upon the equilibrium constant may be extended to the study of aldehydes which show much higher percentage conversion than do those referred to in this paper.

Summary

For the first time a method for the preparation of furfural acetal from the aldehyde and ethanol has been described.

The effect of the ratio of reactants upon the extent of the reaction of benzaldehyde with ethanol, butanol and propanol-2 and of furfural with ethanol has been determined when the ratio of aldehyde to alcohol is varied from 1 to 2 to 1 to 10. The equilibrium constant for the first two of these reactions was found to be identical for the two alcohols but to decrease slightly with increase in ratio of alcohol to aldehyde.[9] The equilibrium constant for the reaction of benzaldehyde with propanol-2 and of furfuraldehyde with ethanol appeared to be independent of the concentration of reactants. The equilibrium constant for the reaction of furfuraldehyde and methanol has been redetermined.

MADISON, WISCONSIN

RESIN STUDIES. I. THE PREPARATION AND AUTOXIDATION OF PRECIPITATED LEAD ROSINATE

BY W. A. LA LANDE, JR.

I. Preparation of Precipitated Lead Rosinate

Introduction.—In attempting to study quantitatively the absorption of oxygen by lead rosinate it was obviously important to begin with a material of known and reproducible composition, preferably a normal salt, which had not been exposed to oxidation. Lead rosinate was made by several of the methods proposed in the literature for the preparation of rosinates and abietates[1] and was found objectionable for two reasons. (1) The rosinate responded positively to the starch–iodide test for peroxides immediately after the preparation was completed. (2) The composition (usually complex) of the precipitates obtained according to the

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[9] The equilibrium constants for the reactions of butanol and ethanol with benzaldehyde are the same only when they are calculated upon the basis of concentrations expressed as mole fractions. They are not identical if the calculation is made upon the basis of concentrations expressed as moles per liter as was done in previous papers in this series.

[1] Pardeller, *Seifensieder-Ztg.*, 1256 (1909); Ellingson, THIS JOURNAL, **36**, 325 (1914); Bontoux, *Rev. chim. ind.*, **28**, 157 (1919); Steele, THIS JOURNAL, **44**, 1332 (1922); Dupont, Desalbres and Bernette, *Bull. soc. chim.*, **39**, 488 (1926); Uzac, *ibid.*, **37**, 1194 (1925); Uzac, *Chimie et industrie*, **14**, 186 (1925).

given directions was not reproducible within a reasonable range. All of the products contained an appreciable quantity of alkali.

In order to provide a suitable material, a study was made of the factors governing the composition of the precipitate formed on adding a solution of a lead salt to a sodium rosinate solution.

Discussion.—From preliminary experiments it was evident that with the ordinary methods of preparation, oxidation of the rosinate began in the early stages of the procedure. Oxidation and absorption of carbon dioxide progressed during the saponification of the rosin and the precipitate was exposed to air during washing, filtration and drying. As a result, in spite of ordinary precautions and reasonably rapid manipulation, the precipitate always responded positively to tests for oxidation. In order to obtain a product uncontaminated by oxidation it was necessary to carry out all steps in the preparation of lead rosinate in the absence of oxygen. Accordingly, the apparatus illustrated in Fig. 1 was devised.

The problem presented by the second objection mentioned above was met by investigating several hitherto apparently neglected factors in the preparation of lead rosinate. It was possible to obtain precipitates of reproducible and nearly theoretical composition only by using very dilute
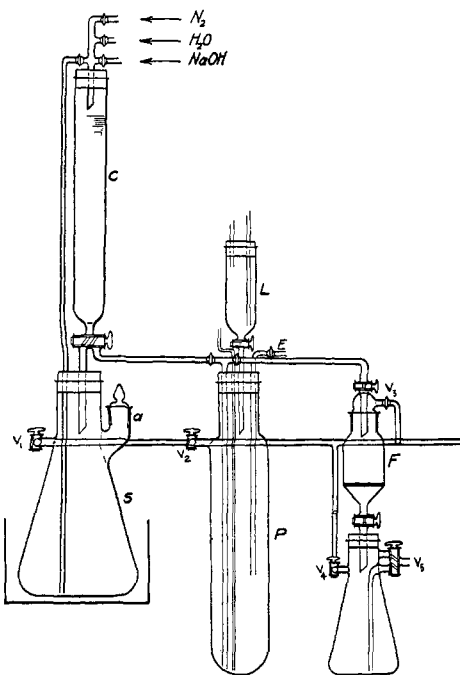

Fig. 1.

solutions of lead acetate and sodium rosinate. Two per cent. solutions of the reactants were found most practical for the precipitation. With more concentrated solutions the precipitate formed was lumpy, bulky and heterogeneous, difficult to wash and purify, and altogether unsuitable for the purpose for which it was intended. The composition of the precipitate was also found to vary with the rate of addition of the lead acetate solution to the sodium rosinate, and with the time and rate of agitation of the reaction mixture. When lead acetate is added dropwise to sodium rosinate solution, several reactions can take place simultaneously. As the solutions mix, an insoluble rosinate tends to be precipitated. Due to its gelatinous, bulky structure the precipitate immediately occludes some of the rosinate

solution and some of the lead acetate solution. This precipitate is of indefinite composition and is further reacted upon by the excess rosinate solution. The composite precipitate at first contains an excess of abietic acid. By agitation with a large excess of lead salt the abietic acid content of the precipitate is transposed to lead abietate. This transposition is a slow one and accounts for the results obtained by varying the time of agitation, i. e., the lead content of the precipitate is increased to a maximum, corresponding to lead abietate, by agitating the acid salt with the excess lead solution. If the lead solution is added slowly the composite precipitate is subsequently very much more slowly (never completely) transposed to the normal salt. In one experiment where the lead solution was added over a period of forty minutes, the precipitate contained only 22% of lead. The best results were obtained by adding the lead solution over a period of four to five minutes. Vigorous and prolonged agitation was absolutely essential during all stages of the preparation. Room temperature was most satisfactory for the preparation of the rosinate. Both lead nitrate and lead acetate were used as precipitants. Previous investigators have usually employed the acetate. No difference in composition of the rosinate dependent on the use of nitrate or acetate was observed.

Experimental

Materials.—Hercules "I" wood rosin of recent manufacture was used in all the experiments: Sap. no., 172.1; acid no., 161.1. Samples in the form of rather large lumps were taken from the interior of a large piece of the rosin and quickly weighed and transferred to the apparatus.

The water used for the preparation of solutions and for the washing of the precipitate was purified by redistilling ordinary distilled water from an alkaline suspension of manganous hydroxide.

Carbonate-free sodium hydroxide was made according to the directions of Küster.[2] The solution was stored in a ceresine lined bottle fitted with the lines and stopcocks necessary for transferring the solution to the various parts of the apparatus, $N = 0.5670$.

Tank nitrogen was bubbled through alkaline pyrogallol solution to remove the gross amounts of oxygen. The remaining traces of oxygen were removed by passing the gas over glowing copper. Tank oxygen was dried by passing the gas through concentrated sulfuric acid, ascarite and calcium chloride.

The organic solvents were dried over sodium and redistilled. The other reagents used in the work were "Baker's Analyzed" brand.

All parts of the apparatus were thoroughly purged with nitrogen before being used.

Seventy-five grams of rosin was charged into the saponifying flask F through "a" (Fig. 1). The equivalent amount of sodium hydroxide and enough water to make a 5% solution were then added through C. Four hundred cc. of this solution was displaced into P, the precipitating vessel, by nitrogen pressure. After diluting the solution until it contained 1.64% of rosin, 1.37 times the equivalent of lead acetate (17.26 g.) in 800 cc. of water was added through L. The reaction mixture was vigorously agitated

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[2] Küster, Z. anorg. Chem., **13**, 134 (1897).

for one hour after the addition of the lead solution, and for five minutes after each subsequent addition of wash water. The washing was considered complete when the decantate failed to give a coloration with sodium sulfide solution. The precipitate was displaced onto the filter F^3 by nitrogen pressure on V_1 and suction on V_5. It was possible to obtain in this way a thick, firm cake of the precipitate. The stopcocks on the filter were then closed and the product kept thus until needed. The precipitate was dried by shaking a portion of it onto a clock glass and quickly transferring it to a phosphorus pentoxide desiccator which was immediately evacuated. The total time of exposure to the air at this point did not exceed twenty seconds. A one-gram sample of the rosinate did not oxidize a starch–iodide solution. After exposing another sample to the air for a few minutes the product liberated iodine from the iodide. Solutions of the rosinate in various organic solvents were perfectly clear—an indication of the absence of any free inorganic compound. After 200 days in an evacuated tube the rosinate had become slightly darker in color. On heating a sample of the rosinate in a capillary tube in a sulfuric acid bath, no visible change occurred until the temperature rose to 70°, then a progressive darkening and shrinking began. There was no definite melting point, but the sample shrunk to small, clear, dark amber globules (140–150°) and then spread around the wall of the tube in a viscous film. This.film became almost black and quite opaque at 160–170°, due in part to a separation of metallic lead, and in part to decomposition of the acid.

Analysis of Lead Rosinate.—The metal content of a rosinate or abietate is a reliable index of its purity. In this investigation the ordinary methods of determination were abandoned in favor of the following procedure.

A weighed sample of the rosinate (0.5 g.) was dissolved in 20 cc. of hot 50% alcoholic 2 N sodium hydroxide. Twice the calculated amount of 50% alcoholic 2 N sodium sulfide was added and after boiling gently for ten minutes the mixture was filtered. The precipitate was first washed with dilute alcoholic sodium hydroxide solution, then with hot water saturated with hydrogen sulfide, and finally dissolved in boiling 1:3 nitric acid. The lead was precipitated electrolytically as lead dioxide. The deposit was dried at 220–230°.

Anal. Subs., 0.4502, 0.5648: PbO_2, 0.1252, 0.1575. Calcd. for this rosinate: Pb, 24.13.[4] Found: Pb, 24.18, 24.02.

These results were checked against those obtained by decomposing samples with concentrated sulfuric acid and a little nitric acid in a Kjeldahl flask. The lead was weighed as sulfate or chromate.

Anal. Subs., (1) 0.9650, (2) 0.7940, (3) 0.6475, (4) 0.6952: $PbSO_4$: (1) 0.3389, (2) 0.2791; $PbCrO_4$: (3) 0.2444, (4) 0.2492. Found: Pb, 24.00, 24.03, 24.20, 24.25.

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[3] This piece of apparatus was made from a Jena glass, tall form Büchner funnel with a sealed-in fritted glass filter plate. The glassblower worked the open end into a bottle neck and fitted it with a ground-in stopper bearing the two stopcocks. Precipitates can be dried very conveniently in inert atmospheres in this type of filter by closing the stopcocks, transferring the apparatus to the oven and connecting the stem of the funnel to the source of the gas.

[4] Calculated from the saponification no., the rosin used contained 92.90% of abietic acid, or 1 g. of rosin = 0.929 g. of abietic acid. This is equivalent to 0.318 g. of Pb. Since the unsaponifiables are co-precipitated, the precipitate will contain 0.318 g. of Pb + 0.929 g. of abietic acid + 0.071 g. of unsaponifiable, or 1.318 g. for each 1 g. of rosin originally present, provided the normal salt forms. The calculated lead content is therefore 24.13%. By the same reasoning the precipitate of rosinate contains 94.7% of normal lead abietate.

The alkali content of the rosinate was determined by Steele's method.[5] One drop of 0.05 N hydrochloric acid discharged the faint pink color produced in the aqueous extract of the ash by phenolphthalein. The amount of alkali in the sample was therefore negligible.

2.   The Autoxidation of Precipitated Lead Rosinate

Introduction.—Maly was probably the first to notice that rosin and abietic acid increase in weight on exposure to the air.[6] Subsequently identified as a process of autoxidation, this phenomenon has been the subject of considerable study, both in the solid acid and in solutions of the acid.[7] On the other hand, little work has been done on the obviously related subject of the autoxidation of metallic rosinates and abietates. To supply some necessary data for an investigation still in progress, the course and extent of the reaction

$$Pb(C_{20}H_{29}O_2)_2 + O_2 \longrightarrow$$
$$\text{solid}$$
$$\text{(as rosinate)}$$
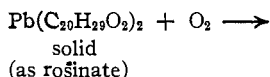
was studied. A solution of the rosinate offers the best means of obtaining rapid and complete absorption of oxygen, but the method does not permit of the obtaining or manipulation of indisputably unchanged intermediate products. Another objection arises from the fact that the degree of absorption is somewhat affected by the solvent used. In the type of system studied in this paper, the reaction proceeds at a conveniently slow rate and the reversibility of the reaction can be directly and easily studied by submitting the reaction mixture to various changes of temperature and pressure. Lead rosinate rather than pure lead abietate was used because results obtained with it had the same significance as those obtained by using pure lead abietate. It was, therefore, unnecessary to execute the much more laborious preparation of the latter compound.

Several methods were tried for following the course of the progressive absorption of oxygen by lead rosinate. Manometric technique was found to be unsatisfactory; the results obtained were not reproducible and the final values were misleading. Frequent shaking of the sample did not improve the results. Since some of the products of the autoxidation of the rosinate liberate iodine from potassium iodide, it appeared possible to follow the course of the oxidation by an iodimetric method. This procedure required too much material and was abandoned. The gravimetric method outlined below was finally adopted as the most practical from the standpoints of convenience, accuracy and economy.

[5] Steele, THIS JOURNAL, **44**, 1332 (1922).

[6] Maly, *Ann.*, **161**, 115 (1872).

[7] Fahrion, *Z. angew. Chem.*, **13**, 1197 (1901); Fahrion, *ibid.*, **20**, 356 (1907); Klason and Kohler, *J. prakt. Chem.*, **63**, 337 (1906); Knecht and Hibbert, *J. Soc. Dyers Colourists*, **25**, 148 (1919); Dupont and Dubourg, *Bull. inst. pin*, **52**, 205 (1928); Dupont and Lévy, *Compt. rend.*, **189**, 763 (1929).

Experimental.—The lead rosinate used in all the experiments was prepared by the method outlined in the first part of this paper. All of the samples were taken at the same time from the same batch of material.

Samples of the rosinate of equal weight (0.4840 g.), in the form of fine powder, were weighed into glass-stoppered weighing bottles, 40 mm. in diameter and 50 mm. in height. The average thickness of the layer of rosinate was 2 mm. Each of the samples thus prepared was used immediately. The stopper of the weighing bottle was removed and the bottle was placed in the vessel shown in Fig. 2. The piece of apparatus was then transferred to the oven or thermostat, and dry preheated oxygen or nitrogen (as the experiment required) passed through at the rate of 300 cc. per hour. This rate provided a slowly but constantly changing atmosphere of the gas, without danger of loss through agitation of the powder. No attempt was made to obtain a fine temperature control, but all of the given temperatures were the same throughout a given run with a maximum variation of $\pm 1°$. Each sample was heated for a timed interval, then allowed to cool in oxygen or nitrogen, and finally weighed after six hours in the desiccator. Before each subsequent exposure to the gas the powder was mixed by rotating the stoppered weighing bottle. In the experiment carried out under pressure the weighing bottle was placed in an Emerson bomb, the pressure raised to the required amount, and the bomb then transferred to the oven.
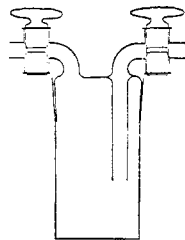
Fig. 2.

Experimental Results.—All the results recorded are average values obtained from at least two experiments conducted under precisely the same conditions.

In Table I showing the increase in weight of lead rosinate in pure dry oxygen at various temperatures, the final value in each sub-table represents the time and percentage increase in weight at which the system came to equilibrium. All runs were continued for at least one hundred hours after this point was reached in order to eliminate the possibility of a false or transient equilibrium. In each sub-table (except 125°) the data between the last result and the one immediately above it have been omitted

TABLE I

INCREASE IN WEIGHT OF LEAD ROSINATE IN OXYGEN AT VARIOUS TEMPERATURES AND AT 28° UNDER 60 ATMOSPHERES' PRESSURE

28°. Sample, 0.4836 g.			65°. Sample, 0.4835 g.		
Total hours	Total increase, g.	Increase in weight, %	Total hours	Total increase, g.	Increase in weight, %
14	0.0003	0.06	1	0.0001	0.021
32	.0013	.26	8	.0056	1.15
47	.0028	.58	26	.0104	2.15
68	.0055	1.14	40	.0128	2.65
90	.0105	2.18	71	.0146	3.02
118	.0150	3.10	95	.0155	3.20
150	.0184	3.80	114	.0162	3.35
184	.0200	4.14	156	.0173	3.57
232	.0214	4.42	204	.0182	3.76
294	.0231	4.78	252	.0186	3.84
911	.0306	6.33	398	.0196	4.05

TABLE I (*Concluded*)

100°. Sample, 0.4840 g.			28°. 60 atm. Sample, 0.4021 g.		
Total hours	Total increase, g.	Increase in weight, %	Total hours	Total increase, g.	Increase in weight, %
3	0.0031	0.64	34	0.0066	1.63
9	.0051	1.04	93	.0149	3.71
22	.0069	1.44	141	.0201	4.77
49	.0077	1.60	189	.0235	5.63
75	.0080	1.66	240	.0253	6.33
100	.0083	1.72	307	.0266	6.62
129	.0085	1.76	362	.0282	7.01
177	.0089	1.84	410	.0297	7.38
218	.0091	1.88	460	.0298	7.42
258	.0092	1.90	508	.0307	7.63

125°. Sample = 0.4838 g.

11	0.0002	0.041
37	.0008	.165
60	.0010	.206
84	.0016	.328
108	.0019	.391
132	.0026	.532

for space reasons. These omitted values when plotted all fall on a curve gently sloping to the maximum or final value. The calculation of the percentage increase in weight is based on the original weight of the sample. The results are plotted in Fig. 3 for the first two hundred hours.
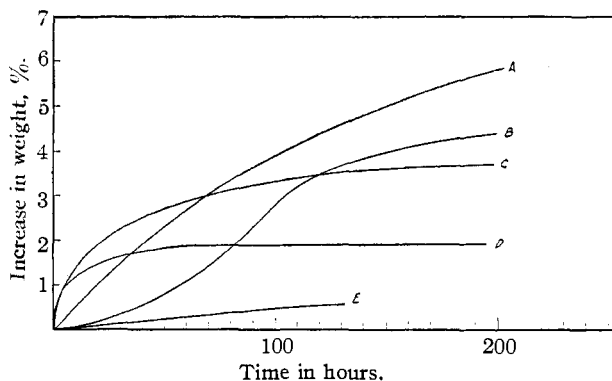

Fig. 3.—Course of the increase in weight of lead rosinate in oxygen at various temperatures and at 28° and 60 atmospheres: A, 28° at 60 atm.; B, 28°; C, 65°; D, 100°; E, 125°.

In Table II the results obtained for maximum absorption at the various temperatures are summarized. For comparison and correction, the results obtained by heating the rosinate in *nitrogen* at the various temperatures are included (Col. 2). These values represent a loss in weight, *i. e.*, the rosinate is appreciably volatile at 100 and 125°. The values for the ap-

parent oxygen absorption at 100 and 125° (Col. 3) have been corrected, in order to take into account the loss in weight of the rosinate when heated to these temperatures in an inert atmosphere. The corrected values are shown in the fourth column and represent the actual oxygen absorption. The molar equivalent of oxygen absorbed is calculated from the weight of oxygen absorbable by a rosinate containing 94.70% of normal lead abietate.

TABLE II

ABSORPTION DATA

T, °C.	Change in weight, % a, in N_2	b, in O_2	a + b Oxygen absorbed, %	Molar equiv. of O_2 absorbed
28 (60 atm.)	−0.00	7.63	7.63	2.04
28	− .00	6.33	6.33	1.59
65	− .00	4.05	4.05	1.08
100	− .31	1.89	2.20	0.55
125	−1.52	0.53	2.05	.51

The relation of the apparent oxygen absorption (Table II, Col. 3) to the actual oxygen absorption (Table II, Col. 4) is shown graphically in Fig. 4.
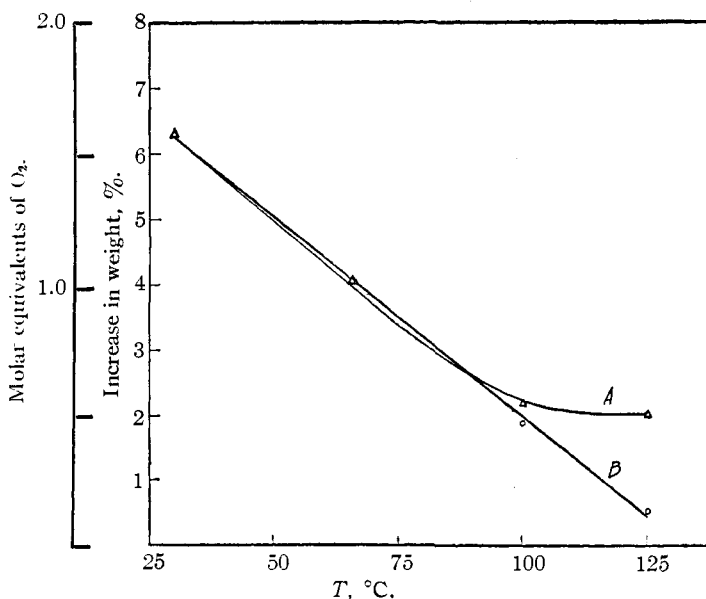

Fig. 4.—Maximum oxygen absorbed at various temperatures by lead rosinate: A, actual O_2 absorbed; B, apparent O_2 absorbed.

The results obtained after heating several of the oxidized samples in nitrogen to constant weight are reproduced in Table III. All the values determined for 100° are corrected for the slight volatility of the rosinate itself at that temperature (see Table II, Col. 2).

TABLE III

EXPERIMENTAL DATA

Oxygen originally absorbed at .... 28° (60 atm.)		28°		65°
Loss on heating in N_2 to constant weight at.. 100°	65°	100°	100°
As % O_2 (of total absorbed)................ 57.0	17.6	48.7	47.0
As molar equivalent of O_2.................. 1.14	0.28	0.77	0.51
Molar equivalent of O_2 remaining........... 0.86	1.31	.82	.57

Discussion of Results.—The results recorded in Tables I and II show that the rate and degree of oxygen absorption by lead rosinate depend, for a given pressure, on the temperature. Dupont and Lévy[8] worked at only one temperature (60°) and it must, therefore, be assumed that this temperature was designedly or fortuitously selected since their final results indicated a sharp end-point when one mole of oxygen had been absorbed. The curve B (Fig. 3) is the familiar S-shaped curve characteristic of auto-catalytic processes. The amount of oxygen absorbed at equilibrium corresponded to three atoms of oxygen. This does not necessarily indicate the formation of a compound $Pb(Ab)_2 \cdot 3O$. It is a great deal more probable that the reaction mixture at this point was a combination of all the possible reaction products, with the final product present in largest amount. The mixture slowly liberated iodine from aqueous iodide, quickly from acidified iodide. The product obtained when the experiment was repeated at the same temperature but under sixty atmospheres' pressure also liberated iodine from aqueous and acidified iodide. The results in this experiment are in good agreement with those obtained by Dupont and Lévy for abietic acid, i. e., each abietate group absorbed one mole of oxygen at equilibrium.

In curves C, D and E there is again an indication that the amount of oxygen absorbed corresponded to one or two atomic equivalents of oxygen. It is more possible however, that the reaction product was a mixture. All of these oxidation products liberated iodine from aqueous iodide (very slowly) and from acidified iodide (more rapidly).

If the degree of oxygen absorption at constant pressure decreases with rising temperature, a reversibility of the initial reaction is indicated. The dissociation of the end-product (or equilibrium product) in the autoxidation of the rosinate evidently proceeds progressively as the temperature is raised. There is an indication that this dissociation is never complete, and that a maximum dissociation is reached when one atomic equivalent of oxygen remains fixed by the rosinate (Fig. 4). The amount of oxygen absorbed in each case is thus an index of the stability (and the concentration) of the end-product at a given temperature, for a constant pressure. This reasoning was applied in an experiment, the results of which are recorded in Table III. If the end-product in the autoxidation of the rosinate at a given temperature and pressure was placed in an atmosphere

8 Dupont and Lévy, *Compt. rend.*, 189, 763 (1929).

of lower oxygen pressure, it slowly lost weight. If, however, the temperature was raised at the lower pressure, the loss in weight occurred quickly. In the experiment, in order to increase the effect, the temperature was raised about 30° and the partial pressure of the oxygen was decreased to zero (100% nitrogen). All the oxidized samples which were treated thus still liberated iodine from iodide although the reaction was much slower compared with the action of the rosinate on the iodide before this treatment, The gas evolved from the oxidized samples was passed over anhydrous copper sulfate and bubbled through barium hydroxide and palladous chloride solutions. There was no indication of the color or turbidity which water, carbon dioxide and carbon monoxide would have produced with these reagents. The gas evolved from two half-gram samples of the oxidized rosinate was passed through the heated, packed tube of a combustion furnace. The effluent gas was received in barium hydroxide solution. No turbidity was observed. The author thus feels justified in assuming that the gas evolved from the oxidized rosinate was pure oxygen. The rosinates again absorbed oxygen when exposed to the gas, but very slowly, an effect undoubtedly due to the change in surface produced by a slight sintering of the powder at the higher temperatures. It was believed before the experiment was tried that the relative amount of oxygen lost and the actual amount remaining fixed would be the same in each case. This would have proved decisively that a stable oxygen compound was formed during the autoxidation. The data obtained (Table III) were not in sufficiently good agreement to be interpreted as substantiating this belief. It is possible that such a compound was formed, but in an amount depending on the conditions of the particular experiment. Hence the amount of oxygen remaining fixed would vary. Another explanation of the apparent non-existence of a relationship among the values obtained for the amount of oxygen remaining fixed at zero oxygen pressure is the possibility of an immeasurably slow but positive dissociation of the more stable oxygen compounds formed during the autoxidation. In other words, these values would approach each other if the conditions were maintained for a sufficiently long time.

According to Dupont and Lévy the autoxidation of abietic acid is accomplished through the agency of an intermediate oxide HAbO, and a peroxide HAbO·O_2, the final product being HAbO$_2$. Unfortunately, the action of this final product on an iodide solution was not investigated. If the autoxidation of lead rosinate proceeds by a similar mechanism, two moles of oxygen should be absorbed by one mole of lead abietate. Actually, this result was obtained in only one instance (Table II), *i. e.*, under the most extreme conditions tried, and the product readily oxidized iodide. This would indicate that the end-product itself is capable of acting as an oxidizer, or that the product obtained under the most extreme conditions

(28°, 60 atm.) was still an equilibrium mixture of end-product and intermediate peroxides. The most obvious interpretation of the data obtained in this investigation would favor the latter conclusion.

The writer takes this opportunity to thank Professor H. S. Lukens for help and suggestions obtained from him during the course of this work. Thanks are also due Mr. J. G. Butz for helpful suggestions.

Summary

A study has been made of some of the factors which influence the composition of the precipitate formed by adding the solution of a lead salt to sodium rosinate solution.

An apparatus has been devised in which all the steps in the preparation of the rosinate may be carried out in an inert atmosphere.

A method for the analysis of the metal content of rosinates has been proposed.

The course, extent and reversibility of the autoxidation of lead rosinate has been studied, using a carefully prepared rosinate of known composition.

The results have been discussed from the viewpoint of the theory suggested by Dupont and Lévy for the autoxidation of abietic acid.

PHILADELPHIA, PENNSYLVANIA

COMPETITIVE HYDROGENATIONS. II

BY F. F. DIWOKY AND HOMER ADKINS

Recently it was shown that there was no apparent relationship between the relative rates of the hydrogenation over platinum of pure compounds taken separately and their relative rates of hydrogenation in mixtures.[1] For example, d-α-pinene was much more rapidly hydrogenated than was cinnamic acid and yet in a mixture of pinene and cinnamic acid the latter was completely hydrogenated before the former took up any hydrogen. It was also ascertained that a reducible substance not undergoing hydrogenation may greatly accelerate the hydrogenation of another compound. For example, pure pinene, which was much more rapidly hydrogenated than was pure allyl alcohol, increased the rate of hydrogenation of allyl alcohol almost seven-fold without itself being hydrogenated to any considerable extent. The results given in this paper are concerned with an extension of this study to the use of nickel catalysts in the hydrogenation of mixtures of reducible compounds.

Originally it was intended to determine (a) the time required for hy-

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[1] Adkins, Diwoky and Broderick, THIS JOURNAL, **51**, 3418 (1929).