[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

IV. The Mechanism of Reaction and of Poisoning in the Dehydroaromatization of *n*-Heptane

BY HUGH S. TAYLOR AND HAROLD FEHRER

In recent publications[1,2,3,4] relative to the dehydrogenation reactions which convert aliphatic hydrocarbons catalytically to aromatic products, marked attention has already been paid to the mechanism of the reaction, with little attention to the progressive poisoning of a catalyst with use which is, thus far, a universal feature of such reactions. We approach these two problems from the standpoint of a wider range of studies with a greater variety of catalysts than chromium oxide, which, hitherto, has been the principal objective of experimental study in the published data. We present data on the comparative rates of reaction of *n*-heptane, heptylene-1 and methylcyclohexane from the standpoint of yields and poisoning and in addition, data on the effect of poisoning by ethylene as a typical olefin. These data lead to certain conclusions with respect to the reaction mechanism in question.

Experimental Details

The apparatus and experimental procedure employed were essentially those described by us in preceding publications[5,6] on *n*-heptane whose characteristics were there described.

Materials.—Heptylene-1 of high purity was supplied to us by Professor G. B. Kistiakowsky of Harvard University, from a sample prepared for calorimetric determination of its heat of hydrogenation. The refractive index corresponded closely with that given by Kistiakowsky for his purest material.

Methylcyclohexane was an Eastman Kodak Co. product of highest purity, judged by its refractive index.

Ethylene of 99% purity or better was used after drying over phosphoric anhydride.

Experimental Results

Dehydroaromatization of Heptylene-1.—In Fig. 1 are presented comparative data for the rate of hydrogen evolution from heptylene-1 and *n*-heptane on passage of the two liquids at a feed rate of 0.3 cc. per minute at 475° after standard revivification over 15 g. of a catalyst containing 90% Cr_2O_3–10% SnO_2, the preparation SnO_2 II of our earlier report.[6] Under these conditions *n*-heptane yields a liquid product containing approximately 17% olefins and 25% aromatics. Hence, some 75/117ths of the hydrogen yield from *n*-heptane would come from further dehydrogenation of heptylene as an intermediate. Over the hour period under study this represents a practically constant rate of some 70 cc. of hydrogen per minute compared with the initial rate on pure heptylene-1 of 100 cc. per minute. The liquid product of a one-hour run with the pure heptylene-1 contained approximately 50% olefins, 10% heptanes and 40% aromatics. Some hydrogen was therefore consumed in this experiment, producing heptane. Nevertheless, it is apparent that a more than five-fold increase in the partial pressure of heptylene does not produce more than a two-fold increase in the initial hydrogen yield accompanying aromatic formation. It is further to be observed that the heptylene dehydrogenation is marked by an extremely rapid poisoning of the catalyst.

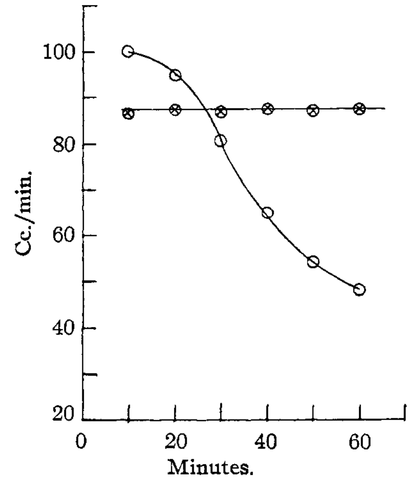

Fig. 1.—Rate of hydrogen evolution at 475°: O, heptylene 1; ⊗, *n*-heptane.

Dehydroaromatization of a Heptane–Heptylene-1 Mixture.—Over the same catalyst, under standard conditions, but at 450°, the reaction of a mixture of 85% *n*-heptane and 15% heptylene-1

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(1) H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **35**, 921 (1939).

(2) R. C. Pitkethly and H. Steiner, *ibid.*, **35**, 979 (1939).

(3) H. Hoog, J. Verheus and F. J. Zuiderweg, *ibid.*, **35**, 993, 1009 (1939).

(4) G. H. Twigg, *ibid.*, **35**, 1006 (1939).

(5) J. Turkevich, H. Fehrer and H. S. Taylor, THIS JOURNAL, **63**, 1129 (1941).

(6) H. Fehrer and H. S. Taylor, *ibid.*, **63**, 1385 (1941).

was compared with that of *n*-heptane. The pertinent data are given in Table I.

TABLE I

DEHYDROAROMATIZATION OF *n*-HEPTANE AND 85% *n*-HEPTANE–15% HEPTYLENE-1 OVER Cr_2O_3-10% SnO_2 (II) AT 450°

Run	Reactant	Rate of gas evolution cc./min. at *t* min. =			Cut no.	Liquid analyses		
		10	20	40		$d^{20}{}_4$	% Olefins	% Aromatics
245	*n*-Heptane	45	52	52	1	0.705	14.2	16.4
					2	.705	14.5	17.4
246	85% Heptane 15% Heptylene	48	48	46	1	.711	14.7	20.7
					2	.708	14.9	20.0

It will be noted that the initial presence of 15% heptylene-1 has a positive, but quite small, influence on the production of aromatics. If, however, the conversion be measured in terms of the rate of disappearance of heptane, it is obvious that the presence of the heptylene has markedly reduced the conversion rate. In pure heptane some 31 mole % of heptane has disappeared while in the heptane–heptylene mixture the heptane changed has fallen to 20 × 100/85 = 23.5%.

Dehydrogenation of Methylcyclohexane.—Comparative data for the rate of hydrogen production by dehydrogenation of heptane and methylcyclohexane are presented in Fig. 2. The experiments were carried out on a standard chromium oxide gel catalyst[5] and at 475°. The rate of hydrogen evolution for methylcyclohexane is more than double the initial rate with *n*-heptane and exceeds even the initial rate in the aromatization of heptylene-1. This is in agreement with the results of Hoog, Verheus and Zuiderweg.[3]

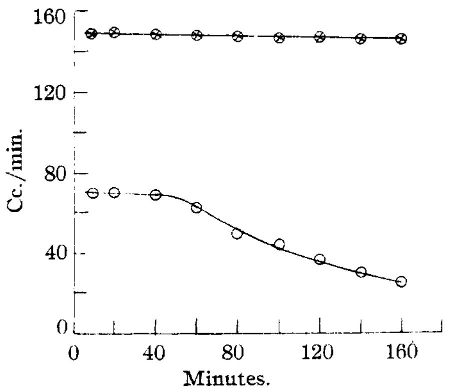

Fig. 2.—Rate of hydrogen evolution at 475°: ⊗, methylcyclohexane; O, *n*-heptane.

In contrast to the experiments with *n*-heptane, no decrease in catalytic activity was observed with methylcyclohexane even after several hours of run. The poisoning of the catalyst in the aromatization of *n*-heptane cannot therefore be due to cycloparaffins, cyclic mono- and diolefins, nor toluene. The inertness of toluene in the heptane dehydrogenation could be independently confirmed by addition to the heptane feed in which it behaves merely as a diluent. The gaseous product, containing more than 99% hydrogen, confirmed the cleanness of the methylcyclohexane reaction. Specific tests for mono- and diolefins disclosed that not more than traces of these substances could be present.

The Poisoning Effect of Ethylene.—The effect of ethylene on a chromium oxide surface was studied to provide information on the poisoning action of the olefin in the heptylene-1 experiments. The work was carried out on a standard chromium oxide gel catalyst, but one of medium activity only, under standard conditions of charge (0.3 cc. liquid per min. per 15 g. catalyst) at 475°. The data obtained are shown in Table II.

TABLE II

POISONING OF CHROMIUM OXIDE CATALYST BY ETHYLENE

Run	Pretreatment	Rate of gas evolution cc./min. at *t* min. =			
		10	20	30	40
178	Standard	41	35	29	23
179	Ethylene, then nitrogen	8	5	2	1
180	Standard	40	28	24	19
181	Ethylene, then hydrogen	8	4	3	2
182	Ethylene plus hydrogen	40	32	25	18

In the final run 182 the gas analysis showed 95.6% hydrogen and the liquid product 10.6% olefins and 11.6% aromatics which is normal for this grade of catalyst.

Run 178 represents a check run with a standard revivification and treatment of the catalyst prior to use. In run 179, after the standard revivification, ethylene was passed over the catalyst at 475° for three hours at a flow rate of six liters per hour. The exit gases were passed through a trap at −79° but no trace of polymerized product was noted. The catalyst was then flushed with pure nitrogen for five hours. On feeding *n*-heptane in standard fashion it was apparent that the ethylene had a very marked poisoning effect, the initial rate of gas yield being cut to one-sixth of normal. Standard catalyst revivification restored activity (run 180). In run 181 it is seen that, after passage of ethylene as in run 179, flushing with hydrogen instead of nitrogen did not serve to eliminate the poisoning effect of the ethylene. In this case, however, a few drops of yellow oily liquid collected in the exit trap. In run 182, after standard revivification, the catalyst was treated for four hours with a 1:4 ethylene–hydrogen mixture. It is apparent from the tabulated results of the ensuing run that hydrogen in excess when simultaneously present suppresses the poisoning effect of the ethylene, presumably by rapid hydrogenation to ethane. Had the poisoning been due to simple adsorption of ethylene the nitrogen flush in run 179 or still more the hydrogen treatment in run 181 would have served to displace the ethylene. The removal of oily liquid by hydrogen in the latter case suggests that a polymerization or carbonization of ethylene occurs on the surface. That hydrocarbon material is present on the catalyst surface after such treatment is shown by the oxidation of the material to form carbon dioxide and water during revivification.

The Variation in Olefin–Aromatic Ratio with Poisoning.—Data on the course of olefin and aromatic production during a run in which *n*-heptane reacted at 475° under standard conditions on a catalyst Cr_2O_3–10% ZrO_2, the ZrIII preparation of our earlier report,[6] are presented in Table III.

TABLE III

OLEFIN–AROMATIC PRODUCTION WITH PROGRESSIVE POISONING

Cut	Olefin, wt. %	Aromatic, wt. %	Aromatic: heptane converted
1	12	38	0.76
2	14	26	.65
3	14.5	16	.53
4	15	10	.40

Each cut analyzed represents one-half hour of operation at 0.3 cc. per min. liquid feed on 15 g. of catalyst. The rate of gas evolution fell from 90 cc. per minute initially to 31 cc. per minute at the end of the two-hour run. The data show that the fall in heptane conversion to one-half value is accompanied by a sharp decrease in aromatic formation while actually the olefin content of the liquid shows a slight rise. The poison affects much more seriously the aromatic formation than the dehydrogenation to olefin.

The Variation in Olefin–Aromatic Ratio with Catalyst and Temperature.—In Table IV data are collected from a number of different sources in our experimental program on the ratio of olefin to aromatic in the products of dehydrogenation of *n*-heptane at 475° under two normal conditions of test with a feed rate of (a) 0.3 cc. and (b) 0.05 cc. liquid per minute per 15 g. of catalyst.[7] The final column gives the cut examined, the number referring to the half-hour period in which it was collected. At the slow rate of feed, owing to slow rate of deterioration of the catalyst, the product examined corresponds essentially to the initial cut at the faster feed rate.

TABLE IV

OLEFIN–AROMATIC PRODUCTION WITH VARYING CATALYSTS AT VARIOUS TEMPERATURES

Catalyst	Feed rate, cc./min.	Temp., °C.	Olefin, wt. %	Aromatic, wt. %	Aromatic: heptane converted	Cut
Standard gel	0.3	475	15	15	0.5	1–4
Cr_2O_3 ex jelly		475	15	13	.46	1–3
Cr_2O_3 gel by alcohol reduction		450	13.3	23.1	.64	1
		475	13.5	41.5	.75	1
		475	13.6	24.3	.63	2
Cr_2O_3 ex acetate		450	12.9	20.3	.61	1
		475	12.8	25.5	.66	1
		500	12.2	29.9	.73	1
Cr_2O_3-10% ZrO_2III		475	12.2	38	.76	1
Cr_2O_3-10% SnO_2I		475	17.2	26	.60	1
		475	16.8	24	.58	2
		475	16.4	19	.42	3
ZnO-Cr_2O_3		475	4.9	8.9	.64	1–2
MoO_3-Cr_2O_3		475	8.0	19.3	.70	1–3
MnO-Cr_2O_3		475	3.1	6.1	.66	1–3
10% Cr_2O_3 on alumina	0.05	475	15.5	26.8	.63	1
10% Cr_2O_3 on alumina		495	13.9	49.2	.78	1
10% Cr_2O_3 on alumina		510	12.3	60.8	.82	1
10% V_2O_5 on alumina	0.05	510	12.7	29.1	.71	1
10% ThO_2 on alumina		555	11.7	16.3	.58	1
15% V_2O_5 on $Al(OH)_3$		510	7.2	75.6	.91	1
15% V_2O_5 on $Al(OH)_3$		490	10.1	36.0	.80	1
CeO_2 gel		510	5.4	12.8	.70	1

Over a variety of chromium oxide catalysts at 475° there is not a great variation in the fraction of heptane undergoing dehydrogenation which is converted to aromatic hydrocarbon at the outset of the reaction. Fractions varying between 0.6 and 0.75 are recorded in the table. This is true irrespective of the extent of dehydrogenation whether great or small. With increase of temperature, the fraction of the heptane reacting to yield aromatic increases markedly. The incorporation of molybdenum and manganese oxides in the chromium oxide gel tends to increase the ratio of aromatic formed even at low total conversions. Cerium and vanadium oxide catalysts give aromatic fractions in the same range as chromium oxide but at higher temperatures. Thoria gives a definitely low ratio even at the highest temperature studied. The favorable influence of temperature on aromatic yield per unit of paraffin

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(7) The data at low speeds are from the dissertation of R. A. Briggs, Thesis, Princeton, 1940. See R. A. Briggs and H. S. Taylor THIS JOURNAL, forthcoming publication.

dehydrogenated parallels the observation of Pitkethly and Steiner[2] on the influence of time of contact. On an unspecified catalyst, presumably chromium oxide at 475°, the ratio of aromatic to heptane dehydrogenated increased steadily with increased time of contact, τ, as the following data show:

τ, sec.	2	5	7.5	20
Aromatic : heptane converted	0.29	0.36	0.49	0.64

Our own observations over a range of temperatures confirm this result.

General Discussion

In preceding discussions of mechanism in this set of dehydrogenation reactions the general conclusion has been reached that the cyclization proceeds through the olefinic stage[3] or the half-hydrogenated state, C_7H_{15},[2,4] regarded as the intermediate step in the paraffin-olefin dehydrogenation. For simplicity, previous authors have assumed that the olefin-forming and cyclization reactions are unimolecular and attempted to draw consequent conclusions. It is clear from the present communication that these assumptions over-simplify the problem and indeed they are not to be expected from previous kinetic experience and data on the adsorption of hydrocarbons.[8] All such evidence indicates that the adsorption of olefins is markedly stronger than that of the corresponding paraffin. This would lead to a dehydrogenation kinetics to the olefin stage unimolecular with respect to the paraffin but inhibited by the olefin formed. The surface of the catalyst would be largely covered with olefin (or half-hydrogenated radical) and dehydrogenation of paraffin would occur on the small fraction of the available surface left bare. Pease's experiments[9] on the hydrogenation of ethylene on active copper catalysts are indicative of this inhibitory action of the olefin and of the weak adsorption of the saturated hydrocarbon, ethane. Our own experiment revealing a lower heptane conversion in 85% heptane–15% heptylene mixtures when compared with conversion with pure heptane is confirmatory of the inhibiting action of the olefin and suggests a paraffin dehydrogenation unimolecular with respect to paraffin and inversely to some power of the olefin. The strong poisoning action of ethylene is also indicative of the marked adsorption of ethylene and any polymeric olefinic products formed from it at the catalyst surface.

With strong adsorption of olefin (or half-hydrogenated radical) at the catalyst surface it follows also that the cyclization of such an intermediate cannot be a unimolecular reaction but will be kinetically somewhere between zero and first order determined by the fraction of the surface covered at the operating pressure. Our experiments on heptylene-1 and heptane–heptylene mixture confirm this. The rate of dehydrogenation increased less than two-fold for a five-fold increase in olefin partial pressure.

In a number of catalytic reactions the rate determining step is the desorption of a reaction product. That is not the case in the present reaction. Toluene is demonstrably without influence, other than that of a diluent, on the rate of reaction. That desorption of hydrogen is not rate controlling is evident from the comparative experiments on the dehydrogenation of methylcyclohexane and heptane which differ markedly in velocity and would be identical were hydrogen desorption the rate determining process. The rapidity of the dehydrogenation of methylcyclohexane accounts satisfactorily for the absence of cycloparaffins in the reaction products from heptane.

The work of Pitkethly and Steiner established that, in a moderate range of variation of heptane–hydrogen pressures, the concentration ratio $[C_7H_{14}]/[C_7H_{16}]$ was approximately a constant and drew the conclusion that the constancy of heptylene concentration which they observed was not due to establishment of the heptane–heptylene equilibrium, $C_7H_{16} \rightleftarrows C_7H_{14} + H_2$. The reverse hydrogenation reaction yielding heptane is, however, occurring as our experiments with heptylene-1 and those of Hoog, Verheus and Zuiderweg indicate. Our results show that, starting with heptylene, the net rate of hydrogenation is approximately 25% of the rate of conversion to toluene under the given conditions. Pitkethly and Steiner derived the constancy of the heptane–heptylene ratio on the assumption that the heptylene was removed as quickly as formed and on the unimolecular reactions of heptylene formation and cyclization. It is evident that the actual state of affairs is more complex. We may generalize by kinetic equations the four reactions under

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[8] J. Turkevich and H. S. Taylor, THIS JOURNAL, **56**, 2254 (1934); J. Howard and H. S. Taylor, *ibid.*, **56**, 2259 (1934).

[9] R. N. Pease, *ibid.*, **45**, 1196 (1923).

consideration: (a) the surface dehydrogenation of heptane to heptylene either unimolecular or inhibited by olefin, k_1; (b) cyclization and aromatization in a reaction between zero and first order, k_2; (c) the carbonization of adsorbed olefin to yield the residue which poisons the surface, in a reaction between zero and first order, k_3; (d) the hydrogenation of olefin to reform heptane, k_4. The kinetic expressions for formation and removal of olefin are

$$+\,d[C_7H_{14}]/dt = k_1[C_7H_{16}][C_7H_{14}]^{-x}$$

$$-\,d[C_7H_{14}]/dt = k_2[C_7H_{14}]^{1-x} + k_3[C_7H_{14}]^{1-x} + k_4[C_7H_{14}]^{1-x}[H_2]$$

When x is unity the dehydrogenation reaction to heptylene is inversely proportional to heptylene concentration, the cyclization and carbonization are zero order. In the hydrogenation reaction (d), the exponent $(1-x)$ satisfies the equilibrium requirements with the assumed inhibition by olefin in the dehydrogenation process. When x is zero we have unimolecular dehydrogenation of heptane and cyclization of olefin as assumed by Pitkethly and Steiner and by Hoog, Verheus and Zuiderweg together with a first order poisoning reaction and a simple bimolecular rehydrogenation process, ignored in former analyses. For any value of x it follows that

$$\frac{[C_7H_{16}]}{[C_7H_{14}]} = \frac{k_2 + k_3 + k_4[H_2]}{k_1}$$

It is evident that such an expression for this ratio is relatively insensitive to variation in the hydrogen pressure, as was found by Pitkethly and Steiner, more especially since our results with heptylene-1 indicate that, under the experimental conditions obtaining, the rate of the hydrogenation process is small compared with that of aromatization. Larger partial pressures of hydrogen should however have a beneficial effect in the over-all reaction since they would tend to decrease the poisoning process by reversing the carbonization reactions without markedly affecting the surface concentration of olefin which gives the cyclization reaction, especially when this latter approximates a zero order process. Such an effect of hydrogen, simultaneously present, was noted in the poisoning experiments with ethylene. Only at very high hydrogen pressures would the hydrogen become detrimental through its influence on the equilibrium process cycloparaffin $\rightleftarrows$ aromatic + hydrogen.

It is clear from this analysis that the slow process in the conversion of heptane to toluene on a clean surface becomes the initial dehydrogenation of the saturated paraffin (k_1). The low sensitivity to variation of hydrogen pressure as observed by Pitkethly and Steiner and our own measurements of the products from heptylene conversion (40% aromatic–10% heptane) show that the sequence of cyclization reactions from heptylene onward are more rapid than rehydrogenation to paraffin. Equilibrium in the system paraffin $\rightleftarrows$ olefin + hydrogen at 475° is so largely on the paraffin side that the hydrogenation process is necessarily rapid compared with the dehydrogenation process, which therefore becomes the rate-determining process. It is, however, interesting to note that this dehydrogenation to olefin is much less sensitive to poisoning than is the aromatization step, which suggests that this latter, although more rapid on a clean surface, requires a configurationally more complex surface, more sensitive to poisoning. This may possibly arise because a different mode of adsorption of the olefin is required for hydrogenation and cyclization.[10] It is obvious, in any case, that such poisoning alters considerably the relative rates of dehydrogenation and cyclization as a run proceeds. Since heptylene is the principal poisoning agent in the several processes it follows that catalysts on which the steady-state concentration of olefin is minimal will probably be the most efficient catalysts for the over-all conversion to aromatics.

This analysis has ignored a side-reaction which does not affect discussion of the mechanism of aromatization, but is of great importance in the economics of the process, namely, the cracking reactions. These are indicated by the presence in the gaseous product of the lower molecular weight saturated and unsaturated hydrocarbons. These cracking reactions may play a part in the deposition of carbon on the surface as is normal in such processes. They possess significance in the formation of aromatics only in so far as they may be a source of the olefins or intermediate radicals that subsequently cyclize. We may indicate one such possibility by a generalized equation of the form

$$C_{n+1}H_{2n+4} \longrightarrow CH_4 + C_nH_{2n} \longrightarrow CH_4 + C_nH_{2n-6} + 3H_2$$

In the catalysts we have studied such side reactions are least important with the chromium oxide preparations.

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(10) We have examined the possibility that this re-orientation of adsorbed olefin determines reaction rate and reached a negative conclusion.

Summary

1. Initial cyclization of heptylene-1 on chromium oxide catalysts is more rapid than that of heptane. The catalysts poison more rapidly.
2. Heptylene-1 in 15% concentration in heptane reduces the over-all conversion to toluene.
3. Methylcyclohexane is more rapidly dehydrogenated to toluene than heptane or heptylene-1 and does not poison the catalyst.
4. Ethylene strongly poisons chromium oxide catalysts by deposition of carbonaceous material on the surface, removable only by oxidation.
5. Simultaneous presence of hydrogen reduces and may eliminate the poisoning action of ethylene.
6. Analysis of the data indicates that dehydrogenation of the heptane is inhibited by heptylene and is the slow process in the whole sequence.
7. Aromatization is more sensitive to poisons than the paraffin dehydrogenation.

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The Crystal Structures of the Tetragonal Monoxides of Lead, Tin, Palladium, and Platinum

BY WALTER J. MOORE, JR.,* AND LINUS PAULING

The crystal structure of red plumbous oxide was first investigated by Dickinson and Friauf,[1] who found the tetragonal unit to have $a_0 = 3.99$ Å. and $c_0 = 5.01$ Å., and to contain 2Pb at $\frac{1}{2}0z$, $0\frac{1}{2}\bar{z}$, with $z = 0.24$, and 2O at 000, $\frac{1}{2}\frac{1}{2}0$. This is a very interesting layer structure, in which each oxygen layer is sandwiched between two lead layers. Subsequently Levi and Natta[2] reported this structure to be incorrect, and assigned to the oxygen atoms the atomic positions $0\frac{1}{2}v$, $\frac{1}{2}0\bar{v}$, with $v \cong 0.76$. This corresponds to a distorted sodium chloride arrangement. A similar structure was reported by them for stannous oxide also. Both the Dickinson–Friauf structure and the Levi–Natta structure are described in detail in the "Strukturbericht."

In 1927 Zachariasen[3] reported that powder pictures of palladous oxide show it to be tetragonal, with $a_0 = 3.029 \pm 0.005$ Å. and $c_0 = 5.314 \pm 0.005$ Å. He concluded that the crystal is probably isomorphous with PbO and SnO, without deciding between the Dickinson–Friauf and Levi–Natta arrangements. It was then pointed out by Huggins[4] that neither of these arrangements provides the bond configuration expected for bivalent palladium, and the structure 2Pd at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, 2O at $\frac{1}{2}0\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$ was suggested and shown to be not incompatible with the reported data.

The present investigation was undertaken to resolve these discrepancies. We have verified the Dickinson–Friauf structure for plumbous oxide, have shown that stannous oxide has the same structure, and have found that palladous oxide is not isomorphous with these crystals, but has the structure suggested by Huggins. We have also found that platinous oxide has this same structure.

Experimental Methods and Results.—Red plumbous oxide was prepared by the action of hot 15 *N* potassium hydroxide solution on the hydroxide, and stannous oxide by boiling a suspension of the hydroxide to which a crystal of stannous chloride had been added.[5] Palladous oxide was prepared by the method of Shriner and Adams,[6] involving fusing palladous chloride and potassium nitrate, and platinous oxide by a similar method. Powder photographs of the substances were made with copper Kα radiation filtered through nickel, in a cylindrical camera with 5-cm. radius. Three films, one behind another, were exposed simultaneously, and the relative intensities of the powder lines were estimated by visual comparisons.

The tetragonal unit of plumbous oxide was found from our films to have $a_0 = 3.947 \pm$

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* National Research Fellow in Chemistry.

[1] R. G. Dickinson and J. B. Friauf, THIS JOURNAL, **46**, 2457 (1924).

[2] G. R. Levi and E. G. Natta, *Nuovo Cimento N. S.*, **3**, 114 (1926).

[3] W. H. Zachariasen, *Z. physik. Chem.*, **128**, 412 (1927); G. R. Levi and C. Fontana, *Gazz. chim. ital.*, **56**, 388 (1926), had previously reported some data without significant interpretation.

[4] M. L. Huggins, *Chem. Rev.*, **10**, 427 (1932); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[5] A. Ditte, *Compt. rend.*, **94**, 792, 864 (1882).

[6] R. L. Shriner and R. Adams, THIS JOURNAL, **46**, 1684 (1924).