ph.D. Dissertation, Ohio State University, 1961; *Dissertation Abstr.*, 22, 3362 (1962); (c) A. Zelyanskaya and L. Kukalo, *Zh. Anal. Khim.*, 18, 726 (1963); (d) M. S. Zakharov, *ibid.*, 18, 450 (1963); (e) K. Sagadieva, *ibid.*, 19, 677 (1964).

(4) Measurements were made with a 10-mv. r.m.s. signal at 50 c.p.s. on air-free solutions thermostated at 30 ± 0.05° using a fairly conventional operational amplifier setup which was, however, either frequency-locked (Hewlett-Packard 302A) or phase-locked (Princeton Applied Research JB4) onto the desired current signal. Owing to observed peak-to-base current ratios, reported peak currents correspond to an arithmetic rather than vectorial correction for capacitance current and are probably correct only to within 5%. Reagent material, triple distilled grade water, and oxine-standardized Ga(III) were employed throughout. All test solutions were 1.8 m*f* in Ga(III) of nominal pH 2.0 ± 0.5 unless noted.

(5) E. D. Moorhead, unpublished results, Rutgers, 1964.

(6) A. J. Engle, *et al.*, *Anal. Chem.*, 37, 203 (1965); see also E. D. Moorhead and W. M. MacNevin, *ibid.*, 34, 269 (1962).

(7) B. Breyer and H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York, N. Y., 1963.

(8) See D. Sellers, *et al.*, *J. Am. Chem. Soc.*, 87, 1206 (1965), and L. Gierst in "Transactions of the Symposium on Electrode Processes," E. Yeager, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 109 ff., for review discussions of ionic strength effects on electrode processes.

(9) K. Krause, *et al.*, *J. Phys. Chem.*, 58, 11 (1954); R. Herber and J. Irvine, *J. Am. Chem. Soc.*, 76, 987 (1954).

Gallium reduction was examined in 0.1 M sodium salicylate (pH 4) in the presence and absence of 1 M KSCN in view of reports[3a,d,e] asserting that the gallium d.c. step is more clearly defined in such media. Admittance curves nearly identical as to position and morphology were obtained for these separate solutions, each giving evidence of two close-lying peaks, which were then made more clearly distinguishable by phase elimination of the 4.5-μa. background current; one such curve is shown as Figure 1B. The current minimum at -0.97 v. vs. s.c.e. coincides closely (considering possible differences in junction potential) with the d.c. half-step value of -0.988 v. reported previously.[10] Though a possible stepwise reduction of Ga(III) is not excluded, it would seem more reasonable at this juncture to suspect that the peaks, located at -0.95 and -1.01 v. vs. s.c.e., correspond to the reduction of two different Ga(III)–salicylate complex ions. This point is being pursued.

(10) E. Vinogradova and N. Chudinova, Zavodsk. Lab., 22, 1280 (1956); Chem. Abstr., 51, 11131b (1957).

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Monocarbahexaborane(7)[1]

Sir:

Over the past several years the discovery and characterization of a considerable number of two-carbon carboranes have been reported.[2] In the course of investigating the products of an electric discharge of 1-methylpentaborane we have isolated a material, CB_5H_7, which represents the first known one-carbon carborane.

Using a silent electric discharge apparatus and techniques previously described,[2a,3] 0.15 mole of 1-methylpentaborane yields 13 mg. of a homogeneous compound: R_v (g.l.c.) = 0.65 (relative to B_5H_9, R_v = 1.00); vapor tension, 503 mm. at 26°; mol. wt. (gas density), 74.4, calcd. 73.0. The ^{11}B n.m.r. of the pure compound displays three sets of doublets (δ^4 +19.1, J = 184 c.p.s.; δ +9.7; J = 162 c.p.s.; δ −2.5, J = 174 c.p.s.) with an area ratio of 2:2:1, respectively, which together with the molecular weight data clearly indicates the presence of five borons. Additionally, the coupling constants for the observed doublets signify the attachment of one terminal hydrogen to each

(1) Based on nomenclature rules adopted for carboranes: R. Adams, Inorg. Chem., 2, 1087 (1963); also, private communication.
(2) (a) R. E. Williams, C. D. Good, I. Shapiro, and B. Keilin, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 14N; J. Am. Chem. Soc., 84, 3837 (1962); ibid., 85, 3167 (1963); (b) T. Onak, R. E. Williams, and H. G. Weiss, ibid., 84, 2380 (1962); (c) T. Onak, F. J. Gerhart, and R. E. Williams, ibid., 85, 3378 (1963); (d) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, Inorg. Chem., 2, 1089 (1963); (e) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, ibid., 2, 1111 (1963); (f) L. I. Zakharkin, V. E. Stanko, V. A. Bratzev, Yu. A. Chapovsky, and O. Yu. Okhlovystin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2238 (1963); (g) D. Grafstein and J. Dvorak, Inorg. Chem., 2, 1128 (1963); (h) H. Schroeder and G. D. Vickers, ibid., 2, 1317 (1963); (i) S. Papetti and T. L. Heying, J. Am. Chem. Soc., 86, 2295 (1964); (j) F. Tebbe, P. M. Garrett, and M. F. Hawthorne, ibid., 86, 4222 (1964).
(3) T. Onak, R. P. Drake, and G. B. Dunks, Inorg. Chem., 3, 1686 (1964).
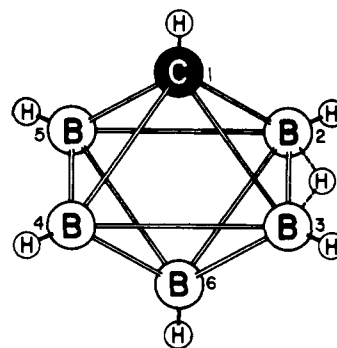(4) Boron trifluoride was used for the external standard.

Figure 1. Proposed geometry of CB_5H_7. Lines drawn between central atoms (C, B) are not meant to indicate localized two-electron bonds.

boron. The infrared spectrum exhibits medium intensity C–H (2960 cm.$^{-1}$), strong B–H (2640 cm.$^{-1}$), and medium B–H$_{bridge}$–B symmetric (2167 cm.$^{-1}$) stretching frequencies. However, a maximum of one bridge hydrogen and one hydrogen bonded to carbon is evident from a ^1H n.m.r. area analysis.

The above evidence requires a molecular formula of CB_5H_7. This is substantiated by a sharp cutoff in the mass spectrum at m/e 74 which corresponds to the $^{12}C^{11}B_5{}^1H_7{}^+$ ion.

On the basis of the proposed octahedral structure[5] for the predicted $CB_5H_6{}^-$, it is expected that the conjugate acid, CB_5H_7, would differ only by a bridge hydrogen linking two adjacent borons. Certainly such a structure is consistent with all available information. From ^{11}B n.m.r. the isomeric possibility depicted in Figure 1 is favored, although placement of the bridge hydrogen between borons 2 and 6 is not excluded if an accidental overlap of resonance lines occurred.

(5) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 89.

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The Selective Photoreduction of Uridine in Polynucleotides

Sir:

Problems dealing with the structure and function of biopolymers require organic reagents and reactions that specifically attack or modify single components of the macromolecule. While selective modifications have been elaborated for proteins,[1] only a relatively small number of such reactions are known for polynucleotides. Compared with the variety of amino acids, the four major base units of DNA and RNA are chemically much less differentiated. This lack of differential reactivity and the restrictions to an aqueous

(1) Cf. B. Witkop, Advan. Protein Chem., 16, 221 (1961).