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<td>著者</td>
<td>Nodzu, Ryuzaburo</td>
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京都大学
THE NODZU LABORATORY

Head: Prof. Dr. Ryuzaburo Nodzu

Since the establishment of the laboratory in 1937, its field of research has been concentrated in the study of reactivities of acetylene and its derivatives. Besides this, however, works have also been done on acetone-formaldehyde resin, on preparation of dioxybenzene monalkyl-ethers and on the natural rubber.

The outlines of these works are as follows:

I. Condensation of Acetylene with Benzene in the Presence of Aluminium Chloride I.

By Ryuzaburo Nodzu and Ri Kan Ei.


There are many reports on the same subject, but the products obtained were differed each other among the examiners, in spite of the fact that all experiments were carried on under almost the same conditions.

In the present work, aluminium chloride was always used 1 to 10 against benzene, and acetylene was passed so long as it was absorbed, at 0-10°, 20-30°, and 80-85°.

At the lower reaction temperature an insoluble solid and a small amount of oily matter were mainly obtained. When the reaction temperature was elevated, a comparatively large amount of oil and soluble resinous matter were found. Especially when the reaction was cut half-way, it resulted in a superior yield of the oily matter. This reaction product was composed of 20% of ethylbenzene, 30% of unsym. diphenylethane, 1% of butenylbenzene, 10% of higher boiling oil, and 40% of soluble resinous solid. The presence of styrol, vinyl-(1-phenyl)-ethylbenzene, diphenyl or dibenzyl was not observed.

II. Condensation of Acetylene with Benzene in the Presence of Aluminium Chloride. II.

By Ryuzaburo Nodzu and Ri Kan Ei.


The resinous solid described in the previous report was oxidized by means of potassium chromate and sulfuric acid under boiling state for 100 hrs., and benzoic acid and a neutral ketone were obtained. This ketone gave benzoic acid, when fused with potassium hydroxide.

On hydrogenation-cracking with nickel or molybdenum oxide as catalyst, ethylbenzene, unsym. diphenylethane, ethyl-(1-phenylethyl)-benzene, and p-di(1-phenylethyl)-benzene were identified in the product.

As a result of these experiments, it was presumed that the resinous matter has the following structure, and that the condensation reaction occurs in the following scheme:
III. Condensation of Acetylene with Benzene in the Presence of Aluminium Chloride III.

By Ri Kan Ei.

In this paper a report is made on the condensation product at the lower reaction temperature (2°C). In this product were found about 60-70% of insoluble solid matter, ethylbenzene, unsym.-diphenylethane, p-(1-phenyl)-ethylbenzene, dimethylidihydroanthracene, a higher boiling fraction, and a resinous matter.

The insoluble solid matter was oxidized by potassium chromate and sulfuric acid, and there were found benzoic acid, acidic ketone and litile amount of anthraquinone carboxylic acid. This ketone was fused with potassium hydroxide, and we obtained again benzoic acid and acidic ketone. We also tried under high pressure and temperature the hydrogenation of this insoluble matter in the presence of molybdenum oxide. We found ethylbenzene, unsym.-diphenylethane, p-diethylbenzene, and 1,2,3,-triethylbenzene.

Consequently, we came to consider that the insoluble solid matter is constructed in the following principle:

IV. Studies on the Condensation Reactions of Acetylene by means of Cadmium Salts.

By Ryuzaburo Nodzu and Sango Kunichika.

We tried preliminary experiments on gaseous condensation reactions of acetylene
with some acidic and basic substances, such as hydrogene chloride, hydrogene cyanide, acetic acid, hydrogene sulfide, phenol, water, alcohol, benzene, aniline, and ammonia, using cadmium salts supported on acid clay as catalyst. The cadmium catalyst had the same anion with that of the reactant, when it was acid. Otherwise, cadmium oxide was used.

The results obtained indicated us the way how to study the condensation reactions with ammonia and water in more detail.

V. Condensation of Acetylene and Ammonia, I.
By Ryuzaburo Nodzu, Sango Kunichika and Eiji Nishimura.

The condensation of acetylene with ammonia was performed under the following conditions: catalyst, cadmium oxide impregnated on acid clay, prepared by ignition of, or precipitation from, cadmium nitrate. Reaction temperature, about 300°.

The principal product was α-picoline, amounting to about 50 % of the oily product, and further, γ-picoline, 2-methyl-5-ethyl-pyridine, 2,3,6-trimethylpyridine, acetonitrile, and ethylamine were confirmed as picrate.

VI. Studies on α, α-Diphenylethane. I. The Pyrolysis.
By Han-Ying Li.

When α, α-diphenylethane was passed into a copper tube, heated about 500°, benzene and styrene was obtained. Besides these products, a small amount of stilbene was also determined. Consequently, we presumed the following decomposition scheme:

Using reduced nickel or zinc oxide as catalyst at about 600°, α, α-diphenylethylene and a little amount of stilbene were obtained.

The cleavage of bond predominated, when acid clay was used as catalyst at 300°, benzene and ethylbenzene were the principal products. Namely, the cleavages of C–C and C–H bonds took place simultaneously.
VII. Studies on \( \alpha, \alpha \)-Diphenylethane II. The Chlorination.
By Han-Ying Li.

At various conditions, the chlorination of \( \alpha, \alpha \)-diphenylethane was studied. Results obtained were as follows:

a). At 0–10°, Solvent (CCl\(_4\)).
Products: monochloro-\( \alpha, \alpha \)-diphenylethane (C\(_6\)H\(_5\))\(_2\)CHCH\(_2\)Cl

b). At 30–60°, (direct sunlight)
Products: \( \alpha, \beta \), \( \beta \)-trichloro-\( \alpha, \alpha \)-diphenylethane (C\(_6\)H\(_5\))\(_2\)CClCHCl\(_2\)

c). At 160–180°, (direct sunlight)
Products: \( \alpha, \beta \), \( \beta \)-tetrachloro-\( \alpha, \alpha \)-diphenylethane (C\(_6\)H\(_5\))\(_2\)CCl\(_2\)

d). At room temperature and 200°, chlorine was passed until absorbed.
Products: \( \alpha, \beta \), \( \beta \)-trichloro-\( \alpha \)-phenyl-\( \alpha \)-(X-chlorophenyl)-ethane, ClC\(_6\)H\(_4\) (C\(_6\)H\(_5\))CClCHCl\(_2\)

\( \beta, \beta \)-dichloro-\( \alpha \)-phenyl-\( \alpha \)-(X-chlorophenyl)-ethylene.
ClC\(_6\)H\(_4\)(C\(_6\)H\(_5\))C=C=CCl\(_2\)

Boiling with alcoholic potash or heating at 200°, \( \alpha, \beta \), \( \beta \)-trichloro-\( \alpha \)-diphenylethane was dehydrochlorinated to \( \beta, \beta \)-dichloro-\( \alpha \)-, \( \alpha \)-diphenylethylene (C\(_6\)H\(_5\))\(_2\)C=C=CCl\(_2\).

VIII. Methylol Condensation of Acetaldehyde.
By Seiichi Fujii.

In this paper studies on the condensation of acetaldehyde with formaldehyde in the presence of calcium hydroxide at 40°, and those on the high pressure hydrogenation of condensation products are described.

1). Hydrogenations of the condensate of 1 mol acetaldehyde with 2.2–2.5 mols formaldehyde.

After the condensation had been completed, the product was concentrated \textit{in vacuo} to a syrup, which contained usually some crystalline substances. This syrup was hydrogenated with the Cu-Cr-oxide catalyt.

a). Hydrogenation at 250°:
Isobutanol was obtained in the yield of more than 70 % of the value calculated from the formaldehyde used.

The result is in favour of the following scheme for the formation of isobutanol.

\[
\begin{align*}
\text{CH}_3\cdot\text{CHO} + 2\text{HCHO} & \rightarrow \text{CH}_3\text{OH} \quad \text{CH}_3\text{OH} \rightarrow \text{CH} \cdot \text{CHO} \rightarrow \text{CH} \cdot \text{CH}_2\text{OH} \\
& \rightarrow \text{CH}_3\text{OH} \quad \text{CH}_3\text{OH} \rightarrow \text{CH} \cdot \text{CHO} \rightarrow \text{CH} \cdot \text{CH}_2\text{OH}
\end{align*}
\]

b). Hydrogenation at 220°.
It was found that the hydrogen absorption occurred stepwise at about 160°,
220°, and 250°. The hydrogenation at 220° gave isobutanol and pentaerythritol.

c). Hydrogenation at 160°.

The result was quite different from those of a) and b). Two kinds of crystals were obtained, one melting at 178° and the other at 258°. The lower melting substance was pentaerythritol, and the higher melting one, tetraglycerol.

2). Hydrogenation of the condensation products of equal mol of both aldehydes.

Analogous experiments were tried out on the condensate above, and isobutanol and a little of propanol were found by the hydrogenation at 250°.

3). The condensation product of 1 mol acetaldehyde and 3 mol formaldehyde gave isobutanol and pentaerythritol on catalytic hydrogenation at 220°C. This fact suggests a new method for synthesizing pure pentaerythritol.

IX. Studies on the Synthesis of Acetaldehyde from Acetylene by the Vapor Phase Method. I.

By Sango Kunichika.


The best catalyst for this subject was found to be cadmium chromate-acid clay, as a result of studies on 20 kinds of catalysts. When this catalyst was used under the conditions: reaction temperature, 250°-300°; space velocity of acetylene, about 2001; mol ratio of acetylene for water, 1:1.5, we obtained the following results: conversion ratio of acetylene per pass, 20-30%; theoretical yield of acetaldehyde, about 85%; durability of the catalyst, considerably long when reactivated occasionally with air and steam; exodus gas, contained CO₂, CO, CH₄, and H₂, which had no bad effect in the repeated use.

X. Studies on the Synthesis of Acetaldehyde from Acetylene by the Vapor Phase Method. II.

By Sango Kunichika.


It was determined that the yellow crystal cadmium chromate, the best catalyst for this subject in the previous report, had the constitution CdCrO₄·2H₂O. By means of the chemical and X-ray analysis as well as the thermal balance measuring on this crystal and its pyrolyzed substances, it was found that the crystal lost its crystalline water below 300°, and remained under the same state of black CdCrO₄ below 500°, until finally decomposed to CdO, Cr₂O₃, and O₂ below 700°.

On the other hand, dehydration curves of various carriers were obtained by means of the thermal balance, which proved that acid clay kept the zeolitic water, supposed to be essential for this reaction, for the longest period.

From these two points of view, the distinctive characteristics of the cadmium chromate-acid clay catalyst are discussed.


By Toshizo Isojima.


Through a silica tube at 400°, which contained various catalyst aq. solution
(30%) of acetaldehyde was passed, and the products were analyzed quantitatively by a volumetric analysis.

Results obtained:
1) In case that ZnO, CdO, PbO, and Fe₂O₃ were used as the catalyst, the conversion ratio of acetaldehyde and yield of acetone were both high.
2) CaO, SnO₂, MnO₂: both values were middle.
3) NiO: the conversion ratio was very much large, but no acetone.
4) Al₂O₃: almost inert.
5) CuO, SnO₂, V₂O₅, MoO₃: a large amount of acetic acid was found.

XII. Catalytic Conversion of Acetaldehyde to Acetone.

By Sango Kunichika and Hirooki Ota.


In the previous report, the most suitable catalyst for this reaction were ferric oxide and zinc oxide. The activity of these catalysts was much affected by the method of their preparation. Fe₂O₃, precipitated by ammonia from ferric chloride and ignited at 600°, gave the higher yield (80%) than those prepared by another method.

Among the mixed catalysts, the mixture of Fe₂O₃ (prepared from ferric chloride and sodium hydroxide) and ZnO (prepared by analogous method) was most effective. Yield, 88%.

As the carrier, activated carbon was best. Fe₂O₃-ZnO-Carbon (50% wt.) gave 72% yield of acetone.

XIII. Synthesis of Acetone from Acetylene.

By Sango Kunichika and Hirooki Ota.


An experiment on the direct synthesis of acetone from acetylene and steam was carried out.

Experimental conditions:
The mixed catalysts of Fe₂O₃ and ZnO in various mol ratios were used. Volume of catalyst: 30 cc.
Division of reaction tube: 25 cm.
Reacting temperature: 450°.
Space velocity of acetylene: 200 L/hr.

Regardless of the mixed ratio of catalyst, the yield (33%) of acetone was maximum at the velocity of water, 30g/hr.

When the mixed catalyst (Fe₂O₃: ZnCrO₄=2:1) was used, and the space velocity of acetylene was about 190 L/hr, the results were favorable. (the conversion ratio of acetylene: 66%, the yield of acetone: 72%).
XIV. Studies on Polyvinylidenechloride. I. Preparation of the Monomer.

By Sango Kunichika and Susumu Hirase.

Vinylidenechloride was prepared by the dehydrochlorination of 1,1,2-trichloroethane, which had been obtained in the liquid phase (using trichloroethane as a solvent) from vinylchloride, containing 10-20 vol.% of acetylene.

A). Trichloroethane.
1. The higher the reaction temperature and also the higher the mol ratio of chlorine for vinylchloride, the more the formation of higher boiling products. The best yield (ca. 90%) of trichloroethane was obtained at a lower temperature (0-20°C), when the mol ratio of chlorine for vinylchloride was 1.2:1.
2. The rate of flow of the mixed gases and the height of the liquid layer did not largely affect the yield.
3. Explosion, due to the presence of acetylene, did not occur, when the content of vinylchloride was more than 70 vol.% of the gas.

B). Vinylidenechloride.
1. Trichloroethane was easily dehydrochlorinated to vinylidenechloride in an yield of about 95% by the action of a slight excess of sodium hydroxide aq. solution (20%). When the concentration of sodium hydroxide was higher, the reaction became difficult because of decrease of the solubility of trichloroethane.
2. Vinylidenechloride was also obtained in a yield of 88% by using milk of lime as a dehydrochlorinating agent.

XV. Studies on the Application of Ketone Resin. III.
The Application of Acetone-Formaline Resin as Adhesive. 3.

By Yasuaki Kozai.

Resin, hardening reagent, and the testing wood plates used in the present experiment were identical with those described in the previous report. The experimental results on resistance against water were as follows: a pressure, 18 kg./cm² at 80-90°C and for about 1 hr, adhesive power of the resin in wet state was about 1/3 (50 kg./cm²) of that in dry state.

XVI. Studies on the Application of Ketone Resin. V.
The Application of Acetone-Formaline Resin as Adhesive. 4.

By Yasuaki Kozai.

In the present paper, influences upon the adhesive strength by the various addition substances to this resin are summarily described.

As addition substances, carbon powder, casein (soya bean and milk), wood powder, kon-nyaku, biocellulose, magnesia and pine resin were tested.
Among them, 5% (wt.) of wood powder, or soya bean casein and 10% of kon-nyaku gave satisfactory results.
Also it was found that saturated aq. solution of sodium hydroxide was the best hardening reagent.

XVII. Studies on the Application of Ketone Resin. VI.
The Application of Acetone-Formaline Resin as Adhesive. 5.
By Yasuaki Kozai.

The influence of heating temperature and duration under atomospheric pressure for applying the resin with half its weight of NaOH(30\% ) was studied.
Adhesive strength 60-80 kg./cm², and wet adhesive strength 25-30 kg./cm², were obtained under the following conditions:

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<td>50 — 60</td>
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<td>60 — 70</td>
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<td>80 — 90</td>
<td>10 ,,</td>
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<tr>
<td>100 — 110</td>
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XVIII. Studies on the Application of Ketone Resin. VII.
The Application of Acetone-Formaline Resin as Abhesive. 6.
By Yasuaki Kozai.

In this paper, the experimental results, using calcium hydroxide as the hardening reagent are summarized.
The adhesive strength is effected by various factors—the degree and duration of compression and heating as well as the amount of calcium hydroxide in the admixtures—and it was found that the following conditions gave a good result for the adhesion of wood. (adhesive strength 150-180 kg./cm², wet adhesive strength about 50 kg./cm².).
a). Adhesive mixture : resin 10 g, Ca(OH)₂(solid) 3-5 g.
b). Specific pressure applied : about 18 kg./cm².
c). This adhesive mixture had a working life ca. 5 days at 5°, ca. 15 hrs at room temperature and its 1 g was able to apply for 50-55 cm². of wood surface.
d). An excellent result was obtained by addition of 1% wood powder (80-120 mesh).
XIX. Alkylation of Dioxybenzenes by p-Toluenesulfonic Acid Ester.

By Ryuzaburo Nodzu, Sango Kunichika and Shinzaburo Oka.


Methyl, ethyl, and butyl esters were prepared by means of 5 N-sodium hydroxide from a mixture of the corresponding alcohol and p-toluenesulfonyl chloride. Yields are methyl ester 85%, ethyl ester 70% and butyl ester 56%, respectively.

Butyl ester and hexyl ester were obtained by using γ-picoline, instead of sodium hydroxide, in the yield of 85% and 82%, respectively.

The alkylation of dioxybenzene was carried out as follows; 0.1 mol natrium was dissolved in 30 cc. absolute methanol, 0.1 mol dioxybenzene and 0.1 mol sulfonic acid ester added, and then heated on a water bath for 2 hrs. The yields of monoalkyl ethers and dialkylethers were about 30-40% and 25-45%, respectively.

XX. Studies on Natural Rubber, I.

On the Viscosity-lowering of Rubber Solution by the Action of Certain Chemicals.

By Ryuzaburo Nodzu and Yasuaki Kozai.

(Read before the Society of Higher-Molecule Chemistry, Nov. 1950.)

The viscosity of rubber solution (solvents: C₆H₆, CCl₄) was lowered in the presence of a little quantity of some inorganic and organic reagents—SnCl₄, AlCl₃, FeCl₃, PCl₅, SOCl₂, CCl₄COOH, CH₂ClCOOH, C₆H₅SH-C₆H₅NHNH₂, Br₂, I₂. Among these, SnCl₄ and I₂ (under sunlight) were most effective. The viscosity-lowering attained quickly to a definite limiting value.

The rubber recovered from the solution (1) of this definite viscosity gave a solution of almost the same viscosity at the same concentration as that of solution (1), and had the same iodine value as the starting rubber which had a viscosimetric mol. wt. 300,000, but a viscosimetric mol. wt. was 15,000.

From these results it was posturated that in the molecule of natural rubber, here and there may be some vulnerable points (probably -O-C- or -N-C- linkage which is formed a priori or a posteriori) against these reagents.