because they vary in the opposite direction to the Q_N values, 1.33 and 1.27, respectively. On the other hand the ΔH values are not anomalous, being 5.36 and 4.79 for quinoline and pyridine, respectively. Unfortunately these values are not conclusive, because the reaction of neutralization is complicated by the displacement of water molecules.

The ΔH values for piperidine and pyrrolidine are lower than expected. The entropy values, on the other hand, are the highest of all the bases. This would indicate that a greater number of water molecules are displaced from these bases.

Acridine is too slightly soluble in water to allow calorimetric measurements to be made. The pK_a value for this base in 50% ethanol, equal to 4.07, is lower than that of pyridine, which is equal to 4.38 when measured under the same conditions. On the other hand, the Q_N value, 1.33, is higher than that of pyridine, 1.27. This anomalous behavior characteristic of the pK_a values in water is also exhibited by the heats of reaction ΔH in 50% ethanol, equal to 3.48 and 5.22 kcal., respectively, for acridine and pyridine. Here, too, the remarks made on quinoline are to be kept in mind.

It is interesting to compare the enthalpies of neutralization of pyridine, 2-, 3-, 4-picoline and 2,6-lutidine with methanesulfonic acid in nitrobenzene, as measured by Brown,[8] with the values obtained by summing up our heats of neutralization with the heats of hydration reported in our previous work.[4] The data obtained are:

	$\Delta H_{CH_3SO_3H}$	Heat of neutr. + heat of hydrat.
Pyridine	−17.1	−16.77
2-Picoline	−18.3	−19.37
3-Picoline	−17.8	−18.88
4-Picoline	−18.4	−19.28
2,6-Lutidine	−19.5	−21.78

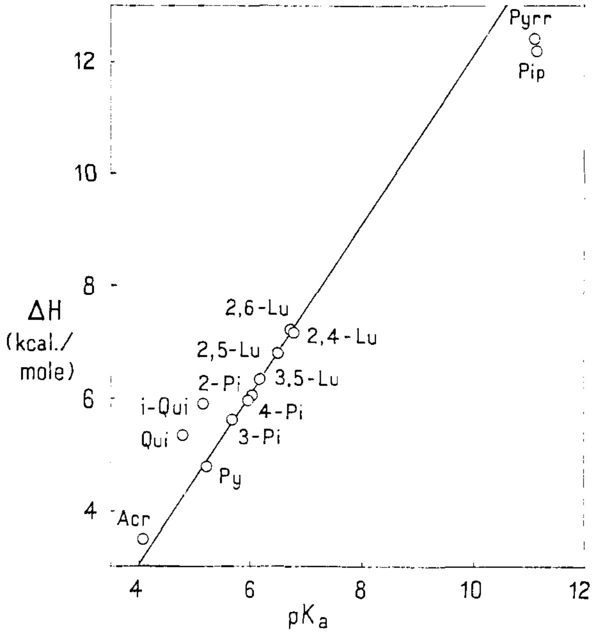

Fig. 1.—Plot of heats of neutralization *vs.* pK_a for the heterocyclic amines.

The agreement between both series is fairly good. Although it is probable that in the systems investigated by Brown, the solvation influences to some extent the heats of neutralization, the satisfactory agreement between the two series of values allows one to suppose that the hydrated proton when it reacts with the base displaces all the water bound to the nitrogen atom.

Acknowledgment.—The authors are indebted to the Italian "Consiglio Nazionale delle Ricerche" for the support of this work.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Chemistry of the Metal Carbonyls. III. The Reaction between Iron Pentacarbonyl and Tetraorganotin Compounds[1,2]

BY R. B. KING[3] AND F. G. A. STONE

RECEIVED DECEMBER 16, 1959

Organotin compounds of the type $R_x'SnR''_{4-x}$ (R', alkyl group; R'', vinyl or phenyl group) react with iron pentacarbonyl in refluxing ethylcyclohexane to give yellow dialkyltin iron tetracarbonyl dimers, $[R_2'SnFe(CO)_4]_2$. Thus reaction between iron pentacarbonyl and either di-*n*-butyldivinyltin, di-*n*-butyldiphenyltin or tri-*n*-butylphenyltin affords di-*n*-butyltin iron tetracarbonyl, a compound identical with that previously obtained from di-*n*-butyltin dichloride and the anion $HFe(CO)_4^-$.

Until recently it appeared that iron would form complexes only with conjugated dienes, these being of the type $L{\cdot}Fe(CO_3)$. It is now evident, however, that under the appropriate reaction conditions iron carbonyls will react with the non-conjugated diene 1,5-cycloöctadiene, forming the very unstable compound $C_8H_{12}{\cdot}Fe(CO)_3$.[4]

The successful preparation of this diene complexe of iron led us to investigate the reaction between iron pentacarbonyl and dialkyldivinyltin compounds in an attempt to prepare compounds of the type $[R_2Sn(CH{:}CH_2)_2]Fe(CO)_3$. It was found that iron pentacarbonyl and di-*n*-butyldivinyltin did indeed react to give a yellow crystalline solid. However, the latter had the composition $C_{12}H_{18}O_4$

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(1) Previous papers in this series: T. A. Manuel and F. G. A. Stone, THIS JOURNAL, **82**, 366 (1960); R. B. King and F. G. A. Stone, *ibid.*, **81**, 5263 (1959).

(2) We are indebted to the Clark Fund of Harvard University for financial support of this work.

(3) National Science Foundation Predoctoral Research Fellow 1958–1960.

(4) T. A. Manuel and F. G. A. Stone, *Chemistry and Industry*, 231 1960.

FeSn rather than the composition $C_{15}H_{24}O_3FeSn$ expected for a diene complex involving the double bonds of the two vinyl groups. Because Hieber and Breu[5] have reported a compound dibutyltin-iron tetracarbonyl, *i.e.*, of composition $C_{12}H_{18}O_4FeSn$, characterized only by iron and CO group analysis, it was of interest to repeat this earlier work to determine whether Hieber and Breu's compound was identical with that obtained from iron pentacarbonyl and dibutyldivinyltin. Furthermore, it was decided to study reactions between iron pentacarbonyl and a variety of tetraorganotin compounds.

Experimental[6]

The tin compounds used in this work were prepared by treating tin tetrachloride or the appropriate organotin chloride with Grignard or lithium reagents.[7,8] The infrared spectra were recorded using a Model 21 Perkin–Elmer double-beam spectrometer with sodium chloride optics.

Preparation of Dibutyltin Iron Tetracarbonyl from Dibutyldivinyltin.—A mixture of 2.5 ml. (3.5 g., 17.9 mmoles) of iron pentacarbonyl and 2 ml. (2.5 g., 8.74 mmoles) of dibutyldivinyltin was refluxed under nitrogen in 40 ml. of ethylcyclohexane. The mixture turned a bright orange, but after about 6 hr. iron began to appear, as is typical of many of the reactions of iron pentacarbonyl with organic compounds. Refluxing was continued for 14 hr. after which time the reaction mixture was cooled to room temperature, filtered under nitrogen, and the solvent removed *in vacuo*. This afforded a light orange residue which was sublimed at 0.1 mm. From 110–140° an oil appeared on the probe of the sublimer and was discarded. Subsequently, 1.0 g. (28.5% yield) of yellow crystals of analytically pure dibutyltin iron tetracarbonyl sublimed at 140° (0.1 mm.).

Anal. Calcd. for $C_{12}H_{18}O_4FeSn$: C, 36.0; H, 4.5; total metal as oxide, 57.6. Found: C, 36.2; H, 4.7; ash, 57.5.

In a representative experiment[9] 43.3 mg. of dibutyltin iron tetracarbonyl dissolved in 1.194 g. of dichloromethane exerted at 25° a vapor pressure 1.55 mm. less than that of pure dichloromethane. This result implies a mol. wt. of 849 (calcd. for $[(C_4H_9)_2SnFe(CO)_4]_2$, 802).

Reaction between Di-*n*-butyltin Dichloride and the Potassium Salt $K_2Fe(CO)_4$.—Repetition of the work of Hieber and Breu[5] afforded a yellow solid which, like the one from iron pentacarbonyl and dibutyldivinyltin, sublimed at 150° *in vacuo*. The infrared spectra (see Fig. 1) of the two solids were the same, as were their individual and their mixed melting points. The identical nature of the yellow solids thus was established.

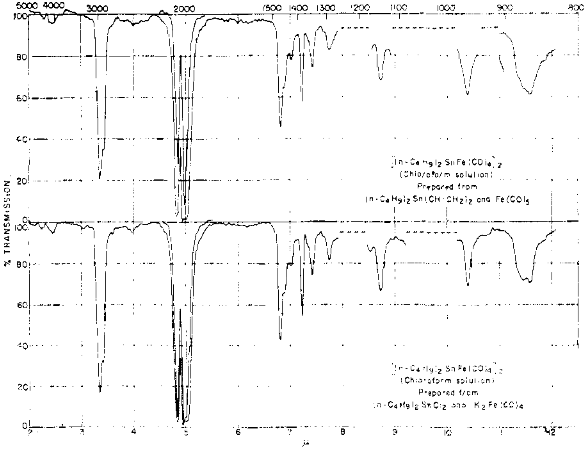


Fig. 1.

Preparation of Diethyltin Iron Tetracarbonyl from Diethyldiphenyltin.—A 2.0 ml. (2.2 g., 6.65 mmoles) sample of diethyldiphenyltin and 2.5 ml. (3.5 g., 17.9 mmoles) of iron pentacarbonyl were refluxed for 10 hr. in 40 ml. of ethylcyclohexane under nitrogen. The reaction mixture was filtered, the red filtrate being collected under nitrogen. Solvent was then removed *in vacuo* leaving a red residue. The latter was shaken with 20 ml. of ligroin (b.p. 66–75°) and the mixture filtered, using a positive nitrogen pressure through a sintered glass disc. The red filtrate was cooled to −78° for 1.5 hr., during which time diethyltin iron tetracarbonyl crystals appeared. These crystals were filtered under nitrogen pressure and dried *in vacuo;* yield 35.9% (0.82 g.). Two recrystallizations under nitrogen from petroleum ether yielded an analytically pure product.

Anal. Calcd. for $C_8H_{10}O_4FeSn$: C, 27.9; H, 2.9. Found: C, 27.9; H, 2.6.

Similar experimental procedures were used to prepare dibutyltin iron tetracarbonyl from dibutyldiphenyltin and dimethyltin iron tetracarbonyl[10] from dimethyldiphenyltin. Analytical data obtained were:

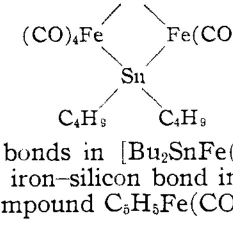
	Carbon, %		Hydrogen, %	
	Calcd.	Found	Calcd.	Found
$[(C_4H_9)_2SnFe(CO)_4]_2$	36.0	36.8	4.5	4.4
$[(CH_3)_2SnFe(CO)_4]_2$	22.7	22.7	1.9	2.1

Reactions between Iron Pentacarbonyl and Other Tetraorganotin Compounds.—Treatment of tributylphenyltin with iron pentacarbonyl under conditions similar to those described above gave an 18% yield of dibutyltin iron tetracarbonyl identified by its infrared spectrum and melting point. Several attempts to prepare dibutyltin iron tetracarbonyl dimer from tetrabutyltin and iron pentacarbonyl gave the desired product only in 0 to 6% yield. The following organotin compounds gave no isolable product with iron pentacarbonyl in refluxing ethylcyclohexane: dibutyldibenzyltin, dibutyldiethyltin, tetraphenyltin, diphenyldivinyltin, tetravinyltin, divinyltin dichloride, dimethyldiperfluorovinyltin,[8] diperfluorovinyldivinyltin.[8] Black insoluble pyrophoric solids and traces of red to orange gummy materials from which nothing could be crystallized were the only products of these reactions.

Discussion

As shown in the Experimental section, the products of the reactions between iron pentacarbonyl and di-*n*-butyldivinyltin and between di-*n*-butyltin dichloride and the salt $K_2Fe(CO)_4$ were identical.

A series of lead compounds $R_2PbFe(CO)_4$ analogous to dibutyltin iron tetracarbonyl was prepared by Hein, Pobloth and Heuser[11] some years ago. These lead compounds were also found to be dimeric. Probably these iron-tin and iron-lead compounds have bridge structures, *e.g.*



The iron–tin bonds in $[Bu_2SnFe(CO)_4]_2$ would be similar to the iron–silicon bond in the cyclopentadienyl iron compound $C_5H_5Fe(CO)_2Si(CH_3)_3$.[12] In

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(5) W. Hieber and R. Breu, *Ber.*, **90**, 1270 (1957).

(6) Microanalyses were performed by Dr. Carol Fitz, Needham Heights, Massachusetts.

(7) (a) D. Seyferth and F. G. A. Stone, This Journal, **79**, 515 (1957); (b) S. D. Rosenberg, A. J. Gibbons and H. E. Ramsden, *ibid.*, **79**, 2137 (1957).

(8) H. D. Kaesz, S. L. Stafford and F. G. A. Stone, *ibid.*, **81**, 6336 (1959).

(9) We are indebted to our colleague Mr. L. Nichols for making a number of molecular weight measurements for us.

(10) This compound was mentioned by Hieber and Breu[5] but no analytical data were given.

(11) F. Hein, H. Pobloth and E. Heuser, *Z. anorg. Chem.*, **248**, 84 (1941); **249**, 293 (1942); **254**, 138 (1947); **255**, 125 (1947).

(12) T. S. Piper, P. Lemal and G. Wilkinson, *Naturwissenschaften*, **43**, 1229 (1956).

the proposed bridge structure for dibutyltin iron tetracarbonyl and its homologs each iron atom has a *pseudo*-inert gas structure. Although the experimental data do not absolutely rule out an alternative bridge structure involving tin–tin and iron–iron bonds as well as tin–iron bonds, this seems less probable.

The organotin compounds, the reaction of which with iron pentacarbonyl was investigated in this work, can be divided into three classes. In the first class all the organo-groups are bonded to tin *via* sp^3-hybridized carbon atoms, in the second class both sp^3 and sp^2-hybridized carbon atoms are bonded to tin, while in the third class of organotin compounds only sp^2-hybridized carbon atoms are bonded to tin. In order for a tetraorgano–tin compound to give appreciable yields of a dialkyltin iron tetracarbonyl when heated with iron pentacarbonyl, it is necessary that it belong to class II above. Dimethyldiperfluorovinyltin is an exception, since it did not give dimethyltin iron tetracarbonyl. However, the chemistry of a perfluorovinyl group bonded to tin is somewhat different from that of a vinyl group. Furthermore, the dimethyl derivative was the only dialkyldiperfluorovinyltin compound treated with iron pentacarbonyl. For these reasons no special significance should be attached to the fact that dimethyldiperfluorovinyltin failed to give the expected compound.

A possible mechanism which would account for the fact that groups bonded to tin through sp^2-hybridized carbon atoms are easily removed by iron carbonyl is one in which the initial step involves formation of an unstable complex between the π-orbitals of the vinyl or phenyl groups and the iron atom.

The three dimeric dialkyltin iron tetracarbonyl compounds reported here are pale yellow crystalline solids which afford yellow solutions in diethyl ether, dichloromethane or isohexane. These solutions undergo extensive decomposition in air after a few hours. The solid compounds themselves are partially decomposed after standing in air for a few days. The partially decomposed compounds are brown and are no longer completely soluble in organic solvents. The pure dialkyltin iron tetracarbonyl compounds can be handled for brief periods in air. However, when prepared from dialkyldiphenyltin compounds and iron carbonyl, the crude products are pyrophoric even after all of the iron metal has been removed. For this reason all manipulations, including crystallizations, must be done under nitrogen.

The melting points of the dialkyltin iron tetracarbonyl compounds decrease with increasing molecular weight: $[(CH_3)_2SnFe(CO)_4]_2$ decomposes above 220°; $[(C_2H_5)_2SnFe(CO)_4]_2$ m.p. 184–185.5°; $[(C_4H_9)_2SnFe(CO)_4]_2$ m.p. 110–112°. In this connection it is interesting that from a reaction between iron carbonyl and dibenzyldivinyltin a yellow oil was obtained. This oil was probably crude dibenzyltin iron tetracarbonyl but it could not be purified. The infrared spectrum of each of the compounds in chloroform solution shows three carbonyl bands. These bands are at 2050, 2020, 1985 cm.$^{-1}$ for the butyl compound, at 2050, 2015, 1985 cm.$^{-1}$ for the ethyl compound, and at 2050, 2010, 1980 cm.$^{-1}$ for the methyl compound.

[CONTRIBUTION NO. 538 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

The Chemistry of Sulfur Tetrafluoride.[1] IV. Fluorination of Inorganic Oxides and Sulfides

BY A. L. OPPEGARD, W. C. SMITH, E. L. MUETTERTIES AND V. A. ENGELHARDT

RECEIVED SEPTEMBER 25, 1959

Sulfur tetrafluoride has been found to be a versatile, easily handled fluorinating agent useful in the preparation of a wide range of inorganic fluorides by replacement of oxygen or sulfur in inorganic compounds. Examples of fluorides prepared from oxides and SF_4 are UF_6, WF_6, IF_5, SeF_4 and GeF_4. Such difficultly obtainable fluorides as SnF_4 and MoF_4 were obtained from the sulfides. The association of SF_4 with certain metal fluorides to form complexes also has been investigated.

Introduction

Sulfur tetrafluoride, a relatively new chemical, has been found to react with most inorganic oxides and sulfides. This general reaction is characterized by replacement of the oxygen or sulfur to give the corresponding fluorides or in some cases the corresponding oxyfluorides, *e.g.*

$$5SF_4 + I_2O_5 \longrightarrow 5SOF_2 + 2IF_5$$

$$6SF_4 + P_4O_{10} \longrightarrow 6SOF_2 + 4POF_3$$

$$SF_4 + SnS_2 \longrightarrow 3S + SnF_4$$

An exception to these class reactions is the oxidation of SF_4 to SF_6 and SOF_4 by strong oxidizing agents such as NO_2 and CrO_3 which will be described in Paper No. V.

In contrast to the reactions of SF_4 with sulfides, the reaction with oxides generally does not consume all of the fluorine bonded to sulfur, and therefore the sulfide fluorination would appear at first glance to be a superior reaction. However, because a number of elements do not form sulfides in the higher oxidation states, such fluorides as WF_6 and IF_5 cannot be obtained by a sulfide fluorination. The merits of the sulfide fluorination reside in the complete utilization of the fluorine atoms in SF_4 and the observed fact that fluorination of sulfides does not stop short of complete replacement as it does in the case of some oxides, *e.g.*

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[1] Paper III, William C. Smith, Charles W. Tullock, Ronald D. Smith and Vaughan A. Engelhardt, THIS JOURNAL, **82**, 551 (1960).