Abstracts

**I. General and Physical Chemistry**

*Studies on the Reactions in Aqueous Solutions by Forming the Interfacial Membrane.* VII~IX.

by Yoshiki INOUE, Akira OSUGI, Takeshi NAGASAKA, Itaru MOTOOKA and Yukio KANAZI

The ion distributions in the both sides of the interfacial surfaces have been studied by the Schlieren Knife Edge method. The interfaces were classified in the following species. The stable intersurface, for example CaCl₂-Na₂CO₃ system:— the ions at the both sides are diffusing smoothly. The trembling one, AlCl₃-NaOH system:— the transport of ions is controlled by driving force. The case such as ZnCl₂-Na₂S system, in which the crackles are issued from the membrane:— the narrow diffusible electrical double layer is observed and this case is similar to that of the ion transport in electrode process. The case such as ZnCl₂-Na₂PO₄ or ZnCl₂-(Na₂)₂HPO₄:— the Schlieren line is similar to the trembling case and the membrane is not formed, the interface spreading.

**IX. The Peculiar Phenomena by Ultraviolet Absorption Spectra of the Membranes, and the Influence of the Surface Active Agents.** (pp. 812~817)

by Yoshiki INOUE and Yukio KANAZI

Various types of interfacial membranes are considered to be due to the electro-double layer and these were studied by ultraviolet spectra.

The results obtained are as follows. The peculiar phenomena depend on the membrane peculiarities which are due to the electro-double layer in the membranes. The rate of the precipitation reaction is indicated by the rate of decreasing of the transmittance qualitatively (the very stable forms). The orientation of CaCl₂ on the membrane is observed on the interfacial membrane of the CaCl₂-Na₂CO₃ system (the very stable forms). From the spectra of AlCl₃-NaOH system, we recognize that the soluble basic aluminium salt is produced from the membrane (the trembling membrane). The spectra of ZnCl₂-Na₂S system which sounds crackles from the surface of the membrane, have very little change of the transmittance, because the strong electro-double layer is formed in this case. Generally, the addition of surface active agents have some influence on the reaction rate.

**The Effects of Gegen Ion on the Critical Micelle Concentration (C. M. C.).** II~IV.

by Kenjiro MEGURO and Tamotsu KONDO

The influence of gegen ions on the micelle formation of cationic surfactants in water has been studied. Dodecyl pyridinium chloride, bromide and iodide were synthesized and their critical concentrations for the micelle formation were determined by measuring the electrical conductance and by the dye method employing the eosine as an indicator. It was found that the chloride gives the largest C. M. C. and the iodide the smallest. The effects of added salts on the micelle formation of these surfactants have also been investigated by making use of the results obtained above.

**III. Effect of Added Salts on the Conductance Curves of Ionic Surfactants.** (pp. 821~823)

The electrical conductances of ionic surfactants in the presence of inorganic salts have been measured. The results obtained were plausibly explained by taking account of ion exchange between gegen ions of surfactant and ions of added salts. The method of "addition of salt" for studying the effects of gegen ion on the micelle formation of ionic surfactant has been criticized.

**IV. Effect of the Size of Gegen Ion.** (pp. 823~825)

The effect of the size of gegen ion on the C. M. C. has been studied. The ammonium and tetra-methyl, -ethyl, and -butylammonium and 1,6-hexane-N,N'-bis-
trimethylammonium dodecyl sulfates were synthesized and their critical concentrations for micelle formation were determined conductometrically and by the dye method. It was found that the larger the size of gegen ion is, the smaller the C. M. C. is and also that a linear relation exists between them. These results have been discussed in relation to the mechanism of micelle formation of surfactant.

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The Solubility of Silver Bromate in Glycerol-Water Mixed Solvent

by Hiroshi MIYAMOTO

Solubilities of silver bromate in glycerol-water mixed solvent were measured at 15, 20, 25 and 30°C. Concentrations of glycerol ranges from zero to 90.713% by weight of the mixed solvent. The solubility of silver bromate was determined volumetrically from the total silver ion using dichlorofluorescein as an indicator. The observed solubilities of silver bromate at 15, 20, 25 and 30°C were 6.07×10⁻³, 3.89×10⁻³, 7.28×10⁻³, 8.59×10⁻³ and 10.02×10⁻³ mol./l., respectively. The observed data were tested by the following equation (Nippon Kagaku Zasshi, J. Chem. Soc. Japan, Pure Chem. Sect.) 68, 19 (1947),

\[
\ln \frac{C_0}{C_1} = \frac{Z\varepsilon^2}{2RT\varepsilon} \Bigg(\frac{1}{D_1} - \frac{1}{D_0}\Bigg) - \frac{Z\varepsilon^2}{2kT} \times \sqrt{\frac{8\pi N Z^2 \varepsilon^2}{10kT} \left( \frac{C_{1/2}^2}{D_1} - \frac{C_{1/2}^2}{D_0} \right)}
\]

The logarithm of solubility is approximately reciprocally proportional to the dielectric constant of the solvent all over the concentration region of glycerol.

The solvation radius of silver bromate, 3~4 Å, was computed using the data and the equation shown above.

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Internal Rotation in α-Chloropropionyl Chloride

by Kunio FUKUSHIMA

Infrared and Raman spectra of α-chloropropionyl chloride have been observed with the object of determining the molecular structure in various states. The normal vibration calculation has been carried out as the seven body problem, regarding the methyl group as a mass point. From the experimental results and the results of the calculation, it has been concluded that in the liquid state the molecules are in three molecular forms, trans, gauche and gauche dash form, of which only the trans form persists in the solid state. In non-polar solution and especially in gas, gauche dash molecules become more in number than in the liquid state. It has been decided that the energy difference between trans and gauche form are nearly equal to zero based on the measurement of the intensity change of infrared absorption bands with the variation of temperature.

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X-ray Studies on the Fine Structure of Polyvinyl Alcohol Film. I. Selective Uniplanar Orientation

by Takani MOCHIZUKI

Polyvinyl alcohol (PVA) films, prepared with usual method, were treated under various heating conditions. In these films, manifest birefringence was observed, which showed that the long axes of the optical indicatrix were arranged in parallel with the film plane. An anisotropic orientation of the crystallites was seen in the X-ray diagrams. The reflection at about 20° (2θ) was separated into two peaks, (101) and (101), and their intensities were measured, using an X-ray diffractometer with narrow slit width. The intensity curves of PVA films were quite different as compared with those of PVA fibers. With the X-ray beam perpendicular to the plane, a random oriented pattern was obtained, in which the intensity of (101) reflection was weaker than that of (101) reflection. With the beam parallel to the plane, (100), (101) and (200) reflections appeared as dense arcs on the equator and the intensity of (101) reflection was stronger than that of (101). From these results, it was concluded that selective uniplanar orientation of the crystallites was observed in PVA film.

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The Chemical Shifts of Alkyl Hydroperoxides

by Shinichi KAMIO

The chemical shifts of the –OOH proton resonance of pure alkyl hydroperoxides (n-propyl through n-octyl and...
2-butyl) were measured for the samples which were synthesized by means of Williams's method.

Alkylhydroperoxides are unstable and the samples are assumed to contain the products of decomposition. It was observed that the $-\text{OH}$ protons are less shielded than $-\text{O}$ protons in alcohols and electronically close to $-\text{COOH}$ protons in so far as the shift values are concerned. As they are diluted in carbon tetrachloride, they shift to the higher side of field just like the other hydrogen-bonded liquids.

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2. Inorganic Chemistry and Geochemistry

Nippon Kagaku Zasshi, 80, 846~849 (1959)
Geochemical Investigation of the Uraniferous Beds of the Ningyo Pass

by Harumi ARAKIT and Kyosuke KUBO

Analyses of rocks from the uraniumiferous conglomerate beds at Ningyo-pass, Tottori, revealed the following. 1) Both U and P are more concentrated in the matrix than in the gravels and in iron sulfide ore over them. Among the gravels, however, porphyritic ones contain more U and P than gravels of andesite, or of other older rocks. 2) U and P are not at all, or incompletely, leached out in the gravels and in iron sulfide over them. 3) The contents of U and P increase with the amount of iron sulfide. 4) The ratio of the contents of U and P to that of iron sulfide are higher in the matrix and in the gravel, than in the iron sulfide which covers the gravel.

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Nippon Kagaku Zasshi, 80, 849~855 (1959)
Synthesis of Erdmann's Type Complexes. IV~V.

by Eishin KYUNO

IV. Synthesis of Potassium Tetraacido-cobaltate(III). (pp. 849~852)

Four cobalt(III) complexes were derived from dichlorodiouacetylenediamine, $[\text{Coen}(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$ and dichlorodiouaquidimine chloride $[\text{Co(NH}_3\text{)}_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$: i) $K[\text{Coen(CO}_3)_2\cdot\text{H}_2\text{O}]$, ii) $K[\text{Co(NH}_3\text{)}_2(\text{CO}_3)_2\cdot\text{H}_2\text{O}]$, iii) $K[\text{Coenox}_2\cdot\text{H}_2\text{O}$, iv) $K[\text{Co(NH}_3\text{)}_2\text{ox}_2\cdot\text{H}_2\text{O}]$.

Absorption maxima of the tetraacido-complexes in aqueous solutions were identical with "blue forms" that had been previously synthesized from the potassium tricarbonatocobaltate(III) in our laboratory. From this fact, it seems that two nitrogen atoms in each complex are located in cis-positions of an octahedron. Backward reaction of the dicarbonatodiammine cobaltate (III) under mild condition resulted in production of familiar Erdmann's salt. From this, it was concluded that an interconversion from cis to trans took place during the reaction. A discussion based upon the infrared spectra was also added.

V. Synthesis of Free Acid-Type Complex. (pp. 852~855)

Three kinds of free acid, i) $\text{H}[\text{Coenox}_2\cdot\text{H}_2\text{O}]$, ii) $\text{H}[\text{Co(NH}_3\text{)}_2\text{ox}_2\cdot\text{H}_2\text{O}]$, iii) $\text{H}[\text{Co(NH}_3\text{)}_2(\text{NO}_2)_2\cdot\text{H}_2\text{O}]$ were prepared from $[\text{Coen}(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$, $[\text{Co(NH}_3\text{)}_2(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$ and NH$_4$ [Co(NH$_3$)$_2$(NO$_2$)$_3$]. Silver and tetramethylammonium salts of ii) and iii) were also prepared from the corresponding potassium salts synthesized beforehand. The pH values of $1\times10^{-4}$ FL aqueous solution of the free acids were 4.9, 3.6 and 4.3 respectively. Absorption spectra of the free acids in solution slightly differed from those of the corresponding salts. Infrared absorption spectra showed that absorption band of the free acids in 1750~1600 cm$^{-1}$, which might be assigned to CO stretching of carboxylate group, shifted to shorter wave lengths and also splitted distinctly into two components of tetracarbonatobium salts. From this fact, it may be assumed that an oxalate group in the coordination sphere of the free acids behaves partially as a monodentate ligand owning to some interactions between the oxalate ion and a proton in outer sphere. Infrared spectra of the dehydrated acids differed from those of the hydrated ones in appearance. From this, it seems that the water of crystallization also contributes to the structure of the acids.

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Geochemical Investigation was made on 34 samples taken from 13 spas located in the Oshima Peninsula, south-western Hokkaido, to find the characteristics of the hot springs of this region. From the results of analyses, the following conclusions were obtained. (a) The spring waters of this area are, in general, rich in residue on evaporation. (b) When the corresponding data were plotted on the Cl-HCO$_3$-SO$_4$ triangular coordinate diagram, it was apparent that most springs are of the Cl-type. Those belonging to the Cl-type are also rich in bicarbonate and free carbon dioxide and sodium.
predominates among major constituents. (c) The carboxylic deposits are often found in these hot springs.

XLIII. On the Hot Springs in South-western Hokkaido. Part 2. The Hot Springs at Shikabe and its Environs. (pp. 862-865)

The results of analyses of 13 hot springs at Shikabe and its environs,issuing along the western coast of Oshima Peninsula, south-western Hokkaido, are shown and the mechanism of emergence and the origin of the chemical constituents are discussed. The increase was observed in chloride and also in boric acid content with rise in temperature. But the negative correlations were found between the contents of chloride and sulfate as well as chloride and bicarbonate. On the Cl-HCO$_3$-SO$_4$ triangular co-ordinate diagram plots representing respective springs fall on a linear line. This shows that the ratios HCO$_3$/SO$_4$ remain nearly constant irrespective of Cl contents. It is concluded from these data that each water is composed from two sources in different ratios of mixing, one being low in temperature and containing bicarbonate and sulfate, and the other high in temperature and rich in chloride. This conclusion is also supported by the results obtained with minor constituents such as Br, I, Li and Ge. The constituents contained in these hot springs are considered to be mainly of volcanic origin.

XLIV. On the Hot Springs in South-western Hokkaido. Part 3. The Hot Springs at Nigorikawa. (pp. 865-871)

The results of analyses of 18 spring waters of Nigorikawa located in the Oshima Peninsula, south-western Hokkaido, are shown. The waters of this area are poor in sulfate though considerably rich in bicarbonate and the contents of these constituents are almost constant in all springs while the chloride content varies greatly over the range from 9 to 2299 mg./l. Thus the equivalent percentages of chloride in total anions (Cl/$\Sigma$ anion) cover the range 2-86. Examining the relations between chloride and some other constituents it is concluded that the waters of Nigorikawa is a mixture of the Cl-type water rich in chloride and high in temperature and the HCO$_3$-type water low in temperature in various proportions. The volcanic emanation is considered to be the main source of constituents of these hot springs and it is rather improbable that they are of fossil origin.

Ultraviolet Spectrophotometric Determination of Bismuth Using Hydrobromic Acid

by Yuraku YAMAMOTO

This report deals with the results of an investigation on the ultraviolet spectrophotometric determination of bismuth using hydrobromic acid as the reagent. Absorption spectra were measured for the bismuth perchlorate solutions containing various concentration of hydrobromic acid, and it was found that two absorption bands with maxima of 256 m$\mu$ and 375 m$\mu$ existed in the ultraviolet region. Though Nielsch and Boltz had already used 373 m$\mu$, it was found that 256 m$\mu$ was more sensitive. Bathochromic effect with increasing acid concentration was observed when hydrobromic acid concentration was low, but the maximum wavelength and the value of absorbance does not change when hydrobromic acid concentration was held higher than 2.6 N. In the spectrophotometric determination of bismuth, the calibration curves were made at two maxima of 256 m$\mu$ and 375 m$\mu$. Effects of temperature, time of standing and diverse ions were investigated. Results obtained were as follows. 1. 1 : 1 concentration of hydrobromic acid are chosen as a working medium. 2. The Beer’s law is followed up to 12 p.p.m. at 375 m$\mu$ and up to 5 p.p.m. at 256 m$\mu$, and the absorbance for 1 p.p.m. of bismuth was 0.2248 (256 m$\mu$) and 0.0839(375 m$\mu$) within the error of 2%. 3. Absorbance is practically constant during 1.5 hr. 4. The temperature coefficient of absorbance was 0.0008 (375 m$\mu$) and 0.0022(256 m$\mu$)/C. 5. Cobalt, manganese, nickel, aluminium and arsenic do not interfere when they are present in the concentration of 100 p.p.m., but iron (III), lead, tin(IV), and antimony(V) interfere con-
The colorimetric determination of small quantity of phosphoric acid forming molybdenum-blue in its extracts was investigated by using some aqueous solutions of inorganic materials as developer. Experiments were carried out by ascending method with Toyo Roshi No. 50, and each metallic ion was identified as sulfide by exposing to hydrogen sulfide gas for about 10 minutes. Since Sb$^{5+}$ and Sn$^{4+}$ cannot be separated from each other, these ions could be separated fairly by reducing them to Sb$^{3+}$ and Sn$^{2+}$ with sodium sulfite. For example, when the solution being prepared by dissolving 3 g. of ammonium carbonate in 20 cc. of 1N ammonia solution was used, the $R_f$ values of these metallic ions are as follows: As$^{3+}$ 0.84 and As$^{5+}$ 0.84, Sb$^{5+}$ 0.26, Sn$^{2+}$ 0.09. $R_f$ values are almost the same when ammonium bicarbonate was used instead of ammonium carbonate.

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Abstracts

The separation of arsenic, antimony and tin was investigated by using some aqueous solutions of inorganic materials as developer. Experiments were carried out by ascending method with Toyo Roshi No. 50, and each metallic ion was identified as sulfide by exposing to hydrogen sulfide gas for about 10 minutes. Since Sb$^{5+}$ and Sn$^{4+}$ cannot be separated from each other, these ions could be separated fairly by reducing them to Sb$^{3+}$ and Sn$^{2+}$ with sodium sulfite. For example, when the solution being prepared by dissolving 3 g. of ammonium carbonate in 20 cc. of 1N ammonia solution was used, the $R_f$ values of these metallic ions are as follows: As$^{3+}$ 0.84 and As$^{5+}$ 0.84, Sb$^{5+}$ 0.26, Sn$^{2+}$ 0.09. $R_f$ values are almost the same when ammonium bicarbonate was used instead of ammonium carbonate.

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Colorimetric Determination of Phosphoric Acid by Molybdenum-blue (Phenylthiosemicarbazide as a Reducing Agent)

by Sumio KOMATSU and Yasuko IWAKUMA

The colorimetric determination of small quantity of phosphoric acid forming molybdenum-blue in aqueous acetic acid solution by using phenylthiosemicarbazide as a reducing agent has been investigated and the following facts were found. Thirty cc. of carbazide solution of 1.5 mg./cc. in 2N acetic acid and 3 cc. of 2.5% aqueous solution of ammonium molybdate are needed to 0.25 mg of phosphorus. Since an excess of molybdate was reduced to blue molybdenum ion by this reagent at higher acidity than 2N, this color reaction was carried out at lower acidity than it. The time to attain the maximum color development was about 5 minutes at room temperature and this color could be kept without undergoing change for 30 minutes. Beer's law was very well followed with phosphorus content from 1 to 12 mg./cc. at the wave length of 750 m$\mu$ and from 0.1 to 5 mg./cc. at 372 m$\mu$. Measuring the absorbance at 372 m$\mu$ had a threefold increase of sensibility over procedures using 750 m$\mu$ and the average error was within ±2%. In order to increase the sensibility, the extraction of molybdenum-blue with ether-iso-amylalcohol mixture of 1:1 by volume was tried. Since molybdenum-blue could not be extracted from only acetic acid medium, sulfuric acid should be added to 2N, to make the extraction possible. For the separation of interfering ions such as Cu$^{2+}$, Ag$^+$, Au$^{3+}$, Hg$^{2+}$, Pt$^{4+}$, Pd$^{2+}$, and Fe$^{3+}$, only the complex phosphomolybdic acid was extracted with iso-amylalcohol, and the colorimetric procedure forming molybdenum-blue in its extracts was tried.

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In order to study the rate controlling step of this reaction, the rate of formation of vinyl acetate was measured by the flow method under various conditions. The reaction velocity was found to be proportional to the concentration of zinc acetate on the catalyst; but when its concentration exceeded 0.3 μg./g. of activated charcoal, the reaction velocity did not increase any more but rather decreased. The activation energy of this reaction was found to be 16.9 kcal./mol. from the results of laboratory scale experiments, and to be 16.1 kcal./mol. in the case of pilot plant scale. These values coincided with that of the chemisorption of acetylene on the same catalyst. The effect of the molar ratio of acetylene to acetic acid on the reaction velocity was reasonably explained by the rate equation previously proposed, which was derived by assuming that the chemisorption of acetylene on the catalyst should be the rate controlling step.

In this investigation indicated that the impurities derived from acetylene consisted of various kinds, but those from acetic acid were few if any; therefore it was considered that the primary action of the catalyst might be concerned with acetylene. Both the measurement of surface area of the catalyst and the various other evidences have shown that the main role of activated charcoal was the chemical activation of zinc acetate by bonding, in addition to the offering of a large surface. Some considerations were given on the cause of this chemical bonding by measuring, for instance, surface area, content of carbonyl group and double bond on the surface quantitatively, and by correlating these values with the activity of the catalyst. The effects of the several complex substances consisting of zinc acetate and aromatic substances, whose functional behaviors could be similar to that of activated charcoal, were examined.

The activity of the catalyst decreased gradually as the reaction proceeded in the synthesis of vinyl acetate. Some considerations were made for this deactivation. The poisonous impurities in acetylene such as PH₃, H₂S etc. could be removed by using oxidizing agents. It was concluded from a number of experiments that, when purified acetylene was used, the main causes of the deactivation of the catalyst might be the polymerized materials derived from acetylene, vinyl acetate, and acetaldehyde on the surface of the catalyst.

The impurities which are accompanied in the vapor-phase synthesis of vinyl acetate were studied by mass, infrared, and ultraviolet spectrometer. Various impurities, which have not been found hitherto, were detected, that is, many olefines with carbon number 4 to 8, and aromatic compounds such as benzene, toluene. Many of them were considered to have come from acetylene. Some consideration was given on the functions of catalyst from the results obtained.

By the condensation of d-limonene and paraldehyde with zinc chloride as a catalyst, 6-ethyliden-1,8(9)-p-menthadien was obtained. From d-limonene and propionaldehyde, 6-propyliden-1,8(9)-p-menthadien was formed. In the solution of acetic acid containing a small quantity of sulfuric acid, cyclic ether C₆H₄(O₂) was obtained from d-limonene and paraldehyde. Similarly cyclic ether C₆H₅O₂ was obtained from d-limonene and propionaldehyde.
Nippon Kagaku Zasshi, 80, 900–903 (1959)

A Study on the Mechanism of Glycolysis. II. On the Rate of Decarboxylation of α-Hydroxy-α-methylacetoacetic Acid

by Takeo NASHIMA

An elucidation of the mechanism of a certain step of glycolysis where C₂-C₃ fission of fructose-1,6-diphosphate is effected by aldolase, was attempted by means of a model experiment. α-Hydroxy-α-methylacetoacetic acid was taken as a model compound. β-Carbon, α-carbon and carboxylic carbon of this acid correspond, respectively, to C₃, C₂ and C₄ atoms of fructose, and the C₂-C₃ fission of the latter corresponds to the removal of carbon dioxide from the former. The rate of decarboxylation of this acid was determined under various conditions, and by comparing it with that of α, α-dimethylacetoacetic acid, it was observed that carbon dioxide was liberated more rapidly from α-hydroxy-α-methylacetoacetic acid than from the α, α-dimethyl compound. Several metal ions, particularly ferrous, ferric, cupric and aluminum ions, greatly accelerated decarboxylation of α-hydroxy-α-methylacetoacetic acid in aqueous solution of pyridine and acetic acid, while it was not the case with α, α-dimethylacetoacetic acid. It was concluded from above observations that the main factors for the cleavage of fructose-diphosphate especially between C₂ and C₃, giving an aldehyde from the C₂-part and an alcohol from the C₃-part, would be as follows: (1) C₂ of the fructose is a ketonic carbon. (2) C₃ of the fructose has a hydroxyl group attached to it. (3) Certain metal ions catalyze the cleavage of fructose-diphosphate. The yield of carbon dioxide from α-hydroxy-α-methylacetoacetic acid was less than one half of the anomalously small amount observed from α, α-dimethylacetoacetic acid. It was supposed that the replacement of the a-hydroxy- and a-carboxyl groups by metal ions makes the bond between C₂ and C₃ stronger, so that the removal of carbon dioxide is made difficult.

This may be conceivably because of the large steric hindrance of this group, just like in case of the a-toly group. But the effect of the a-hydroxyl group is larger than p-hydroxyl group, probably owing to chelate ring formation. For example, the absorption maxima of I, III, X and XII are (222, 270, 300 mμ), (222, 272, 322 mμ), (245, 282 mμ) and (250, 265, 314 mμ) respectively.

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Nippon Kagaku Zasshi, 80, 906–909 (1959)

On Reduction of Residual Oxidant in tert-Butyl Chromate-oxidation

by Takayuki SUGA

Oxalic acid and hydrazine sulfate are usually used as reducing agents for the residual oxidant in tert-butyl chromate-oxidation. The present author made a further study concerning reduction of the residual oxidant by these reducing agents.

Reduction with oxalic acid: Oxidation of cyclohexene, reported previously by R. V. Oppenauer et al. (1949), was re-examined, and it was found for the first time that hydroquinone (in a considerable amount), quinhydron and cyclohexenyl acetate were detected besides cyclohexenone and p-benzoquinone. It was clarified that hydroquinone was formed by reduction of p-benzoquinone with oxalic acid used as a reducing agent for the residual oxidant. Consequently, when a compound of quinone series is formed in the oxidation, it is necessary to give much consideration for treating reaction products and dealing with experimental results.

Reduction with hydrazine sulfate: when a carbonyl compound, which is apt to react with hydrazine sulfate (e.g. benzaldehyde), is obtained from the oxidation, the reaction mixture should be steam-distilled in presence of mineral acid after reduction of the residual oxidant. Because, if this treatment is omitted, a carbonyl compound can not be isolated in free form but is obtained as the derivative (e.g. dibenzalhydrazine). It is therefore undesirable to use hydrazine sulfate as a reducing agent for the residual oxidant when the carbonyl compound, which can not be steam-distilled or is unstable to mineral acid, is formed in tert-butyl chromate-oxidation.

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Nippon Kagaku Zasshi, 80, 909–913 (1959)

Reaction of d-Limonene with Japanese Acid Clay. III. Liquid Phase Reaction in the Presence of a Small Amount of Water

by Hisashi KOMAE

Limonene was heated with Japanese acid clay (5%) at 150°C for 1 hr. in an autoclave, in the presence of 0.1, 0.5 or 1.0 mol. of water per mol. of limonene, respectively. In the presence of 0.1 mol. of water, limonene was attacked almost entirely. The more the

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Studies on 2-Amio-4 or 5-aryl Substituted Thiazoles. II. Reaction in the Presence of a Small Amount of Water

by Jiro OKAMIYI

Various 2-aminothiazole compounds were prepared, on which ultraviolet absorption spectra were measured. The compounds included: 2-NH₂-4-α-C₆H₅-5-C₆H₅-C₃NS (I, mp. 208°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (II, 201°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (III, 222°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (IV, 163°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (V, 223°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (VI, 248°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (VII, 260°C, dec.), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (VIII, 208°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (IX, 201°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (X, 212°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (XI, 210°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (XII, 139°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (XIII, 120°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (XIV, 284°C), 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (XV, 171°C) and 2-NH₂-4-C₆H₅-5-C₆H₅-C₃NS (XVI, 198°C). The effect of the α-naphthyl group upon the absorption spectra is smaller than expected.

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amount of water, the less the activity of the catalyst; in the case of 1.0 mol. of water limonene was not changed. While only a small portion of limonene was changed by 0.5 mol. of water, further treatment of the product (polymer-freed and containing 90.3% of limonene) for 9 hr. resulted in the formation of the following compounds: α-terpinene, p-cymene, terpinolene, α-καταλ. p-methylenadiene, α-καταλ. p-methylenadiene, γ-terpinene, d-α-terpinene, 1,8-cineole and polymer. Five consecutive treatments of limonene with the catalyst and water led to the formation of p-cymen, p-methylen-3 and a large amount of polymer. Optical rotation and bromine value of the products (polymer-freed) decreased as the reactions were repeated but diene value, which was changed in parallel with the intensity of the band at 265 mμ, was the largest at the 4th reaction. At the 5th reaction, optical rotation fell to about zero and bromine value decreased to about one-fourths of the original value. These results give the additional support to the reaction mechanism proposed in the previous paper.

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I. Oxidation of R-Homocampheniloneenolacetate by Hydrogen Peroxides. (pp. 913~915)

by Yoshiteru HEYA and Yuichi WATANABE

The oxidation of R-homocampheniloneenolacetate with H₂O₂ in acetic acid afforded following compounds. Unsaturated monocarboxylic acid, two kinds of hydroxy-carboxylic acids, and their lactones.

The reaction processes of affording these products were discussed.

II. Reduction of Camphorenolacetate and R-Homocampheniloneenolacetate by Lithium Aluminium Hydride. (pp. 915~917)

by Yoshiteru HEYA and Yuichi WATANABE

When camphorenolacetate was reduced with large amounts of LiAlH₄, camphor and iso-borneol were produced, but when R-homocampheniloneenolacetate was reduced under the same condition, the main product was R-homocamphenilone. This substance was presumed to be the exo-type alcohol.

Using small amounts of LiAlH₄, the main products from both enolacetates were ketones.

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Oxidation of Cyclohexanol, trans-1,2-Cyclohexanediol, and Cyclohexanone with tert-Butyl Chromate

by Tokayuki SUGA

Oxidation reactions of cyclohexanone, cyclohexanol, and trans-1,2-cyclohexanediol with tert-butyl chromate were studied. Oxidation of cyclohexanone (at 35°C for 48 hr.) gave only a very small amount of adipic acid, and it was found that cyclohexanone was fairly stable to this oxidant and 1,2-cyclohexanediol was not obtained unlike the case where the oxidation is carried out with selenium dioxide. When cyclohexanone was oxidized at 35°C for 6 hr., it was entirely converted into cyclohexanone alone. Even when cyclohexanone was allowed to be oxidized at 35°C for 48 hr., cyclohexanone was obtained, accompanied by only a very small amount of adipic acid, which was probably the further oxidative fission product of 1,2-cyclohexanediol formed from cyclohexanone by oxidation. As the result it was found that tert-butyl chromate is an useful oxidant for the oxidation of a saturated cyclic secondary alcohol to the corresponding ketone. trans-1,2-Cyclohexanediol was also oxidized at 35°C for 3 hr. Any corresponding 1,2-diketone was not obtained, but a large amount of adipic acid was formed together with a small amount of adipic ester of the diol. It was found from this result that the oxidant is not suitable for the oxidation of a cyclic α-γlycol, such as trans-1,2-cyclohexanediol in which two secondary hydroxyl groups attach to adjacent carbon atoms, to its corresponding α-diketone. The author considers that the ester obtained was formed by the oxidation of the intermediate, hemiacetal, which was produced from the reaction of the diol with adipaldehyde, which was formed from the diol by glycol fission (probably via a radical).

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Studies on the Cleavage of Molecules by Catalytic Hydrogenation. XXV~XXVI.

by Ken-ichi WATANABE, Isamu NIIKURA and Kazuo HATA

XXV. Ortho Effect in Catalytic Hydrogenation of Aromatic Nitriles. Part I. (pp. 921~923)

by Ken-ichi WATANABE

It was previously reported that aromatic nitriles were hydrogenated to the corresponding methyl compounds and ammonia in vapor phase using nickel-copper-kieselguhr catalyst, and any substituent in the ortho position restrained the hydrogenolysis of nitrile group by steric effect. In the present experiment, still larger effect was observed by two substituents both ortho to the nitrile group. In the hydrogenation of 2,6-dimethoxybenzonitrile, the normal hydrogenation product (2,6-dimethoxytoluene) was scarcely found, alternatively yielding a considerable quantity of 2,6-dimethoxybenzene. The hydrogenation of 2,4,6-trimethyl-benzonitrile gave poor yield of isodurene. In both cases, the reactions were very complicated.

XXVI. Catalytic Hydrogenation of p-Methoxybenzonitrile (pp. 923~924)

by Isamu NIIKURA, Ken-ichi WATANABE and Kazuo HATA

Catalytic hydrogenation of p-methoxybenzonitrile was studied, and the effect of methoxyl group was discussed.
in comparison with the previous result of α-methoxybenzonitrile. Main reaction was the hydrogenolysis of nitrile group to produce p-crenyl methyl ether and ammonia. But some side reactions were observed simultaneously, and a small quantity of toluene, aniline and phenol was also identified. When the reaction temperature was high (above 300°C), a considerable quantity of anisole was obtained. Hydrogenation of nitrile group was found to be somewhat restrained owing to competitive hydrogenolysis of methoxyl group.

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VII. On the Reactions of α-Amino-γ-valerolactone. (pp. 924-933)

α-Amino-γ-valerolactone hydrobromide reacts with sodium cyanate to give α-ureido-γ-valerolactone, and free α-amino-γ-valerolactone with phenylisocyanate to give α-phenylureido-γ-valerolactone. In a similar way, α-thioureido-γ-valerolactone derivatives were obtained from α-amino-γ-valerolactone with phenyl- and methyl-thioisocyanate. When boiled in hydrochloric acid, α-ureido-derivatives were converted to β-hydroxyethylhydantoins but α-thioureido-derivatives did not undergo analogous transformation. In this work this transformation mechanism, and the tendency to ring-formation of lactone, hydantoin and thiohydantoin from α-amino-γ-valerolactone derivative were discussed.

VI. On the Reactions of α-Amino-γ-butyrolactone with Aromatic Aldehydes. (pp. 924-929)

It was shown that α-amino-γ-butyrolactone underwent aldol-type condensation with aromatic aldehydes to give α-benzalamino-α(1-hydroxybenzyl)-γ-butyrolactone derivatives. These condensation products with benzaldehyde and p-nitrobenzaldehyde were found to be threo-form compounds. The product obtained from benzaldehyde was hydrolyzed to give α-amino-α(1-hydroxybenzyl)-γ-butyrolactone hydrochloride, but the p-nitro derivative was decomposed to α-amino-γ-butyrolactone hydrochloride and p-nitrobenzaldehyde by hydrochloric acid.

VII. On the Reactions of α-Amino-γ-valerolactone. (pp. 929-933)

A few ring-opening reactions of α-amino-γ-valerolactone, prepared from levulinic acid, were shown. This valerolactone derivative underwent analogous reaction to α-amino-γ-valerolactone (cf. V.) to give 2,5-bis-(β-chloropropyl)-3,6-diketopiperazine (IX), β-bromopropylhydantoin (XIII) and ethyl γ-bromovalearate (VI) but no ring-opening reaction with sodium methyl mercaptide. These halogenated compounds were easily dehydrohalogenated in the presence of methyl mercaptide and IX gave 5,5-dimethyl-3,4,3′,4′-tetrahydrodihydro-l,3-furanone (XXV).
The Syntheses of Dihydro-1, 4, 5, 8, 9, 10-hexaazaanthracene-2, 6-dicarboxylic Acid and its Derivatives

by Sumio NOGUCHI

As a part of the studies of heterocyclic compounds which have conjugated double bond of -C=N-, dihydro-1, 4, 5, 8, 9, 10-hexaaazaanthracene-2, 6-dicarboxylic acid (VII), its diethyl ester (VIII) and 1,10-dihydro-1, 4, 5, 8, 9, 10-hexaaazaanthracene (X) were synthesized. Fluorurubin (IV) gave VII on oxidation with potassium permanganate. The compound (VII) underwent decarboxylation by vacuum sublimation, giving X. It was proved that the compound (VII) is an effective reagent for detecting Ag⁺ and Cu²⁺. When the concentration of Cu²⁺ is reduced less than 1000 ppm, it behaves as a special reagent for Ag⁺ at pH 1.

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Toluene Used as a Solvent in tert-Butyl Chromate-oxidation

by Takayuki SUGA

Oppenauer et al., Anales Asoc. Quim. Argentina 37, 246 (1949), and Roth, U.S. Patent 2,758,111 (1956), reported that toluene can be used as a solvent in tert-butyl chromate-oxidation. However, there was not reported any experimental example. The author, therefore, investigated whether toluene can be used as the solvent or not. A toluene solution of tert-butyl chromate containing acetic acid and acetic anhydride was maintained at 55°C for 4 days and then at a room temperature for 8 days. Also, toluene was treated with a carbon tetrachloride solution of the oxidant containing no acid. In the above two cases toluene was oxidized by tert-butyl chromate yielding benzoic acid (3.90 and 1.14%), benzyl acetate (0.14 and 0.14%), benzaldehyde (0.08 and 0.08%), acetone (0.12 and 1.14%) and isobutyraldehyde (0.004 and 0.18%). It is consequently undesirable to use toluene as the solvent in tert-butyl chromate-oxidation. The author is of opinion that acetone and isobutyraldehyde were probably derived from tert-butanol in oxidation process.

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