

relation

$$D(\text{H-A}) = D(\text{X-H}) - D(\text{X-HA}) - \Delta H \quad (5)$$

Since $-\Delta H$ is positive, $D(\text{H-A})$ is greater than zero if $D(\text{X-H}) - D(\text{X-HA})$ is either positive or negative but less than $-\Delta H$. An approximation of $D(\text{X-H})$ and $D(\text{X-HA})$ may be obtained from the Morse potential for XH and X-HA treated as diatoms and the vibrational frequencies $\nu(\text{X-H})$ and $\nu(\text{X-HA})$. For OH bonds for example it turns out that $D(\text{X-H}) - D(\text{X-HA})$ is about 5 to 25 kcal./mole in agreement with the expectation that the XH bond in the complex is longer and weaker than XH in the free molecule. Experimental values for $-\Delta H$ probably are in the range of 2 to 8 kcal./mole (if the solution values can be taken as a guide) so that the bond dissociation energy of the free radical HA is about 7 to 33 kcal./mole in the gas phase.

Perhaps low temperature hydrogen atom reactions in the gas phase or e.s.r. experiments on H atoms trapped in an inert matrix containing a diluted proton acceptor could reveal the presence of such radicals.

If the Morse function is a valid description for $D(\text{X-H})$ and $D(\text{X-HA})$, equation 5 gives a relationship between ΔH and the difference in stretching frequencies $\nu(\text{X-H}) - \nu(\text{X-HA})$. This is being investigated in more detail both experimentally and theoretically.

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DIVISION OF PURE CHEMISTRY
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COMPLEX FORMATION BETWEEN ETHYLLITHIUM AND *t*-BUTYLLITHIUM

Sir:

Cosolution of ethyllithium and *t*-butyllithium in benzene leads to the formation of complex organolithium compositions, differing from either pure component, containing both types of alkyl groups bonded to lithium. Pure ethyllithium^{1,2} and *t*-butyllithium³ exist as six-fold and four-fold polymers, respectively, in benzene solution. Apparently carbon-lithium bond breaking takes place in this solvent, leading to exchange of alkyl groups between polymeric organolithium molecules when both compounds are present. The new compounds which are produced are believed to be electron-deficient polymers of the type $(\text{EtLi})_n(\text{t-BuLi})_{m-n}$, where m is a small number such as 4 or 6.

Ethyllithium alone is sparingly soluble in cold benzene, but its solubility is greatly enhanced in benzene solutions of *t*-butyllithium. Evaporation of the benzene from a solution of both compounds leaves a low-melting white solid residue. The white solid is highly soluble in pentane, unlike ethyllithium which is virtually insoluble in this solvent. The complex is also much more volatile than ethyllithium. It distills readily at 70° and 0.1 mm., forming colorless crystals. Gas chromatographic analysis of the hydrocarbons formed by hydrolysis of several samples of the distilled material show that its composition can vary. The ratio of ethyl to *t*-butyl groups in the resublimed composition is nearly the same as that in the original solution. Benzene solution with ethyllithium:*t*-butyllithium ratios of 1:1 and 1.8:1 gave distilled products with ethyl:*t*-butyl ratios of 1.1:1 and 1.7:1, respectively: m.p. 68–72° and 56–59°.

- (1) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).
- (2) R. West and W. Glaze, *ibid.*, **83**, 3580 (1961).
- (3) M. Weiner, G. Vogel and R. West, *Inorg. Chem.*, **1**, 654 (1962).

The infrared spectrum in the CsBr region of a benzene solution containing a 1:1 mixture of ethyllithium-7 and *t*-butyllithium-7 exhibits a strong broad band centered around 500 cm^{-1} , not found in the spectra of either of the components. Ethyllithium and *t*-butyllithium have strong absorption bands at 538 and 480 cm^{-1} , respectively, attributed to vibrations of the carbon-lithium framework. Summation of optical densities of spectra of ethyl- and *t*-butyllithium-7 show that the 500 cm^{-1} band does not result from overlapping of the bands of these components. The 500 cm^{-1} band in the $\text{EtLi}^7\text{-t-BuLi}^7$ complex shifts to about 514 cm^{-1} in a 1:1 solution of EtLi^6 and t-BuLi^7 . This band may be tentatively assigned to carbon-lithium framework vibrations in one or more new organolithium species containing both ethyl and *t*-butyl groups.

The characteristic triplet and quartet pattern in the hydrogen n.m.r. spectrum of ethyllithium⁴ in benzene is not changed by addition of *t*-butyllithium, and the peak positions are only slightly shifted. This finding is not inconsistent with complex formation, but does suggest that, if ethyl groups exist in different environments in the solution, exchange must be rapid compared to the relaxation time. On the other hand, the singlet at $\tau = 9.01$ in the proton n.m.r. spectrum of pure *t*-butyllithium in benzene is split into a doublet in solution containing ethyllithium. A 1:1 mixture of the two compounds gives *t*-butyl peaks at $\tau = 9.08$ and $\tau = 9.31$, with relative intensity about 7:2. Thus *t*-butyl groups appear to be present in at least two environments.

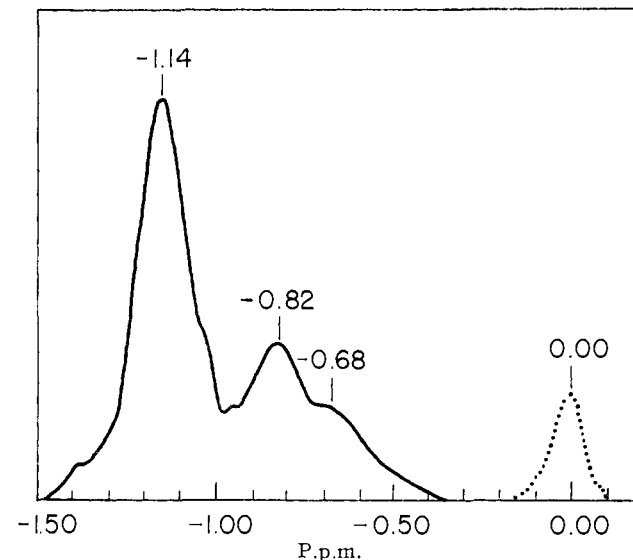


Fig. 1.—Lithium-7 n.m.r. spectra: solid line, 1:1 mixture of ethyllithium and *t*-butyllithium, each 8% by weight in benzene; dotted line, aqueous lithium nitrate solution as external reference.

Indication of the chemical interaction of ethyllithium and *t*-butyllithium in solution is also obtained from the lithium-7 n.m.r. spectrum. Pure ethyllithium and *t*-butyllithium in benzene give only single lithium resonances at -1.29 and -0.64 p.p.m., respectively, referred to aqueous lithium nitrate solution. A 1:1 mixture of the two compounds in the same solvent gives a spectrum consisting of three bands at -1.14 , -0.82 and -0.68 p.p.m., with relative intensities about 5:2:1. In the mixture, lithium atoms must be present in at least three different environments, between which exchange is slow compared to the relaxation time.

- (4) T. L. Brown, D. W. Dickerhoof and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

As yet it is not known whether the formation of mixed organolithium compounds will occur generally. Preliminary results indicate that *t*-butyllithium enhances the solubility of phenyllithium in benzene, but only to a limited extent.

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**ADSORPTION ON INORGANIC MATERIALS. V.
REACTION OF CADMIUM SULFIDE WITH COPPER(II),
MERCURY(II) AND SILVER(I)^{1,2}**

Sir:

In continuation of our studies of the adsorption and ion exchange properties of insoluble inorganic materials, we have examined a number of sulfides for possible chromatographic use. The present note deals with the properties of cadmium sulfide which was found to be an excellent "adsorbent" for heavy metal ions such as Cu(II), Hg(II) and Ag(I) which form highly insoluble sulfides. While the reaction of CdS with ions of this type has long been known,³ apparently it has not been recognized before that the reaction is fast enough for chromatographic use in aqueous media.

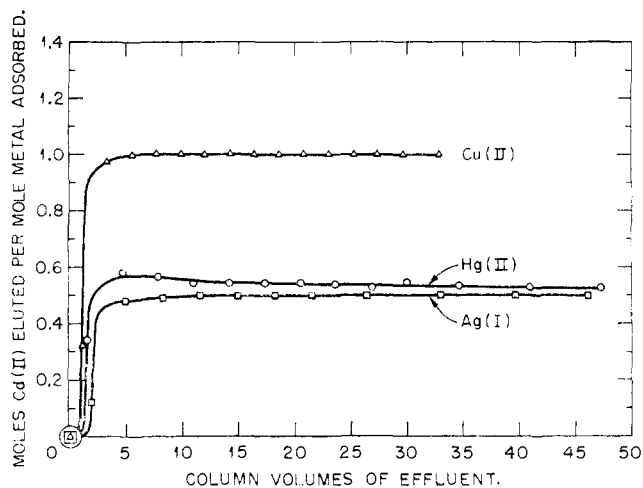


Fig. 1.—Reaction of various heavy metal ions with cadmium sulfide columns (25°; columns: ca. 0.2 cm.² × 2 cm., flow rate ca. 2 cm./min.).

Cadmium sulfide was prepared by addition, with continuous stirring, of excess ammonium sulfide to a 0.2 M cadmium nitrate solution. The resulting precipitate was collected by filtration and washed with water, 0.2 M HNO₃, and again with water. The material was dried at 25°, ground, and sieved (mesh size, 80–170). This sieved material gave columns which have good flow characteristics. The columns had a cross-sectional area of ca. 0.2 cm.² and were ca. 2 cm. high. X-Ray crystallographic examination of the material⁴ revealed only lines of the cubic CdS; the crystallite size was about 90 Å.

(1) This document is based on work performed for the U. S. Atomic Energy Commission and for the Office of Saline Water, U. S. Department of the Interior, at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

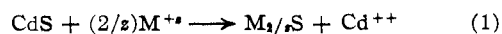
(2) Previous paper: H. O. Phillips and K. A. Kraus, *J. Am. Chem. Soc.*, **84**, 2267 (1962).

(3) E. Schürmann, *Lieb. Ann.*, **249**, 326 (1888).

(4) We are indebted to Robert L. Sherman of ORNI. Analytical Chemistry Division for the crystallographic examinations.

When dilute (*e.g.*, tracer) or concentrated (*e.g.*, 1 M) solutions of silver, copper or mercury nitrates, with or without supporting electrolyte (NaNO₃, HNO₃), were passed through columns of cadmium sulfide, quantitative removal of the ions from the solution was obtained as determined by radiometric analysis of the effluent (Ag¹¹⁰, Hg²⁰³, Cu⁶⁴). The adsorption reaction is insensitive to the anions present in the solution; in the case of Ag(I) (0.05 M), excellent adsorption was found even from 0.1 M Na₂S₂O₃ in which Ag(I) is strongly complexed.

Adsorption of these ions by cadmium sulfide might be expected to result principally from displacement reactions of the type



To establish the stoichiometry of the reaction, a series of column experiments was carried out with 0.050 M AgNO₃–1.0 M NaNO₃, 0.052 M Cu(NO₃)₂–0.004 M HNO₃ and 0.050 M Hg(NO₃)₂. The effluent was analyzed for Cd(II) by EDTA titrations⁵ while absence of the other heavy metal ions was confirmed radiometrically. Except for a slight delay in Cd(II) breakthrough, the reaction with Ag(I) and Cu(II) follows equation 1 quantitatively as shown in Fig. 1. With Hg(II), the effluent Cd(II) concentration was substantially less than expected from equation 1.

Qualitatively, excess adsorption of Hg(II) over that expected from equation 1 would be expected if there is at least partial formation of double salts of the type (HgS)_n·HgX₂. White double salts with composition (HgS)₂·HgX₂ are well known.⁶ Treatment of CdS and HgS columns with excess of Hg(II) solutions yielded white or gray solids, suggesting formation of such double salts. However, the amount of Hg(II) adsorbed by CdS in the experiment described in Fig. 1 is in excess of that expected for formation of (HgS)₂·Hg(NO₃)₂; perhaps basic double salts containing a still larger Hg/S ratio are formed.

The reaction between CdS and the heavy metal ions often goes essentially to completion under the usual conditions of column operation. Thus silver uptake as high as 13.2 moles per kilogram of CdS was achieved with a 0.21 cm.² × 1.45 cm. CdS column with 0.05 M AgNO₃–1 M NaNO₃–0.001 M HNO₃ at a flow rate of 5 cm./min. This uptake is equivalent to a 94% conversion to Ag₂S. Conversion to CuS is somewhat slower; at the same flow rate using a similar column and 0.052 M Cu(NO₃)₂–0.004 M HNO₃, 4.7 moles of Cu(II) was adsorbed at 50% breakthrough, which is equivalent to 70% of theoretical (6.92 moles per kg.).

The extreme rapidity with which the adsorption-displacement reactions proceed is probably the most striking feature in the chromatographic application of CdS. Thus, using 0.05 M Ag(I) and Cu(II) solutions, quantitative adsorption was found with 2 to 3 cm. columns at flow rates up to 50 cm./min. During the adsorption, a color change occurs from orange to black; the boundary remains remarkably sharp at flow rates as high as 25 cm./min. With Hg(II) the reactions are more complicated and not quite as fast. A red HgS, which often forms first, slowly converts to the black sulfide and it in turn converts still more slowly (at room temperature) to the white double salts.

Cadmium sulfide, in view of its high capacity, applicability to dilute and concentrated solutions, and very favorable exchange kinetics thus seems to be a very

(5) C. N. Reilly, R. W. Schmid and F. S. Sadek, *J. Chem. Educ.*, **36**, 555 (1959).

(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 4, Longmans, Green and Co., New York, N. Y., New Impression, 1952, p. 961.