higher than in the other runs. The curve in Fig. 1 was drawn from the equation

$$R \ln P = \frac{-155550}{T} - 3.452 \times 10^{-3} T + 41.60 \quad (1)$$

The coefficient of the term in $1/T$ is ΔH_0^0, and the other constants were obtained by expressing the difference in the free energy function as a linear equation in T and substituting this expression in the equation

$$R \ln P = \left(\frac{F^0 - H_0^0}{T}\right)_{\text{Solid}} - \left(\frac{F^0 - H_0^0}{T}\right)_{\text{Vapor}} - \frac{\Delta H_0^0}{T} \quad (2)$$

Errors.—The standard deviations of the experimental variables for single observations are estimated as follows:

Temperature	±3.4°
Time	±5 sec.
Weight loss	±0.0001 g.
Sample dimensions	±0.0025 cm.[2]

Comparison with Earlier Data.—The vapor pressure of molybdenum has been previously determined by Norris and Worthing[13] and by Jones, Langmuir and MacKay.[14] Norris and Worthing gave no experimental data in their paper, so that it is difficult to evaluate their results. From their empirical equation for the rate of evaporation of a molybdenum filament, calculation of an average ΔH_0^0 yields 147.6 kcal. There is an increase with temperature in ΔH_0^0 of about 5 kcal. from 1600 to 2400°K. Jones, Langmuir and MacKay's data, taken with the free energy data calculated by Richert,[10] yield an average ΔH_0^0 of 152.8 ± 1.6 kcal., which is in better agreement with our value of 155.55 ± 0.19 kcal. Values of ΔH_0^0 calculated from their data show a trend of about 7 kcal. from 2070 to 2504°K., whereas there is no appreciable temperature trend in our data. Some of the discrepancy may be due to the pressure of residual gases in their system during bakeout; their reported maximum was 10^{-3} mm., as compared to the maximum of 5×10^{-5} mm. in our system.

(13) L. Norris and A. G. Worthing, *Phys. Rev.*, **4**, 323 (1933).

(14) H. A. Jones, I. Langmuir and G. M. J. MacKay, *ibid.*, **30**, 201 (1927).

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE LABORATORY OF NORTHWESTERN UNIVERSITY]

Hydrogenation of Organo-tin and Lead Compounds under Pressure[1]

BY LEON L. GERSHBEIN[2] AND V. N. IPATIEFF

Both tin tetraphenyl and lead tetraphenyl undergo hydrogenation under an initial pressure of 60 atm. and at temperatures around 200° to yield the respective metal and benzene, only traces of diphenyl occurring in the reaction mixtures; copper powder has no effect on the nature of the hydrocarbons produced. Similarly, with the tin tetraethyl and tin tetraisobutyl, reaction with hydrogen yields principally ethane and isobutane, respectively.

Although the hydrogenation of a few organo-tin and lead compounds under high temperature and pressure has been studied, there appear to be discrepancies, especially with the lead derivatives, as regards the formation of hydrocarbons and the effect of metals.

A study of the conditions involved in the hydrogenation of the tetraethyl, tetramethyl and the tetraphenyl of lead under pressure was carried out by Ipatieff, Razuvaev and Bogdanov[3]; in all cases, metallic lead deposition occurred. Although the hydrocarbons were not characterized in the tetraalkyl experiments, lead tetraphenyl produced benzene and insignificant amounts of diphenyl. It is of interest to note that a variety of hydrocarbons result from heating lead tetraethyl at 250–300° in the presence of hydrogen and ethylene.[4] Dull and Simons observed the formation of diphenyl in quantitative yield when lead tetraphenyl was decomposed in the absence of catalyst or hydrogen.[5]

According to Zartman and Adkins,[6] zinc di-*n*-butyl and magnesium diphenyl when heated in copper liners under hydrogen pressure in the presence of nickel catalyst give rise mainly to *n*-butane and benzene, respectively. However, the tetraphenyl and tetra-*p*-tolyl of lead were converted to diphenyl and 4,4′-dimethyldiphenyl, respectively; lead tetraheptyl to a lesser degree, formed *n*-tetradecane and traces of heptane at 200° and under an initial hydrogen pressure of 100 atm. A further claim that lead tetraphenyl is quite stable at this temperature and pressure in the absence of nickel, is in marked contrast to earlier findings where almost, if not complete hydrogenation, was demonstrated.[3] Furthermore, Razuvaev and Koton[7,8] mention that the addition of such metals as nickel catalyzes the formation of benzene, contrary to the results of Zartman and Adkins.

In the present investigation, the dependence of metallic tin deposition on solvent (decalin, dioxane, benzene and xylene), temperature (150–225°) and duration of heating of tin tetraphenyl was explored; Table I shows the results obtained with the compound at an initial hydrogen pressure of 60 atm. In all cases, benzene was the principal hydrocarbon produced with diphenyl occurring in only minute amounts; in no run was complete hydrogenation

(1) Presented before the Organic Division of the American Chemical Society, Boston, Massachusetts, April, 1951.

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(3) V. N. Ipatieff, G. A. Razuvaev and I. F. Bogdanov, *Ber.*, **63B**, 335 (1930).

(4) H. S. Taylor and W. H. Jones, THIS JOURNAL, **52**, 1111 (1930).

(5) M. F. Dull and J. H. Simons, *ibid.*, **55**, 4328 (1933).

(6) W. H. Zartman and H. Adkins, *ibid.*, **54**, 3398 (1932).

(7) G. A. Razuvaev and M. M. Koton, *Ber.*, **66B**, 854 (1933).

(8) M. M. Koton, *ibid.*, **66B**, 1213 (1933).

observed. This is apparently true for even higher temperatures. Thus, in a preliminary report by Koton[9] with tin tetraphenyl in xylene at an initial hydrogen pressure of 50 atm., the separation of tin in 24 hours was 63% at 250° and 71% at 375°. That the reaction was not pyrogenetic was demonstrated in the present as well as in the last study by the absence of any change when hydrogen was omitted. Although Koton[10] observed no decomposition of the tetraphenyl under hydrogen pressure at 150°, 38.6% of the latter in decalin solution underwent hydrogenation to metallic tin as given in Table I.

TABLE I

DISPLACEMENT OF METALLIC TIN FROM TIN TETRAPHENYL[a,b]

Experiment	Time, hr.	Temp., °C.	Solvent[c]	Metallic tin displacement, %
2-60[d]	15	150	Decalin	38.6
3-63	15	200	Decalin	76.9
1-53	8	200	Dioxane	61.4
4-65[e]	15	200	Benzene	44.9
8-82	9	225	Xylene	76.3

[a] In each case, the initial hydrogen pressure was 60 atm. [b] Except for very small amounts of diphenyl, benzene comprised the chief hydrocarbon. [c] The volume of solvent averaged 50 ml. [d] A total of 2-4 g. of tin tetraphenyl was employed in each hydrogenation. [e] Only diphenyl was analyzed in the hydrocarbon mixture.

In agreement with earlier work,[3] lead tetraphenyl in ethanol when heated at 200° for 19 hours at an initial hydrogen pressure of 60 atm. was converted into lead to the extent of 97%. As in the case of tin tetraphenyl, benzene and traces of diphenyl were produced. The incorporation of copper powder comprising 25% the weight of lead tetraphenyl (or 10% in the case of tin tetraphenyl) did not alter the distribution of hydrocarbons. The latter experiments were included in the light of the Zartman and Adkins results with copper liners. It is of interest that the increased metallicity encountered with lead contributes to the greater ease of hydrogenation of its tetraphenyl in contrast to tin.

As the hydrocarbon mixtures from the hydrogenation of lead or tin alkyls have been little studied, tin tetraisobutyl and tin tetraethyl in the absence of solvent were submitted to hydrogenation at 300-310° for 20 hours at an initial hydrogen pressure of 100 atm. In both cases, metal was deposited. A total of 79% of the tin tetraisobutyl was converted into isobutane, 9% into isobutylene and possibly 2% into the corresponding C_8-hydrocarbons. Tin tetraethyl underwent at least a 67% conversion into ethane; some methane and only traces of propane and butane were produced. Thus, similar to the aryl compound, the hydrogenation proceeds under pressure with the formation of the corresponding hydrogenated residue, RH, to almost complete exclusion of R-R.

Experimental

Materials.—The organo-tin and lead compounds were prepared by reaction of the Grignard reagent from the appropriate organic bromide with stannic chloride or anhydrous lead chloride, respectively.[11] Redistillation of the alkyls and two recrystallizations of the tetraphenyls followed. Constants: tin tetraethyl, b.p. 180.5-181°, $n^{19.5}$D 1.4718; tin tetraisobutyl, b.p. 155-155.5° (24 mm.), n^{20}D 1.4760; both the tin and lead tetraphenyls melted at 229° (uncor.). All solvents were distilled before use. Copper powder was prepared by the reduction of the oxide with hydrogen at 250°.

Hydrogenation Procedure.—A rotating Ipatieff bomb of 450-ml. capacity was employed in all runs. A weighed amount of the organo-metallic compound together with solvent was introduced into a glass liner equipped with a stopper containing a coiled capillary inlet tube. The liner was placed in the bomb, the latter tightened and the system flushed with tanked hydrogen at a pressure of 50 atm. Hydrogen at the specified pressure was then pumped into the system. Heat was supplied to the rotating autoclave by a thermostatically controlled furnace. In most runs, the reaction was allowed to proceed for a given period of time without interruption. At the conclusion of the experiment, the gas was discharged prior to opening of the bomb. Where the gaseous mixture was to be analyzed, the gas was slowly passed through a series of condensing tubes immersed in liquid air, and the non-condensable gases were periodically sampled and pooled over salt solution.

Analysis of Products. a. Metal.—In the majority of cases, metallic tin occurred as a button of high purity. This together with smaller tin particles was washed with copious amounts of benzene as were the walls of the liner containing a thin film of the metal, and the latter was dissolved in hydrochloric acid, and analyzed and weighed as SnO_2. Metallic lead was dissolved in acid and determined gravimetrically as the sulfate.

b. Benzene and Diphenyl.—Benzene was obtained by fractionation of the liquid product, and then was characterized by constants and nitration.[3] Where dioxane or alcohol was employed, benzene appeared in a layer upon the addition of excess water to the distillate. Working of the still residues gave rise to very small amounts of diphenyl (under 4% and averaging 1-2%). No depression in melting point occurred on admixture with an authentic sample.

c. Gaseous Product.—The components of the condensable gas mixture were determined by Podbielniak distillation. Samples of non-condensable gases were analyzed in an Orsat assembly, the paraffin content being ascertained by combustion.

Hydrogenation of Tin and Lead Tetraphenyls.—A series of experiments was carried out with tin tetraphenyl at an initial hydrogen pressure of 60 atm. Relevant data including the percentage displacement of metallic tin appear in Table I. The following exemplifies one of the runs:

Experiment 3-63. Tin Tetraphenyl.—A total of 2.238 g. of tin tetraphenyl in 55 ml. of decalin (boiling range 185-195°) was hydrogenated at 200° for 15 hours at an initial pressure of 60 atm. of hydrogen. The reaction product contained a button of metallic tin which on analysis corresponded to 0.479 g. (76.9% conversion). Fractionation of the liquid contents yielded 0.80 g. of a cut boiling 81-90°, n^{21}D 1.4981, which was identified as benzene. Aside from some tin tetraphenyl, less than 30 mg. of diphenyl resulted on processing of the residue.

Experiment 12-56. Lead Tetraphenyl.—When 5.141 g. of lead tetraphenyl in 45 ml. of absolute ethyl alcohol was heated for 19 hours at 200° and an initial hydrogen pressure of 60 atm., small particles of lead were deposited. The latter after solution in nitric acid yielded 2.935 g. of lead sulfate (or 1.998 g. of lead), indicating a 96.7% conversion of the lead tetraphenyl. Traces of diphenyl (< 40 mg.) occurred in the alcohol solution.

Experiments 10-73 and 11-71. Effect of Copper Metal.—The hydrogenation of mixtures containing 8.76 g. of lead tetraphenyl and 2.19 g. of copper powder in 60 ml. of absolute ethyl alcohol or 2.39 g. of tin tetraphenyl and 0.24 g. of copper in 70 ml. of decalin (at 200° for 9 hours; initial hydrogen pressure, 60 atm.) gave rise to products very low in diphenyl. The gray metal mixture in the tin tetraphenyl run appeared to be more homogeneous than that of the lead-copper mixture.

Hydrogenation of Tin Tetraisobutyl.—A total of 26.85 g. (79.4 millimoles) of tin tetraisobutyl was heated in the ab-

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(9) M. M. Koton, *J. Gen. Chem.* (*U. S. S. R.*), **2**, 345 (1932).

(10) M. M. Koton, *ibid.*, **4**, 653 (1934).

(11) E. Krause and A. von Grosse, "Die Chemie der metall-organischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937.

sence of solvent for 20 hours at 300–310° (initial pressure, 100 atm. of hydrogen). The condensable gas, 5.51 l. (S.C.; 246 millimoles), analyzed as follows on Podbielniak distillation: propane, 1.6%; isobutane, 85.7%; *n*-butane, 3.1%; isobutylene, 2.5%; C_5-, 0.6%. The non-condensable gases contained 39 millimoles of paraffin (index, 3.34), undoubtedly, mainly isobutane. The over-all conversion into this hydrocarbon was 79%. Although the metal was not analyzed, the contents were rinsed with portions of absolute ether totalling 100 ml., and the latter distilled. After removal of the ether, 0.41 g. of a fraction boiling 107–110°, $n^{24}D$ 1.3882, was obtained which contained small amounts of olefin as based on reaction with bromine. This product might comprise mainly 2,5-dimethylhexane or diisobutyl (b.p. 109°, $n^{20}D$ 1.3930[12]) together with unsaturated hydrocarbons.

Hydrogenation of Tin Tetraethyl.—Under the same conditions as those of the last experiment, 16.07 g. (66.4 millimoles) of tin tetraethyl yielded 4.93 l. (S.C.; 220 millimoles) of condensable gas with the following composition: methane, 9.8%; ethane, 83.3%; propane, 4.1%; butane, 1.7%; C_5-, 1.1%. The conversion to ethane amounted to 67%. As losses occurred on analysis of the non-condensable gas sample, this value may be greater. Liquid hydrocarbons were absent.

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(12) G. Egloff, "Physical Constants of Hydrocarbons," Vol. 1, Reinhold Publishing Corp., New York, N. Y., 1939, p. 53.

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[Contribution from the Laboratory of Physical Chemistry, University of Wisconsin]

Boundary Spreading in Sedimentation Velocity Experiments. I. The Enzymatic Degradation of Serum Globulins

By J. W. Williams, Robert L. Baldwin, Winifred M. Saunders and Phil G. Squire

By analysis of the way in which a boundary in the velocity ultracentrifuge spreads with time, it is possible to sort out the effects of diffusion and of size and shape heterogeneity. When the molecules sediment and diffuse independently of each other the following equation holds: $\sigma^2/2t = D^* = D + D\omega^2 s_m t + (p^2\omega^4 x_m{}^2 t/2)$. In this expression σ^2 is the second moment of the boundary gradient curve, t is the time, D^* and D are the apparent and true weight (refractive) average diffusion coefficients, p is the standard deviation of the distribution of sedimentation constant in a system which is heterogeneous as regards molecular mass and shape, s_m is the mean sedimentation constant, ω is the angular speed of rotation and x_m is the distance of the centroidal ordinate of the boundary from the center of rotation of the ultracentrifuge.

Since the boundary spreading due to differences in sedimentation constant is proportional to $x_m t$, while that due to diffusion is closely proportional to $t^{1/2}$, then as $t \rightarrow \infty$ the relative effects of diffusion in modifying the shape of the boundary disappear and there can be obtained a distribution of sedimentation constants of the molecules in the system. In addition, it is possible to obtain the standard deviation of the sedimentation constant distribution from the slope of the plot of the apparent diffusion coefficient, D^* *vs.* $x^2{}_m t$.

This approach has been used in the study of the heterogeneity in pepsin-digested γ-globulin systems. The γ-globulin fractions used as starting materials showed measurable heterogeneity by this boundary spreading technique. One, a mixture of γ_1- and γ_2-globulins, showed greater heterogeneity in its sedimentation behavior after pepsin digestion than the other, a γ_1-globulin preparation. The pepsin digestion method of Pope has been adapted to produce a material of reasonably high physical homogeneity.

The term homogeneity is used in several ways in protein chemistry. In biochemistry it is often employed to indicate that the molecules are alike in regard to properties, such as biological activity, which are of particular interest to the biochemist; it is frequently assumed that such molecules have the same origin. In physical chemistry it is easier to give quantitative meaning to the term homogeneity since it is possible with certain methods, such as sedimentation velocity, sedimentation equilibrium, diffusion and electrophoresis, to measure the extent of the physical heterogeneity of the protein without further fractionation.

There are at least three reasons why studies of heterogeneity are being made today. First, (and this applies equally to all quantitative measurements on proteins—physical, chemical or biological) the meaning of physical constants obtained with a protein system depends upon its heterogeneity. For example, the molecular weight of a mixture, in unknown amounts, of hemoglobin and γ-globulin, calculated from iron content or from osmotic pressure measurements, has little meaning. If, however, some method is available for determining the amount of each, the molecular weight of the mixture has more value; from the iron determination the minimum molecular weight of the hemoglobin could then be found or the molecular weight of one could be calculated from the osmotic pressure measurements, knowing the molecular weight of the other. Second, in order to follow certain processes of interest both to the physical chemist and to the biochemist it is necessary to measure changes in the heterogeneity of a protein system. Such a process is the denaturation and digestion of serum globulin by pepsin, which will be discussed here. Third, such studies are necessary in deciding whether or not living organisms produce absolutely homogeneous proteins, a question of considerable interest to the biochemist. The results of Alberty, *et al.*,[1] have suggested that most proteins, even those of very mild treatment in preparation, show measurable heterogeneity in electrophoresis. Of course, allowance must be made for the fact that the methods of fractionation or separation may have produced the observed heterogeneity.

Theory

Boundary Spreading (RLB, JWW).—We have been led to study whether the contributions of molecular mass and shape heterogeneity and of diffusion to the spreading of the sedimentation velocity boundary could be sorted out to provide a means for the quantitative description of each effect. From our remarks it will be evident that some progress has been made in this direction.[2]

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(1) R. A. Alberty, *et al.*, This Journal, **70**, 1675 (1948); *J. Phys. Colloid Chem.*, **52**, 217, 1345 (1948).

(2) R. L. Baldwin and J. W. Williams, This Journal, **72**, 4325 (1950).