Anal. Calcd. for $C_{14}H_{20}N_2$: C, 77.8; H, 9.3; N, 12.95. Found: C, 77.70; H, 9.55; N, 12.24.

The hydrazone was not purified further, but used directly to prepared dicyclopropylmethane (XII).

Dicyclopropylmethane (XII). (a) **From the Hydrazone.**—Sodium (2 g.) was dissolved in 100 ml. of diethylene glycol, and to this solution there was added 25 g. (0.2 mole) of dicyclopropyl ketone hydrazone. The solution was heated to 190–210° for 45 minutes and the product distilled as formed (4.2 liters of nitrogen were evolved). After drying (potassium carbonate) and redistillation there was obtained 9.0 g. (47%) of dicyclopropylmethane, b.p. 102° at atmospheric pressure, $n^{25}D$ 1.4228.

Anal. Calcd. for C_7H_{12}: C, 87.4; H, 12.6. Found: C, 87.72; H, 12.43.

(b) From the Ketone.—A mixture of 35 g. (0.32 mole) of dicyclopropyl ketone, 300 ml. of diethylene glycol, 40 g. of potassium hydroxide and 40 ml. of 85% hydrazine hydrate was heated for one hour at 130°. The excess hydrazine and water were removed until the pot temperature reached 180°, where it was maintained until all the product had distilled. The distillate was extracted with ether and, after drying (potassium carbonate) and removal of the solvent, there was obtained 19 g. (63%) of dicyclopropylmethane.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Reactions of Sodium Metal with Aromatic Hydrocarbons[1,2]

BY DONALD E. PAUL, DAVID LIPKIN AND S. I. WEISSMAN

RECEIVED MAY 9, 1955

The stoichiometry, optical absorption spectra and electrical conductivity of the products of the reaction of metallic sodium with aromatic hydrocarbons in tetrahydrofuran solution were studied. The results indicate that products containing one mole of sodium per mole of hydrocarbon are formed, in agreement with the conclusions arrived at by paramagnetic resonance absorption measurements. A relationship was found between the absorption spectra of reaction products and their parent hydrocarbons. The absorption spectra also were used as an analytical tool for the study of equilibria involving pairs of aromatic hydrocarbons and their corresponding negative ions. The results of these measurements give the following order of increasing electron affinities: benzene $\ll$ phenanthrene $<$ naphthalene $<$ anthracene, naphthacene. A mechanism is proposed for the reaction of a negative ion hydrocarbon free radical with various reactants (*i.e.*, carbon dioxide, water).

A brief description has been given of a reaction of sodium metal with aromatic hydrocarbons in the presence of solvents such as 1,2-dimethoxyethane and tetrahydrofuran.[3] In this paper we report the results of a more detailed study of some of the properties of the reaction products. Recently Holmes-Walker and Ubbelohde[4] described the results of an investigation of the solid reaction products obtained from the same kinds of reactants in different solvents.

In preparing solutions containing the products of the alkali metal–hydrocarbon reactions, high vacuum techniques were used similar to those employed by Kraus in his classical studies of the metal–ammonia systems and by Lewis, Lipkin and Magel[5] in their studies of triarylmethyls.[6]

The experiments were performed with tetrahydrofuran (THF) and, to a lesser extent, 1,2-dimethoxyethane as solvents. These solvents were both purified in the same way. The ether was first distilled from a mixture of activated alumina and sodium hydroxide pellets. The distillate, which was collected in a receiver containing sodium chips and anthracene, was redistilled into a solvent storage bulb on the vacuum line after standing in contact with the sodium and anthracene for at least one hour. The storage bulb contained a sphere of liquid sodium–potassium alloy and anthracene.

All the aromatic hydrocarbons used in this work, with the exception of triphenylene,[7] were Eastman Kodak Co. "white label" materials. Purification by recrystallization yielded samples with melting points in good agreement with values reported in the literature.

Composition of the Reaction Products

Scott, Walker and Hansley[8] have reported that the reaction between sodium metal and naphthalene in 1,2-dimethoxyethane, under an atmosphere of nitrogen, yields an intense green product in which the molar ratio of sodium to naphthalene is one. The data of Chu and Yu[9] for a number of aromatic hydrocarbons also indicate the formation of reaction products containing one mole of sodium per mole of hydrocarbon.

We have measured the molar ratio for the reaction between sodium metal and anthracene in THF under high vacuum conditions. The measurements were made as follows: a known volume (containing approximately 1.5×10^{-3} to 5.5×10^{-3} mole of solute) of a standard solution of anthracene in cyclohexane or benzene and a capillary containing a large excess of sodium metal were introduced into a dumper on the vacuum line. After evaporation of the solvent, anthracene was carefully sublimed from one portion of the dumper to another and the sodium then was volatilized from the capillary to form a mirror on the walls. THF from the storage bulb was distilled into the dumper and the resulting blue solution, after sufficient time for complete reaction of the hydrocarbon had elapsed, was either decanted or poured through a glass wool filter into a receiver. Solvent was distilled back into the dumper and any product remaining there poured into the receiver. The receiver was sealed off, broken open and a few drops of water immediately added to its contents. The mixture was quantitatively transferred, with enough carbon dioxide-free water to reduce the concentration of THF below

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[1] Taken in part from a thesis submitted by Donald E. Paul to the Graduate Board of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This research was supported, in part, by a Universal Match Company Fellowship, by the joint program of the United States Atomic Energy Commission and the Office of Naval Research, and by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

(3) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

(4) W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.*, 720 (1954).

(5) G. N. Lewis, D. Lipkin and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

(6) Holmes-Walker and Ubbelohde[4] did not use high vacuum techniques and it is possible that their results were complicated by the products resulting from decomposition of the metal–anthracene complex. In our experiments sodium metal films remained bright indefinitely, even in the presence of solvent. Furthermore, solutions of our reaction products have remained unchanged for almost a year.

(7) We wish to thank Mr. Wm. E. Emerson for the preparation of the sample of triphenylene.

(8) N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

(9) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).

50%, to the cup of a micro-titration apparatus first described by J. S. Dixon.[10] The sodium hydroxide formed was determined by titration in an atmosphere of carbon dioxide-free nitrogen with the use of a glass electrode for detection of the end-point.

The average of twelve separate determinations of the molar ratio of sodium to anthracene is 1.14 ± 0.06. We believe that because of the large standard deviation and the nature of the systematic errors of the method, no significance should be attached to the deviation of the ratio from unity. It is worth noting that this ratio of unity was obtained at much lower concentrations than those used by Scott, Walker and Hansley[8] and by Chu and Yu.[9]

The combined evidence of the data cited above on the composition of the reaction products, the observations on the magnetic properties,[3,9,11] the polarographic reduction studies on aqueous dioxane solutions of aromatic hydrocarbons,[12] and the potentiometric titration experiments in 1,2-dimethoxyethane as solvent,[13] clearly indicates that the primary products obtained in the reactions of sodium metal with aromatic hydrocarbons are free radical negative ions.[14]

Optical Absorption Spectra of the Free Radicals

The reaction products in THF solution are all deeply colored. The color of the product formed with napthalene is green; with anthracene, brilliant blue; with phenanthrene, olive green; with triphenylene, lavender; with naphthacene, blue green; with stilbene, dark green in the presence of an excess of stilbene but red in the presence of an excess of sodium[15]; and, with dibenz[a,h]anthracene, dark green.[16]

Quantitative optical absorption spectra of solutions of the various reaction products were measured in a model DU Beckman spectrophotometer equipped with a thermostated cell compartment. Pyrex absorption cells with 0.1 cm. path length were used for most of the measurements. Preparation of the sealed-off cells for the absorption measurements was accomplished by the procedure described previously for determination of the molar ratio. After the absorption spectrum of a particular solution had been determined, the level of the solution in the cell was marked. The cell was then opened and the content of reaction product determined by titration with acid (see above). The volume of solution was determined by filling the cell to the mark from a graduated pipet. In those cases where molar extinction coefficients are given, the concentration of reaction product was calculated on the assumption that the hydrolysis of one mole of reaction product yields one mole of hydroxide ion.

The absorption spectra of the free radicals in THF solution are given in Figs. 1–3.[17] The molar extinction coefficient, ϵ (defined by $\log_{10} I_0/I = \epsilon cd$, with c, the concentration, in moles per liter and d,

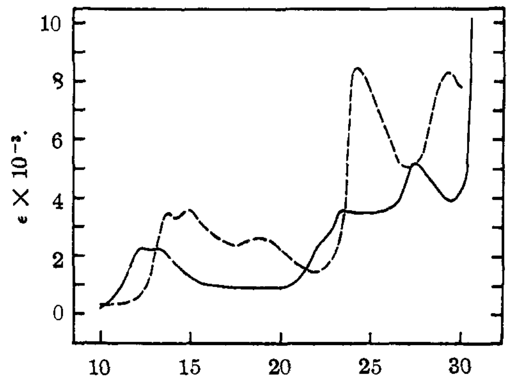

Fig. 1.—Absorption spectra of sodium naphthalenide (solid curve) and sodium triphenylenide (dashed curve) in THF.

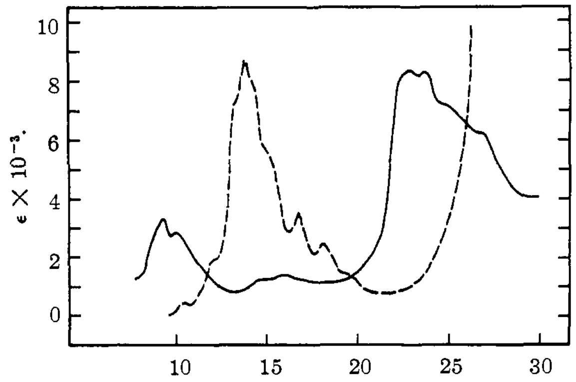

Fig. 2.—Absorption spectra of sodium phenanthrenide (solid curve) and sodium anthracenide (dashed curve) in THF.

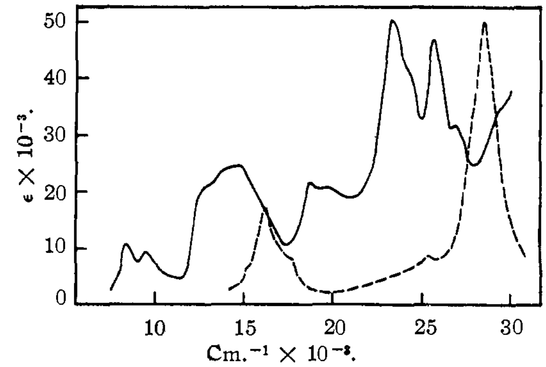

Fig. 3.—Absorption spectra of sodium dibenz[a,h]-anthracenide (solid curve, ordinates are in arbitrary units) and sodium naphthacenide (dashed curve) in THF.

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[10] J. S. Dixon, Ph.D. Thesis, Washington University, June, 1953.

[11] T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953); S. I. Weissman, J. Townsend, D. E. Paul and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953).

[12] (a) S. Wawzonek and H. A. Laitinen, THIS JOURNAL, **64**, 2365 (1942); (b) G. J. Hoijtink, *et al.*, *Rec. trav. chim.*, **73**, 355, 895 (1954).

[13] G. J. Hoijtink, *et al.*, *ibid.*, **74**, 277 (1955).

[14] It is suggested that the names of these free radical negative ions be derived from the names of the corresponding hydrocarbons by substituting the suffix -ide for the terminal -e in the name of the parent hydrocarbon.

[15] The dark green and the red substances may be rapidly and reversibly transformed into each other. The former exhibits paramagnetic resonance absorption while the latter does not. It is concluded, therefore, that the dark green color corresponds to the species $(C_6H_5CH{=}CHC_6H_5)^-$ and the red color to $(C_6H_5CH{=}CHC_6H_5)^{=}$. The fact that stilbene forms two different products on reaction with metallic sodium has been observed by H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953), and by J. W. B. Reesor, J. G. Smith and G. F. Wright, Abstracts of Papers Presented at the September 1954 Meeting of the American Chemical Society, p. 28-O.

[16] These are the colors of the primary reaction products. Occasionally these colors change more or less rapidly with time, presumably because of secondary reactions catalyzed by traces of impurities.

[17] The spectra given in these figures were obtained on solutions which were found to show paramagnetic resonance absorption.

the path length, in cm.), is plotted against frequency in cm.$^{-1}$. The spectrum of sodium naphthalenide in 1,2-dimethoxyethane is essentially the same as in tetrahydrofuran.

A study was made of the validity of the Beer–Lambert law for solutions of sodium naphthalenide and anthracenide in THF. The former was found to obey this law over the concentration range 0.130×10^{-3} to 8.67×10^{-3} *M* and the latter over the concentration range 0.46×10^{-3} to 3.4×10^{-3} *M*.

In the ultraviolet, close to the limit of our measurements (*ca.* 31,000 cm.$^{-1}$), the absorption peaks of the free radical negative ions are close in position to, but not exactly coincident with, those of the corresponding hydrocarbons.[18] This approximate coincidence may arise from the fact that the introduction of an extra electron into a conjugated hydrocarbon does not produce large changes in the positions of its energy levels. The unpaired electron may be pictured as occupying the first vacant orbital of the hydrocarbon. An energy level scheme, based on this picture, is given in Fig. 4.

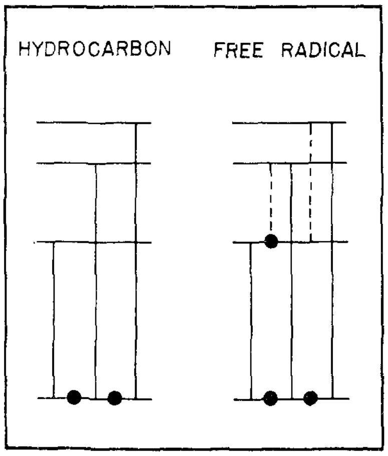

Fig. 4.—Diagrammatic representation of the energy levels in aromatic hydrocarbons and their corresponding negative ion free radicals.

This diagrammatic representation corresponds to the observation that the free radical negative ions have absorption characteristics approximately similar to those of the parent hydrocarbons, plus a region of absorption at lower frequencies. McClure has summarized[19] the energy level scheme of a number of hydrocarbons. Using the data presented in his paper, we have estimated the positions of the absorption bands to be expected in the free radical ions. The calculated absorption band frequencies are given in Table I.

TABLE I

ABSORPTION FREQUENCIES OF NEGATIVE ION FREE RADICALS

Compound	Calcd. frequencies (cm.$^{-1}$)	Compound	Calcd. frequencies (cm.$^{-1}$)
Naphthalene	2,800	Triphenylene	3,800
	13,500		9,200
	20,700		23,100
	27,900	Naphthacene	4,900
Anthracene	12,500		15,600
	19,300		21,100
	27,300		22,400
Phenanthrene	4,600		26,300
	10,800	Dibenz[a,h]anthracene	3,870
	18,600		6,360
	24,900		18,780
	28,100		24,640
			28,910

Conductivity Measurements

Scott, Walker and Hansley[8] reported the qualitative observation that solutions of sodium naphthalenide in 1,2-dimethoxyethane are electrically conducting. Since their solutions may have contained small amounts of ionic impurities, we measured the conductivity of solutions of sodium anthracenide in THF.

The solutions were prepared by the techniques described above and the conductivities were determined in a conductivity cell filled *in vacuo* and sealed off. The electrodes, which were made of shiny platinum, were about two centimeters in diameter and were spaced about one centimeter apart. The measurements, made at 34.35° at 500 cycles per second, are summarized in Table II.

TABLE II

CONDUCTANCE OF SODIUM ANTHRACENIDE IN THF

Concn., moles/l. ($\times 10^3$)	Equiv. conductance
10.23	2.493
2.67	5.61
1.80	6.52
1.32	7.58
0.705	9.64

Equilibrium Measurements

In an attempt to estimate relative electronegativities of aromatic hydrocarbons in tetrahydrofuran solution, we have studied three equilibria of the type

$$X + Y^- = X^- + Y \qquad (1)$$

The pairs studied (X and Y in the above equation) were naphthalene–anthracene, naphthalene–phenanthrene and anthracene–naphthacene.

The measurements were carried out as follows: one of the hydrocarbons of the pair was completely converted to free radical as previously described. A portion of this free radical solution was decanted from the excess sodium metal into a Pyrex absorption cell (0.1 cm. path length) containing a known weight of the second hydrocarbon. Equilibrium was established very rapidly, even at the melting point of tetrahydrofuran (−108°). The cell was sealed off and the optical density of the solution was measured at two wave lengths (see Table III) in order to determine the concentrations of the two negative ions. Equilibrium quotients for equation 1 were calculated from the above data. In each case X^- and Y^- were determined spectrophotometrically as mentioned above, $(X^- + X)$ were known from the weight of X originally introduced into the cell, and Y was assumed to be equal to X^-.

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(18) Two lines of evidence indicate that these peaks are not due to unchanged hydrocarbons, but are characteristic of the free radicals themselves. First, in the case of anthracene it was found that the negative ion free radical did not show the fluorescence of the parent hydrocarbon. Further, it was demonstrated that unchanged anthracene was detectable by its fluorescence in the presence of a large excess of anthracenide. Second, a comparison of the magnitude of the ultraviolet extinction coefficients of the hydrocarbons with the observed absorbency of the free radical solutions indicated clearly that this absorption could not be due to unchanged hydrocarbon.

(19) D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951); H. B. Klevens and J. R. Platt, *ibid.*, **17**, 470 (1949).

TABLE III[a]

EQUILIBRIUM DATA FOR THE REACTION $X + Y^- = X^- + Y$

Reactants	Naphthalene–anthracenide	Naphthalene–phenanthrenide	Naphthacene–anthracenide
Frequencies (cm.$^{-1}$) used for meas. of X^- and Y^-	12,500 15,270	10,000 12,350	12,050 13,340 17,550
$K_{308°K}$	$1.4(\pm 0.9) \times 10^{-4}$	8.4 ± 3	1.3[b]
d ln K/d $(1/T)$	-1.2×10^3	-1.1×10^3	-1.6×10^3

[a] Although the data are not sufficiently reliable to permit an accurate calculation of entropy changes, they suggest that the relative electron affinities of aromatic hydrocarbons in THF are in large part determined by an entropy, rather than energy, factor. [b] See text.

The determination of the equilibrium quotient for the naphthalene–anthracene pair was complicated by the fact that a very large excess of naphthalene was required to yield measurable amounts of the naphthalenide free radical. In order to avoid appreciable decomposition of the free radicals, it was necessary to subject the naphthalene to stringent purification. This was accomplished by treating the naphthalene with a THF solution of sodium naphthalenide, removal of the solvent, and careful sublimation of the naphthalene from the residue. This was followed by a second sublimation of the naphthalene. A small portion of this purified naphthalene was then converted to the free radical and the resulting solution was decanted from the excess sodium. This solution, together with the bulk of the purified naphthalene, was transferred to the absorption cell which already contained a known weight of anthracene. After distillation of the required amount of THF, the absorption cell was sealed off.

In the above naphthalene-anthracene measurements the weight of purified naphthalene introduced into the absorption cell could not be readily determined by direct weighing. The mole fraction of naphthalene in each sample was estimated by determination of the temperature at which the solution became saturated with naphthalene. In order to calculate the mole fraction, it was assumed that the solution was ideal.

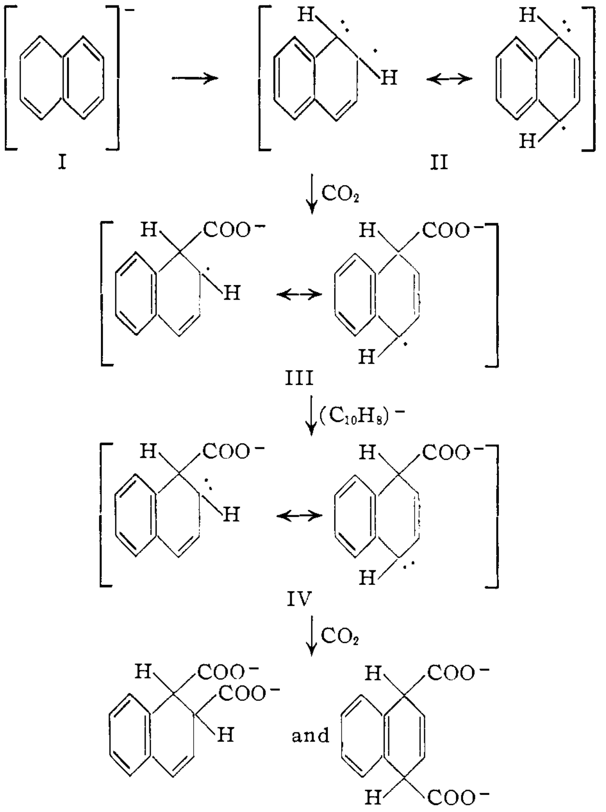
A summary of the equilibrium data for reactions corresponding to equation 1 is given in Table III. The concentrations of the various components were in the range 10^{-4} to 10^{-2} M, except for the naphthalene in the naphthalene–anthracene pair. The mole fraction of naphthalene in this system was about 0.25.

The equilibrium quotients given in Table III are subject to various sources of error. Probably the principal source of error lies in the spectrophotometric determination of X^- and Y^-. This is due, in part, to the overlapping of the spectra of the various pairs. Further, there are difficulties in the preparation of stable, dilute solutions of the hydrocarbon free radicals. Finally, the equilibrium quotient for the anthracene–naphthacene system may be in error by an order of magnitude both because of the uncertain purity of the naphthacene and the possibility of formation of a doubly charged negative naphthacene ion.

Although our equilibrium data are subject to various uncertainties as discussed above, they do yield a qualitative order of electron affinity for the hydrocarbons dissolved in THF. The order of increasing affinity is benzene[20] << phenanthrene < naphthalene < anthracene, naphthacene.[21] This order agrees with the order of decreasing half-wave reduction potentials found for aromatic hydrocarbons in aqueous dioxane by Wawzonek and Laitinen.[12a] It is of interest to note that Levy and Szwarc[22] suggest essentially the same order for the "methyl affinity" of aromatic hydrocarbons, while Burkitt, Coulson and Longuet-Higgins[23] give a similar order for the polarization energies. Also, Marvel and Anderson[24] have found that anthracene undergoes copolymerization with 1,3-butadiene while, in contrast, benzene, naphthalene and phenanthrene do not copolymerize.

Mechanism of the Reactions of the Negative Ion Free Radicals with Various Reagents

In the reactions of the negative ion free radicals with substances such as carbon dioxide or water two facts stand out: first, dihydro or substituted dihydro derivatives of the parent aromatic hydrocar-



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[20] In solutions containing a high concentration of benzene in THF we have observed the formation of a pale yellowish-green color. The solutions exhibit paramagnetic resonance absorption.

[21] This variation in electron affinity suggests the use of the corresponding negative ions as reducing agents of graded oxidation–reduction potentials. The reductive dephenylation of phenyl esters of phosphoric acids by means of sodium naphthalenide will be described in a forthcoming paper.

[22] M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954).

[23] F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

[24] C. S. Marvel and W. S. Anderson, THIS JOURNAL, **76**, 5434 (1954).

bons are formed[8,25]; second, in the absence of excess sodium metal, half of the original hydrocarbon is recovered unchanged, while in the presence of excess sodium the original hydrocarbon is completely converted to the dihydro derivative.[25a,c] The first fact led previous investigators to the conclusion that disodium addition products, rather than negative free radicals, were formed in the reaction of sodium metal with aromatic hydrocarbons. The second set of observations remained unexplained.

A mechanism for the reactions of aromatic hydrocarbon free radicals with substances such as carbon dioxide or water, which is consistent with the observations described above, is shown in formulas I–VI. The conversion of I to III involves an activated state, two of whose possible resonance structures are represented by II. Conversion of II to III is simply a reaction between a Lewis base and acid. It is assumed that I → III is a relatively slow reaction because both I and carbon dioxide require activation. The interchange of an electron between III and $(C_{10}H_8)^-$ to give IV is assumed to be very rapid.[26] The final step (IV → V and VI) is assumed to be slow compared to III → IV, but rapid compared to I → III. This is not an unreasonable assumption, since the conversion of IV to V and VI involves only the activation of the carbon dioxide. It is apparent from the given reaction scheme that in the absence of excess metallic sodium, for each mole of I converted to V and VI one mole of naphthalene is reformed in the step III → IV.

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(25) (a) W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936); (b) A. Jeanes and R. Adams, This Journal, **59**, 2608 (1937); (c) J. F. Walker and N. D. Scott, *ibid.*, **60**, 951 (1938).

(26) R. L. Ward and S. I. Weissman, *ibid.*, **76**, 3612 (1954).

St. Louis 5, Missouri

[Contribution of Branch of Coal-to-Oil Research, Bureau of Mines, and the Department of Chemistry of the University of Pittsburgh (Contribution No. 959)]

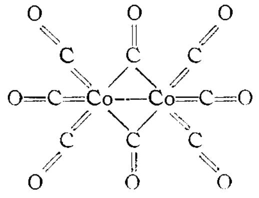
Acetylenic Dicobalt Hexacarbonyls. Organometallic Compounds Derived from Alkynes and Dicobalt Octacarbonyl[1,2]

By Harold Greenfield,[3] Heinz W. Sternberg,[3] Robert A. Friedel,[3] John H. Wotiz,[4] Raymond Markby[3] and Irving Wender[3]

Received July 15, 1955

It has been found that acetylene and substituted acetylenes, RC≡CR′, readily displace the two bridge carbonyl groups in dicobalt octacarbonyl, $Co_2(CO)_8$, to yield a new type of organometallic compound, $RC_2R'Co_2(CO)_6$. The structure and properties of these "acetylenic dicobalt hexacarbonyls" are discussed.

Recent investigations[5,6] have shown that dicobalt octacarbonyl (I), like iron enneacarbonyl,[7] contains two types of carbonyl groups, *i.e.*, bridge and terminal carbonyl groups.



I

It has now been found that the two bridge carbonyl groups in I can be replaced by alkynes. The reaction, which proceeds smoothly and quantitatively at room temperature, can be represented by equation 1

$$RC{\equiv}CR' + Co_2(CO)_8 \longrightarrow \underset{II}{RC_2R'Co_2(CO)_6} + 2\overline{CO} \quad (1)$$

The reaction is general and occurs with all types of alkynes (see Table I). If the alkyne contains two triple bonds, each triple bond reacts with a mole of dicobalt octacarbonyl. This is the case even with conjugated diacetylenes, where a steric effect might have been expected.

The acetylenic dicobalt hexacarbonyls are generally deeply colored. In the ultraviolet region diphenylacetylene dicobalt hexacarbonyl has a broad band near 2800 Å. with a molar extinction coefficient, ϵ, of about 21,000. An interesting property of the acetylenic dicobalt hexacarbonyls is their weak intermolecular forces of attraction. This is indicated by their high volatility, high solubility in organic solvents and the ease with which they can be eluted from a column of activated alumina. For example, acetylene dicobalt hexacarbonyl, with a molecular weight of 312, distils at 64 to 66° at 3.5 to 4 mm. pressure. Diphenylacetylene dicobalt hexacarbonyl, with a molecular weight of 464, sublimes at 90° at 1 mm. pressure, and can be eluted from a column of activated alumina with a small volume of an aliphatic hydrocarbon solvent; 1,7-octadiyne tetracobalt dodecacarbonyl, with a molecular weight of 678, is soluble in pentane at room temperature.

Magnetic susceptibility measurements on diphenylacetylene dicobalt hexacarbonyl indicate that this compound is diamagnetic.

The Infrared Spectra of Acetylenic Dicobalt Hexacarbonyls.—The infrared spectrum of dicobalt octacarbonyl (I) contains a group of three bands at 4.83, 4.89 and 4.94 μ and a single band at

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(1) For a preliminary communication, see H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, This Journal, **76**, 1457 (1954).

(2) This paper is based, in part, on the Ph.D. Thesis of Harold Greenfield, University of Pittsburgh.

(3) Branch of Coal-to-Oil Research, Bureau of Mines, Bruceton, Pa.

(4) Department of Chemistry, University of Pittsburgh.

(5) J. W. Cable, R. S. Nyholm and R. K. Sheline, This Journal, **76**, 3373 (1954).

(6) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *ibid.*, **77**, 3951 (1955).

(7) R. K. Sheline, *ibid.*, **73**, 1615 (1951).