

0.5 g. of the catalyst at 310–320° for forty-five minutes, the product distilled (b. p. 272–278° at 3 mm.) from the catalyst and then recrystallized from benzene-alcohol, 4.37 g. (88%) of 5-methyl-1,2-benzanthracene melting at 155–157° was obtained.

Dehydrogenation was also accomplished by heating 0.5 g. of the hydrocarbon mixture obtained by the potassium acid sulfate treatment with 0.07 g. of sulfur at 250° for ten minutes. Copper powder was added to the hot mixture to combine with the excess of sulfur and the product was sublimed under reduced pressure; by recrystallizing the sublimate from benzene-alcohol, 0.35 g. of 5-methyl-1,2-benzanthracene melting at 156.5–157° and 0.05 g. melting at 154–156° was obtained. Cook reports 157.5–158.5° for the melting point of the pure hydrocarbon.

Summary

1-Methyl-, 1-ethyl- and 1-*n*-propyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene have been obtained in crystalline form and tested for oestrogenic activity. The carbinols can be converted rapidly to 1-alkylphenanthrenes in one operation by means of a palladium-charcoal catalyst. 1-*n*-Butylphenanthrene and 1-phenylphenanthrene have been prepared for the first time. A rapid preparation of 5-methyl-1,2-benzanthracene by means of the catalyst is described.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Balandin Multiplet Hypothesis of Dehydrogenation of Cycloparaffins

BY HUGH S. TAYLOR

The ready dehydrogenation of cyclohexane in contact with palladium and metals of the platinum group at 300° was demonstrated by Zelinski¹ in 1911. This test was applied by him to the determination of hexahydroaromatics in Caucasian petroleum when he observed that cycloheptanes² and cyclopentanes¹ do not undergo dehydrogenation under the given conditions. Since these initial efforts, a great deal of experimental research has been devoted, in the laboratories of Zelinski and his collaborators, to test of the dehydrogenation activity of the platinum metals and of nickel, in many derivatives of the cycloparaffins, hydrogenated polycyclic hydrocarbons and heterocyclic derivatives. A few of these researches pertinent to the subsequent discussion may be summarized.

Zelinski and Delzowa investigated the derivative 1,1-dimethylcyclohexane³ and found that, even with a platinum catalyst extremely active for cyclohexane, no dehydrogenation of the 1,1-dimethyl derivative occurred. The conclusion was reached that such cyclo compounds, doubly substituted on a single carbon atom, are not to be regarded as hydroaromatics in contrast to the cases of *o*-, *m*-, and *p*-disubstituted cyclohexanes which readily yield the dehydrogenated disubstituted benzenes. In the same year Zelinski studied⁴ the so-called octanaphthene

and nonanaphthene fractions collected from petroleum sources and found that, when hydroaromatics were removed carefully, the residues were not susceptible to dehydrogenation on the platinum metals at 300°. The nonanaphthenes were thought to be homologs of cyclopentane but the inertness of the eight-membered cyclic compounds was later confirmed by the work of Zelinski and Freimann⁵ who found that a synthetic preparation of cyclooctane only undergoes partial dehydrogenation with the loss of one molecule of hydrogen, and the formation of a bridged-ring structure (1, 5) or, by rearrangement, methylcycloheptane, which was not further dehydrogenated.

Zelinski and Levina showed⁶ that although cyclopentane was not dehydrogenated on the platinum metals at 300°, nevertheless, cyclopentadiene, in the presence of hydrogen at 160°, is hydrogenated on platinized charcoal yielding cyclopentane with simultaneous formation of the tricyclic structure, tricyclodecane.

Zelinski and Balandin⁷ showed that dehydrogenations of piperidine, cyclohexane and decalin all occurred readily on palladium, platinum or nickel and that the apparent activation energy was dependent only on the catalyst, not on the substrate. On platinum, activation energies between 18 and 19.9 kcal. were found, with nickel 9.7–10 kcal., and with palladium 15.3–16.3 kcal.

(1) Zelinski, *Ber.*, **44**, 3121 (1911).

(2) Zelinski, *ibid.*, **45**, 3878 (1912).

(3) Zelinski and Delzowa, *ibid.*, **56**, 1716 (1923).

(4) Zelinski, *ibid.*, **56**, 1718 (1923).

(5) Zelinski and Freimann, *ibid.*, **63**, 1485 (1930).

(6) Zelinski and Levina, *ibid.*, **66**, 477 (1933).

(7) Zelinski and Balandin, *Z. physik. Chem.*, **126**, 267 (1927).

Mention also must be made of the phenomenon of "irreversible catalysis" investigated by Zelinski and Glinka.⁸ They found that two molecules of cyclohexadiene reacted on platinum catalysts to form one molecule each of benzene and cyclohexene. More recently Zelinski and Pawlow⁹ showed a parallel "irreversible catalysis" involving three molecules of cyclohexene to yield one molecule of benzene and two of cyclohexane. In this work Zelinski found that the "irreversible catalysis" occurred more rapidly on a catalyst than either hydrogenation or dehydrogenation.

With this background of experimental research of the Zelinski school, Balandin¹⁰ attempted to formulate a general theory of heterogeneous catalytic action, since known as the "multiplet hypothesis," which was specially adapted to the interpretation of data of the types just discussed, especially decomposition and dehydrogenation. Balandin proceeded from two postulates (a) that the binding between two atoms in an adsorbed molecule may be broken if they are attracted by two different catalyst atoms and (b) that a bond may be closed between atoms of an adsorbed molecule bound to the same catalyst atom. Catalysis arises, according to this view, through the geometrically determined action of various catalyst centers, hence the term multiplet hypothesis. Similar views had earlier been formulated in less detail by Burk¹¹ under the title "multiple adsorption."

The attractiveness of the Balandin view lay in its application to the dehydrogenation of cycloparaffins. The activity of catalysts in the dehydrogenation of hexahydroaromatic compounds was associated with the geometric structure of the catalysts. The six-membered cyclohexane ring was associated with the octahedral face of a face-centered cubic metal lattice, this face having a triangular atomic lattice so disposed that the atoms at the corner of the triangle could adsorb a cyclohexane molecule at the mid-points of each alternate C-C bond, with, at the same time, adjacent catalyst atoms suitably placed to attract to themselves two hydrogen atoms from adjacent CH₂ groups in the ring. This specialized geometrical concept led to the conclusion that face-centered cubic metals are es-

pecially favorable materials for dehydrogenation of hexahydroaromatics and that, further, their lattice constants must lie within certain limits. Actually, dehydrogenation was found with metals between the lattice limits 1.397 Å. (Pd) and 1.237 Å. (Ni) while metals only slightly outside these limits (Sn = 1.40 Å.) are inactive.

The development of the theory led to many definite conclusions, the more important of which may be summarized. (1) All six hydrogen atoms must be split off simultaneously from hexane and, in general, from all saturated six-membered rings. (2) Five- and seven-membered hydrogenated rings are not suitable for dehydrogenation for geometric reasons. There are no lattices with the symmetry 5 or 7. (3) Although the three-membered ring may be accommodated on a triangular lattice the position of the active centers is not favorable for dehydrogenation. (4) Geometrical considerations of substrate and catalyst determine the lattice limits discussed above. (5) Substitution of methyl for one hydrogen in the ring in no way hinders dehydrogenation, since the molecule can be adsorbed with six hydrogens favorably located. (6) 1,1-Dimethylcyclohexane cannot be disposed suitably on the triangular lattice and so dehydrogenation is difficult. (7) *trans*-Disubstituted cyclohexanes should not suffer dehydrogenation unless they can first be converted to the *cis* form. (8) Polycyclic six-membered rings can be disposed on such a surface as readily as cyclohexane. Similar dehydrogenation characteristics must be expected. (9) The geometrical disposition of adsorbed cyclohexadiene and of cyclohexene gives a ready geometric interpretation of "irreversible catalysis." (10) Heterocyclic six-membered hydrogenated ring systems are also suitable geometrically for such dehydrogenation. (11) An obvious alternative disposition of the six-membered ring on the triangular lattice suggests the mechanism of ring-splitting in accord with experimental observations.

It is at once clear how these conclusions fit the experimental observations of Zelinski's researches as already outlined and led to further efforts at experimental check. Zelinski and Margolis¹² compared the dehydrogenations of *cis* and *trans o*- and *p*-dimethylcyclohexanes, but found no difference in their behaviors on platinized charcoal at 300°. They found, however, in their prepa-

(8) Zelinski and Glinka, *Ber.*, **44**, 2305 (1911).

(9) Zelinski and Pawlow, cited by Balandin and Brussow, *Z. physik. Chem.*, **B34**, 96 (1936).

(10) Balandin, *ibid.*, **B2**, 289 (1929).

(11) R. E. Burk, *J. Phys. Chem.*, **30**, 1134 (1926).

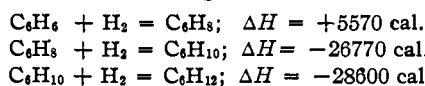
(12) Zelinski and Margolis, *Ber.*, **65**, 1613 (1932).

rations, by hydrogenation of the corresponding xylenes, evidence for isomerization from *cis* to *trans* on osmium at higher temperatures (150°) than that required for preparation of the *cis* form (50–70°). On nickel, at 175°, the *trans* form is obtained by hydrogenation and the *cis* form is converted to *trans* on the same catalyst. There is, therefore, a possibility that the similarity of behavior in the two forms can be associated with an isomerization equilibrium. Ehrenstein and Bunge¹³ found that *cis*- and *trans*-decahydroquinoline were equally easily dehydrogenated on platinum contacts; the *trans* form was resistant to dehydrogenation on palladium, although the *cis* form was dehydrogenated readily on the same metal. The reason for the difference between platinum and palladium was not elucidated.

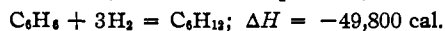
A more serious comment on the Balandin theory was raised by Lazier and Vaughen,¹⁴ who found that cyclohexane could be dehydrogenated on chromium oxide catalysts, especially of the gel type, which did not possess the face-centered lattice structure or the sextet-type orientation postulated for the metal catalysts. Balandin and Brussow¹⁵ recently met this objection by calling attention to the possibility of a doublet orientation to a catalyst which involves a side-wise adsorption of the cyclohexane ring and which would catalyze a step-wise dehydrogenation, two atoms at a time. Such an orientation would not require the specialized crystalline structure necessary for the sextet orientation. Lattices of other symmetry classes would suffice. The requirement that only six-membered rings could be dehydrogenated would no longer hold and five- and seven-membered rings should be attacked as well as the hexagonal rings. Their test of these points on catalysts of chromium and molybdenum oxide led them to the conclusion that experiment verified these consequences of doublet orientation. Further comment on this conclusion will be deferred until a point of view has been set forth with regard to the dehydrogenation reactions in cyclic polymethylene systems which has hitherto been overlooked.

Comparative studies of catalytic efficiency in systems of the type here under discussion must all satisfy the general criterion of catalytic action, namely, that the reaction occurring is accompanied by a free energy decrease, that it is thermodynamically possible. In the system benzene-

hydrogen-cyclohexane it was shown experimentally by Dougherty and Taylor¹⁶ that the equilibrium changes rapidly from the cyclohexane to the benzene side in the temperature range of 100 to 300°. No corresponding measurements have been found in the corresponding five- and seven-membered ring systems. In the interval, the development of the quantum mechanical concept of resonance or conjugation energy has demonstrated that the benzene ring possesses a high degree of stability associated, in the main, with the alternating double-single bond linkages of the two Kekulé structures for the molecule. This degree of stability is greater than that found, as yet, with any other conjugated system. It is excellently exhibited by the data on heats of hydrogenation of benzene and its partially hydrogenated products, as determined recently by Kistiakowsky and his co-workers.¹⁷ This is shown in the following data from this source.

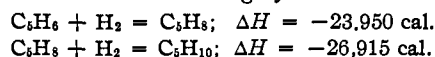


By summation, for the total process, one obtains

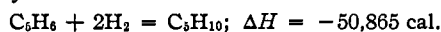


The heats of hydrogenation of cyclohexene and cyclohexadiene are not markedly different from that of a normal ethylenic linkage. On the contrary, the hydrogenation of benzene to cyclohexene is changed by reason of the conjugation energy of benzene from a negative to a positive value of $\Delta H = +5570$ cal.

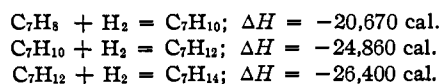
No similar stabilization can be anticipated in the five- and seven-membered ring systems and this is confirmed by data from the same source as the preceding and by the, as yet, unpublished data kindly supplied by Professor Kistiakowsky.¹⁸ For the five-membered ring system we have



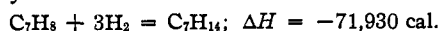
and, by summation



Correspondingly, for the seven-membered ring systems



and, by summation



(16) Dougherty and Taylor, *J. Phys. Chem.*, **27**, 533 (1923).

(17) Kistiakowsky, Ruhoff, Smith and Vaughn, *THIS JOURNAL*, **58**, 137, 146 (1936).

(18) Private communication.

(13) Ehrenstein and Bunge, *Ber.*, **67**, 1715 (1934).

(14) Lazier and Vaughn, *THIS JOURNAL*, **54**, 3080 (1932).

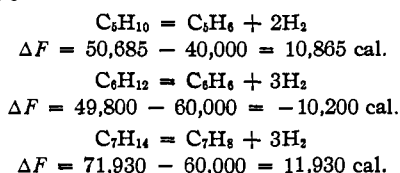
(15) Balandin and Brussow, *Z. physik. Chem.*, **B34**, 96 (1936).

In the cases of the hydrogenation of both C_6H_6 and C_7H_8 , we have evidence in the low heats of hydrogenation of some stabilization due to resonance, in neither case comparable, however, with that in the case of benzene.

Now, it is precisely this degree of stabilization in the case of benzene which is the important factor in determining the ready dehydrogenation of cyclohexane to benzene. This can be seen from a consideration of the free energy equation for the several dehydrogenation processes at the temperature of $600^\circ K.$, a temperature close to that employed by Zelinski in his standard dehydrogenation technique (300°). Employing the thermodynamic equation in the form

$$\Delta F = \Delta H - T\Delta S$$

we make the assumption, in the absence of actual data, that the entropy change approximates to 33.3 entropy units for each hydrogen molecule eliminated. This assumes that the entropy change is approximately that of the hydrogen produced, $S_{298}(H_2) = 31.2$, and that the entropies of the hydrocarbons do not differ significantly. Using this value for ΔS , $T\Delta S$ then amounts to 20 kcal. per hydrogen molecule eliminated at $600^\circ K.$ It then follows that, in every case but the dehydrogenation of cyclohexadiene to benzene, the free energy change is positive. In the exceptional case it is strongly negative, $\Delta F = -5570 - 20,000 = -25.57$ kcal. This approximation also ignores the change of ΔH with temperature. For the over-all processes, in the three cyclic systems, the data give



The unique characteristics of the dehydrogenation of cyclohexane compared to cyclopentane and cycloheptane are thus strikingly shown. Quite abnormal variations in the entropy changes would be necessary to change the conclusions. In other words, the stabilization energy of the benzene molecule, ~ 35 kcal., is equivalent to an entropy change of 50–60 units at 300° .

We are therefore led to the conclusion that the absence of dehydrogenation at 300° in cyclopentane and cycloheptane systems arises from the thermodynamic limitations of the systems and does not arise from any stereochemical factors

involving catalyst and substrate structures. The argument of Balandin on this latter basis is thereby markedly weakened.

The invalidity of the Balandin hypothesis emerges, however, from the observation that the catalyst employed by Kistiakowsky and his colleagues for the calorimetric determinations on hydrogenation of the cyclopentenes and cycloheptenes was the Co-Ni catalyst, studied by Long, Frazer and Ott¹⁹ in their researches on metal lattices of the Balandin face-centered cubic type. It is quite obvious that the configurational characteristics of a catalyst which are adequate for a given process of hydrogenation cannot be unsuitable for the reverse process of dehydrogenation. The impossibility of the structural explanation strengthens further the thermodynamic explanation suggested. This is confirmed by the research of Zelinski and Levina already cited⁶ in which it was shown that the structure of the platinum catalyst was compatible with the hydrogenation of cyclopentadiene to cyclopentane at 160° . Platinum should therefore not be configurationally unsuitable, in the reverse dehydrogenation process, when thermodynamically possible.

It now remains to show how the thermodynamic limitations on these dehydrogenation processes account for the other characteristics that have been cited in support of the configurational concepts of Balandin. The absence of intermediate dehydrogenation products in the case of cyclohexane is at once evident from observation of the relevant heat data. Neither in the case of cyclohexene nor cyclohexadiene can we expect more than a minute concentration at equilibrium at 300° . In none of the cases where little or no resonance stabilization is involved can we expect equilibrium concentrations of unsaturated product very different from those we would expect in the paraffin-ethylene series at the same temperature. It is the final stage, yielding benzene, with its abnormal ΔH value which acts to displace these equilibria to the completely unsaturated side.

The dehydrogenation of 1,1-dimethylcyclohexane is entirely analogous to the reaction $C_6H_{12} = C_6H_6 + 2H_2$. This system derives no advantage from the resonance stabilization of benzene, $\Delta F = 55,370 - 40,000 = +15,370$ cal., and the equilibrium concentration of diene nec-

(19) Long, Frazer and Ott, *THIS JOURNAL*, **56**, 1101 (1934).

essarily will be small. Only with catalysts, of which nickel may be an example, which have strong tendency to break carbon-carbon bonds, making possible the simultaneous removal of methane, would the advantage of the resonance energy be obtainable. Platinum and palladium are not suitable catalysts for such carbon-carbon ruptures.

Thermodynamically, the difference between dehydrogenations of *cis* and *trans* disubstituted isomers of cyclohexane involves only the small differences of free energy between the two forms and not the structural considerations advanced by Balandin. This conclusion is in accord with the general results of the investigations previously cited in this respect.

The phenomenon of "irreversible catalysis" discovered by Zelinski is in best agreement with the thermodynamics of these systems. The "irreversible" conversion of cyclohexadiene and of cyclohexene to benzene and cyclohexane is in each case determined favorably as to equilibrium by the stabilization energy of the benzene formed. The effect should be most pronounced in the case of cyclohexadiene, of which reaction it is known that, on platinum catalysts, the change to benzene and cyclohexane is observable at -78° . Since the evidence indicates that it is not the structural characteristics of the catalyst that determine the "irreversibility," the observation that these irreversible catalyses proceed more rapidly than the corresponding hydrogenations or dehydrogenations points strongly to an inhibitory action of hydrogen in these latter processes. It is to such an effect of hydrogen that Lourdu and Taylor²⁰ have ascribed the different activation energies in the case of metal and hydrogenating oxide catalysts such as chromium oxide. This conclusion is also in best agreement with the observations of Zelinski and Balandin that the apparent activation energies of dehydrogenation of piperidine, cyclohexane and decalin were the same on a given catalyst but varied from one catalyst to the other. Since the configurational state of the catalyst is not decisive, it would appear that the adsorption characteristics of the catalyst for the common factor, the hydrogen, determine the apparent activation energy.

With respect to the dehydrogenation studies of

(20) R. P. Lourdu and Taylor, *Bull. soc. chim. belg.*, forthcoming publication (1938).

Balandin and Brussow on chromium oxide catalysts it should be observed that their evidence for the presence of the intermediates cyclohexene and cyclohexadiene was very inconclusive; nor, on the thermodynamic basis, should there be more than traces of these present. Their experiment to show that pentamethylene rings are dehydrogenated on chromium oxide is also inconclusive, since it is known that, on this catalyst, in the range $400-450^{\circ}$, ready dehydrogenation of paraffinic hydrocarbons occurs. It was not shown that the hydrogen formed came from the 30% pentamethylene content of the Caucasian petroleum sample employed. At the higher reaction temperatures ($400-450^{\circ}$) prevailing in these oxide-catalyzed dehydrogenations conditions are, however, thermodynamically more favorable to all the dehydrogenation processes than at the temperature of 300° used by Zelinski. Comparatively, however, the dehydrogenation of the six-membered rings is still overwhelmingly the most favorable.

In conclusion, it may be emphasized that the point of view here presented is not to be regarded as suggesting that dehydrogenation of hexahydroaromatic compounds does not involve a planar adsorption of the six-membered ring molecules to be dehydrogenated. That may be the most favorable configuration for the process. The paper does, however, insist that the geometrical relations of substrate and catalyst do not account for the absence of catalytic efficiency in the five- and seven-membered rings and that the hydrogenation experiments with such ring systems when unsaturated indicate that the geometrical structure of the catalyst is not an essential determining factor.

Summary

1. Data of Zelinski on catalytic dehydrogenation of saturated cyclic ring systems have been summarized.
2. The data have been correlated with the Balandin multiplet hypothesis of heterogeneous catalytic action.
3. The dehydrogenation reactions have been examined from the standpoint of equilibrium using newer heat data.
4. It has been concluded that dehydrogenation of cyclopentanes and cycloheptanes at 300° is thermodynamically unfavorable, while that of cyclohexane to benzene is favorable due to the

resonance stabilization of the benzene molecule.

5. The available data on dehydrogenation of these ring systems can be accounted for satisfactorily on the basis of probable equilibria.

6. The Balandin multiplet hypothesis thereby loses its principal support.

7. The Balandin hypothesis is invalidated by the observation of catalytic hydrogenation of unsaturated cyclopentenes and cycloheptenes on catalysts configurationally unsuitable on the basis of the multiplet hypothesis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

Studies on Phosphorescent Zinc Sulfide¹

BY WILLIAM H. BYLER

Introduction

The purpose of this work was to develop a controlled method of preparation of phosphorescent zinc sulfide so that a defined group of preparations could be studied for correlation of certain luminous properties among themselves and with the composition and method of preparation of the phosphors. Efforts to correlate the results of different investigators have sometimes been futile because radical differences in luminous properties may result from very slight differences in composition or method of preparation of the materials. By this approach, it was hoped that new light might be thrown on the problems of the necessary conditions for phosphorescence and the nature of the mechanisms of luminescence processes. A simple, objective method of measurement of luminosity was developed in order to facilitate the study.

Preparation of Phosphorescent Zinc Sulfide.—The method employed in this work involved heat treatment of sulfide which was precipitated from ammoniacal solution, washed, filtered, dried at 105°, ground and passed through 200-mesh silk. The calcined material was soaked in water, dried, and passed through 200-mesh silk. Copper solution was added before the precipitation and flux in the dry state was mixed into the wet sulfide.

The difficulty of obtaining a uniform product is due to the effect of variable composition resulting from slight differences in method of preparation, to the marked effect of mere traces of certain metals, and to the important influence of physical state on luminous properties. Using constant heat treatment, the effects of the last two of these factors are usually not revealed except by measurement of luminosity but the first effect sometimes may be recognized by casual examination of color or tendency of the lumpy product to separate into individual crystals.

It is known that the color may be varied widely by variation of composition and heat treatment, but these

factors may be held constant within the limits of control and the color still vary somewhat. Guntz² demonstrated the important role of zinc oxide in color determination and variations observed in the preliminary stages of this work may be explained on that basis. The amount of zinc oxide in the finished material may be influenced by (1) the character of the atmosphere in the furnace, (2) the reaction of zinc sulfide with water which is present in the dried material in a hydrate, (3) the reaction of the retained ammonium chloride with zinc oxide, and (4) the reaction of zinc oxide with zinc sulfide. The atmosphere in the gas furnace was kept slightly oxidizing and lids were placed loosely on the crucibles. Uniform washing conditions and timing of the filtration process were depended upon to regulate the amount of foreign salts retained by the sulfide.

Ease of disintegration of the lumps in water is significant because the amount of handling required to get the product into powder form is reflected in the quality. There is some evidence that intergrowth of crystals is promoted by a large excess of ammonium chloride. This may be due to reaction of the ammonium chloride with zinc sulfide or oxide to produce zinc chloride. This salt adsorbed on the surface of zinc sulfide crystals would promote cementing.

Metals of the iron group are particularly active as poisons. It is important to use pure starting material and to be on guard against contamination at every step. Any cobalt and nickel present in the electrolytic zinc was plated out almost completely on the zinc during the solution process. Any iron remaining was removed by precipitation as ferric hydroxide.

The physical state of the finished zinc sulfide crystals is largely controllable through regulation of the heat treatment. Calcination temperature could be controlled to within less than 5°. But the physical condition of the dried zinc sulfide is subject to significant variation. When a large excess of hydrogen sulfide is used, the washed precipitate filters quite slowly and shrinks to a brittle, green-yellow mass when dried. When the excess of hydrogen sulfide is small, the filtration is much faster, the shrinkage on drying is not so great, and the dried lumps are snow-white. Difference in color can be explained on the basis of difference in sulfur content. Differences in speed of filtration and density are probably due to difference in particle size or extent of aggregation of particles

(1) From a thesis submitted to the faculty of the Graduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) A. A. Guntz, *Ann. chim.*, **5**, 157 (1926).