



HOKKAIDO UNIVERSITY

Title	Summary International Reports, Aug. 1973-Jul. 1974
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 14(1), 135-149
Issue Date	1975-03
Doc URL	https://hdl.handle.net/2115/37934
Type	other
File Information	14(1)_135-150.pdf



Sixth International Conference on
Organometallic Chemistry, University
of Massachusetts, Amherst, Massachu-
setts, U.S.A., August 13-17, 1973

A Convenient and General Synthesis of Acetylenes *via* the Reaction of Iodine with Lithium 1-Alkynyltriorganoborates

Akira SUZUKI, Norio MIYAURA, Shigeo ABIKO
and Mitsuomi ITOH

Treatment of lithium 1-alkynyltriorganoborates with iodine under mild conditions produces the corresponding internal alkynes in essentially quantitative yields (eq. 1).



The most general method previously available for the synthesis of acetylenes involves the reaction of alkali metal acetylides with organic halides or sulfates. However, this synthesis is really satisfactory only for primary alkyl groups which readily undergo nucleophilic substitution reactions. On the other hand, the present synthesis is free of this limitation. Secondary and aryl groups appear to be introduced as easily as primary groups. Consequently, the present method provides a range of applicability far broader than the procedures previously available.

XIth International Symposium on Free
Radicals Berchtesgaden-Königssee, Ger-
many Sept. 4-7, 1973

E.S.R. Spectra of Diborane Radicals in Solid State

A. HASEGAWA* and J. SOHMA

E.S.R. spectra of the radicals produced from γ -irradiated diborane in polycrystal or single crystal were investigated. From the analysis of the results of the single crystal, the radical was identified as a neutral diborane radical, $\cdot\text{B}_2\text{H}_5$, which was produced by extracting one of the two bridging hydrogen atoms of diborane. The E.S.R. parameters were determined for the two boron atoms as well as the bridging hydrogen in $\cdot\text{B}_2\text{H}_5$ radicals, which are in the two different sites in the crystal, by the analyses of the spectra from the single crystals. For the terminal hydrogen, which gives the small coupling, the coupling constant was determined to have an orientation in which the four terminal hydrogen became equivalent. The major portion of the spin density on the radical is equally shared by the two boron atoms while a considerable portion exists

* Faculty of Science, Hiroshima University, Hiroshima, Japan.

on the bridging hydrogen atom, and a small portion with negative sign exists on the four terminal hydrogens. The orbitals of the unpaired electrons on the two borons in the radicals are in the same plane and form an angle of 73° . These results are in good agreement with those from INDO calculation for the radical. The structure of the radical was discussed in comparison with radicals having a similar structure.

International Symposium on Macromolecules; Aberdeen, Scotland Sept. 10-14, 1973

ESR Studies on the Free Radicals Produced by Mechanical Fracture of Solid Polypropylene

M. SAKAGUCHI and J. SOHMA

The species of the primary free-radicals produced by mechanical fracture of isotactic polypropylene were identified by ESR spectra analysis. It was found through this identification that macroscopic fractures of solid polypropylene caused microscopic ruptures of the polymer chains, namely the scissions of the C-C chains. Two characteristic features, which are not observed in radicals formed by γ -irradiation, were found in the radicals produced by mechanical fracture of the polypropylene, namely a high reactivity to oxygen and anomalous behaviour in radical decay. The radicals produced by the fracture rapidly reacted with oxygen and were converted into peroxy radicals of polypropylene before decaying out. The high reactivity is assumed to be related to the ready accessibility of oxygen molecules to the radicals. The second characteristic behaviour of the radicals formed by the fracture was the anomalous increase of the radicals which were observed in the temperature range of 150° – 200° K. It may be surmized that the oxygen and the electric charge exerted certain effects on the decay and also on the formation of radicals by fracture.

XIth International Conference on Phenomena in Ionized Gases, Prague, Czechoslovakia, 10-14 September, 1973

The Development of Steady State Ionization Currents Between Parallel Plates in Hydrogen

M. SHIMOZUMA, Y. SAKAI, H. TAGASHIRA
and S. SAKAMOTO

The growth of steady state ionization currents between parallel plates in gases is often represented by the Townsend equation and Lucas equation. In the present paper, the experimental ionization current growth between parallel plates in hydrogen was

analysed by three methods: (a) a linearized least square method, (b) Gosseries plot and (c) a plot proposed by a group in Keio University. The result of the analysis clearly showed that the ionization current growth was represented far better by the Lucas equation, in which the secondary ionization coefficient by non-resonant photons was treated as a function of the electrode separation, than the conventional Townsend equation in which plane electrodes with very large area and a constant secondary ionization coefficient (γ_T) are assumed. Our present results support the previous investigation by Tagashira and Lucas.

IUPAC International Symposium on
Macromolecules Aberdeen England 10-
14, September 1973

Orientation of (101) Plane in Cellulose Regenerated from Viscose Film with ZnSO_4

Sadayoshi WATANABE, Jisuke HAYASHI, Junyo NAKAGAWA
and Masashi ASANO

Department of Applied Chemistry

Viscose film regenerated in a coagulation bath to which ZnSO_4 is added shows (101) orientation plane of cellulose crystallite in parallel with the film surface.

By adding a concentrated aqueous solution of ZnSO_4 to an aqueous solution of NaOH , $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ deposited in plate crystal form with the layer of water of crystallization in parallel with the crystal surface. It was observed that the crystallite on the regenerated viscose film is of this basic zinc sulfate and the surface of plate crystal lies in parallel with the film surface.

A possible mechanism of such an orientation is as follows. NaOH in viscose reacts with ZnSO_4 in the coagulation bath to form the crystallite of basic zinc sulfate on the viscose film.

The crystalline of the cellulose xanthate grows up epitaxially on the crystalline of the basic zinc sulfate in the following manner. The lattice plane contained hydrophobic groups of the cellulose xanthate is put on the lattice plane contained the water of crystallization and lies in parallel with the film surface, because the lattice parameters of these two planes are quite similar.

Therefore, the (101) plane of OH groups in cellulose crystallite retains the orientation of the plane of the hydrophobic groups in cellulose xanthate in parallel with the film surface.

IUPAC International Symposium on
Macromolecules Aberdeen England 10-
14 September 1973

Memory of Chain Configuration during Reaction of Cellulose and Cellulose Derivatives

Jisuke HAYASHI, Sadayoshi WATANABE
and Akinori SUEOKA

Department of Applied Chemistry

The meridional diffraction of cellulose III and IV were quantitatively examined and was found to be dependent on the origin. The intensity ratio $R(=I_{(020)}/I_{(040)})$ is 2, 1/2, 1/8, and 2/3 for cellulose III prepared from cellulose I, III from II, IV from I, and IV from II, respectively.

Referring to the transformation between these crystalline modifications, these may be classified into two families; the cellulose I family consisting of cellulose I, III_I and IV_I and the cellulose II family consisting of cellulose II, III_{II} and IV_{II}. The transformation occurs within each family. It occurs from each of I family to cellulose II, but not from II family to I family.

According to these results, the chain configuration of cellulose is considered to be different between cellulose I and II families. The former has a "bent" type and the latter has a "bent-twisted" type onfiguration.

The irreversible transformation reaction from cell I to II corresponds with the irreversibility of the transformation from the cell I family modification to the cell II family. Therefore, the reason for the irreversibility should not be ascribed to the more stable intermolecular hydrogen bond of cell II, but rather to the more stable molecular chain conformation of the cell II family.

IUPAC International Symposium on
Macromolecules Aberdeen England 10-
14 September 1973

Plane Lattice Structure in the Amorphous Region of Cellulose Fibers

Sadayoshi WATANABE, Jisuke HAYASHI
and Shigeyoshi MASUDA

Department of Applied Chemistry

When cellulose fibers are treated with concentrated aqueous solution of AcOK, washed with benzene and dried at 100°C~160°C, a new strong meridional diffraction (I_0) corresponding to (101) of cellulose I or II is produced. However, I_0 changed inc-

reasingly into a new first layer diffraction ($d=9.5 \text{ \AA}$) (I_1) with the rise of drying temperature. In addition, some new diffractions appeared at 160°C , however these were weak. The treatment with AcOK caused no change in the crystallinity of the fibers, which may indicate that the new diffractions are due to the AcOK-Cellulose addition product formed in the amorphous region of fibers.

As a result of calculations of the structure factor of AcOK-Cell, it was shown that an imperfect crystal structure with only I_1 was present. It was further shown that this is the plane lattice structure that retains regular order within (200) and shows a disorder in relative arrangement between (200) planes.

This fact was confirmed by optical diffraction photograms for the two dimensional plane lattice model. It is believed that the plane lattice structure which is special type of crystal defects is the representative structure in the amorphous region of cellulose fibers.

IUPAC International Symposium on
Macromolecules Aberdeen England 10-
14 September 1973

Study on Crystal Structure of Cellulose II

Jisuke HAYASHI and Sadayoshi WATANABE
Department of Applied Chemistry

A possible model for the crystal structure of cellulose II was studied. Use of models proposed by earlier workers with "bent" form chains having two-fold screw axis showed discrepancies between the observed and calculated intensities.

In our previous work, it was suggested that the crystal structure of cellulose trinitrate derived from cellulose II deviates from five-fold screw structure on account of the chain configuration of cellulose II with "bent and twisted" form. Actually, (010) diffraction was found by Fortisan to have a high crystallinity.

The agreement between the observed and calculated intensities was improved by the adoption of a "bent and twisted" form chain model, which is a modification of the two-fold screw structure. The cellulose structure with $\phi_1=30^\circ$, $\phi_2=45^\circ$, $\theta_1=50^\circ$, $\theta_2=20^\circ$, antiparallel chains, and a r-shift of 0.1850 gave a better agreement ($R=26.5\%$).

The proposed model also showed better agreement with the infrared data. The observed dichroism for the CH_2 stretching, bending and wagging modes agree with that expected from the orientation of the CH_2 group in the model. Two parallel dichroism bands of OH stretching correspond to two kinds of $\text{O}_3\rightarrow\text{O}_5$ bond in "bent and twisted" form chains.

International Association for Bridge
and Structural Engineering Symposium
on "Resistance and Ultimate Deforma-
bility of Structures acted on by Well
Defined Repeated Loads". 13-14, Sept.
1973, Lisbon Portugal

Strength and Lateral Deformability of Columns of Reinforced Concrete at Shear Failure

Kazuo OHNO, Takuji SHIBATA
Takashige HATTORI

In the design of structural members, it should be intended that the brittle failure such as shear failure might not occur in the ultimate state, to insure the ductility of structures. This could be obtained by making the flexural strength of members to be less than the shear strength.

In cases where the shear strength is unavoidably less than the flexural strength, the column should be endowed with sufficient deformability to follow the response lateral deformation of the entire structure.

In this paper, equations to assess the shear strength and the ultimate lateral deformability at shear failure of reinforced concrete columns are proposed. These equations were derived from the investigation of test data which have been presented in Japan since 1961. The differences between two types, monotonic increase and repeated reversal, are obscure in the shear strength or the ultimate lateral deformability.

The International Symposium RILEM/
IUPAC on Pore Structure and Proper-
ties of Materials, Prague, September 18
to 21, 1973

The Influence of Pore Structure of Concrete Made with Absorptive Aggregates on the Frost Durability of Concrete

Yoshiro KOH and Eiji KAMADA
Department of Architecture, Faculty of Engineering

The behaviors of hardened cement paste and concrete made with three kinds of absorptive coarse aggregates during freezing and thawing were studied to clarify the influence of pore structure on the frost durability of concrete. The relation between the pore size distribution measured by the high pressure mercury penetration method and the length change during freezing and thawing measured by a dilatometer with

the aid of differential transformer was discussed. The increase of frost deterioration with the lowering of freezing temperature can be explained in terms of quantity of freezable water in capillaries becoming gradually larger as already shown in Helmuth's paper. Our experiments suggest that the freezing of water in fine capillaries can not occur until the freezing temperature becomes somewhat lower than the calculated temperature shown in Helmuth's paper.

5th European Congress of Corrosion,
Paris (France), 24th-28th September,
1973

Layer Structure on the Passivation Film on Iron in Acidic and Basic Solutions

Norio SATO and Tetsuji NODA

An ellipsometric study of the passive oxide film formed on iron in phosphate and borate solutions at pH ranging from acid to base was carried out. No magnetite layer was found in the film. It was shown that the film consists of an inner layer of γ -ferric oxide and an outer layer of hydrated ferric oxide. The inner layer is not influenced by the solution pH or anions, and was determined by the overpotential of oxide film formation. A high electric field of an order of 10^6 V/cm was found to exist in the inner layer. The outer layer is under the influence of the solution environment and it dissolves in acid solutions at pH less than 4. It was also shown that the water content in the outer layer increases as the solution becomes alkaline.

CAD/CAM Conference, Society of
Manufacturing Engineers, Detroit,
U.S.A., Oct. 1-3, 1973

Practical Approaches for an Integrated CAD/CAM System

Norio OKINO, Hiroshi KUBO
Department of Precision Engineering

This paper describes practical approaches to three problems in CAD/CAM. First, in the system design of CAD/CAM, the author has proposed a new concept called "Designer's assistant" and has shown a practical system called TIPS-1 which is designed by this concept. Then, in graphic software, a new shape description language and a processing method of graphics were proposed which were designed to solve such difficult problems as hidden lines or contours. Finally, a trial on the personal NC-drafter

was introduced as an example of a practical approach to hardware for CAD/CAM. This might be an effective apparatus for a designer instead of CRT or other mechanical displays.

International Congress on Fluidization
and its Application, Toulouse, France,
October 1-5, 1973

Modeling of Catalytic Fluidized Bed Reactors

Haruo KOBAYASHI, Tadatoshi CHIBA

This paper describes a new model for catalytic reaction in gas-fluidized beds, referred to as "Bubble Flow Model". Since all parameters involved in the model are essentially correlated to the diameter of bubbles and since the bubble diameter with due allowance to its growth is estimated from the operating conditions alone, it is possible to predict the degree of chemical conversion with no adjustable parameters.

The effect of bubble size distribution on the reactor performance is as illustrated and it was shown that when the reaction rate is relatively fast, the difference in conversion becomes remarkable in both cases whether the distribution of bubble size is taken into account or not. The effect of gas adsorption is shown to be small unless the reaction rate is very high.

Experimental data available from various investigations were used in order to examine the validity of the proposed model in the prediction of catalytic conversions for various first-order irreversible reactions. It was found that the model could successfully predict the conversions over a wide range of operating conditions.

4th International Conference on Crystal
Growth Tokyo, 26 March 1974

Modes of Grain Growth in Worked Alloys

Hitoshi NAKAÉ, Dept. Precision Engineering.

The phenomena involved in the grain growth of cold rolled dilute alloys of iron were treated on the basis of an analogy of crystal growth. The migrating boundary was associated with an interface between a growing crystal and a medium from which the crystal grew. Then, the deviation in composition from a nominal one resulted in the regions of either side of the migrating boundary at ascending temperature according to the mode of crystal growth. These regions were conjectured to be subjected to a phase transformation at their deviated compositions other than the nominal ones.

The influences of this phenomenon on the grain growth of cold rolled 3.25% Si-Fe and 3.25% Al-Fe alloys were that 1) the growth rate dropped slightly at A_3 transformation corresponding to iron, 2) the growth of cube on edge texture was enhanced in Si-Fe alloy with sulfur addition at a point corresponding to the eutectic point of S-Fe alloy system and 3) the growth of cube texture was enhanced at the temperatures exceeding three eutectic points in Si-Fe alloy and along the solidus in Al-Fe alloy.

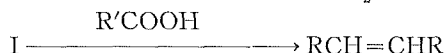
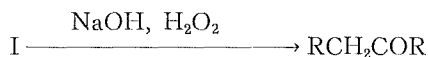
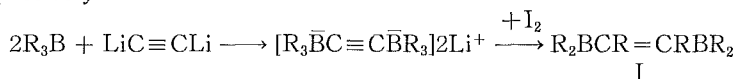
The development of cube texture in 3.50% Ge-Fe alloy, and that of cube on edge texture in 3.25% Si-Fe alloy with small additions of aluminium or germanium were also ascribed to the above considerations.

Second International Meeting on Boron Chemistry, University of Leeds, England, March 25-29, 1974

**Organic Syntheses Using Complexes Obtained from Dilithium
Acetylide and Organoboranes. Syntheses of Ketones,
 RCH_2COR and Symmetric Alkenes, $RCH=CHR$**

Akira SUZUKI, Norio MIYAURA, Shigeo ABIKO
and Mitsuomi ITOH

Treatment of complexes formed from organoboranes and dilithium acetylide with iodine under mild conditions should give bis(dialkylboryl)alkene (I). Alkaline hydrogen peroxide oxidation or protonolysis with carboxylic acid of such intermediates produce the corresponding ketones, RCH_2COR or symmetric olefins, $RCH=CHR$ in good yields, respectively.



The Second International Conference
on Solid Surfaces, Kyoto, Japan. March
25-29, 1974

**Attenuation of Elastic Surface Waves by
Anharmonic Interactions**

Tetsuro SAKUMA and Tsuneyoshi NAKAYAMA

Based on the theory of surfons, we present a formalism to calculate the attenuation rate of elastic surface waves at low temperatures in high frequency regions. A

general formula for the attenuation rate due to the cubic anharmonic terms in the elastic energy of an isotropic elastic continuum is given by means of a temperature-dependent Green's function. In a frequency region between 20 and 40 GHz at $T=1^\circ\text{K}$, our results show quite different frequency and temperature dependence $\omega^{1+n} T^{4-n}$ ($1.9 \lesssim n \lesssim 2.2$) from that obtained in low frequency regions.

U.S.-Japan Joint Conference on "The Comparative Investigation of New Materials by Thermoanalytical Techniques". Akron, Ohio, U.S.A. April 8-12, 1974

Studies on Catalysts and Catalytic Reactions by Gas-flow DTA and High-pressure DTA

Tadao ISHII

Gas-flow DTA (applicable from static atmosphere to fluidized bed state) and high-pressure DTA (applicable up to 200 kg/cm² and 500°C) were developed and applied to the following and the characteristics of the apparatus and the catalytic action under working condition were discussed.

(I) Gas-flow DTA: 1) thermal dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, oxidation of UO_2 and decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 2) DTA studies of V_2O_5 - M_2SO_4 catalysts ($\text{M}=\text{Li}, \text{Na}, \text{K}$ and Cs) for SO_2 oxidation, 3) thermal decomposition of KClO_4 by Fe_2O_3 catalysts with different preparing histories.

(II) High-pressure DTA: 1) liquid phase high pressure hydrogenation of aromatic substances such as benzene, phenol and diphenylether, by commercial catalysts, 2) high pressure coal hydrogenation by various catalysts, Fe_2O_3 , Fe_2O_3 -S, red mud, red mud-S, FeS , ZnCl_2 , ZnO , ZnS , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, SnO_2 , SnS , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{27}$.

International Discussion Meeting on Studies of Lattice Distortion and Local Atomic Arrangements by X-ray, Neutron and Electron Diffraction. 29 April-3 May, 1974, Jülich, Federal Republic of Germany

A Study on the Fine Structure in Metastable β_1 crystal of Cu-40 wt % Zn Alloy

K. TAKEZAWA and S. SATO

Very fine contrasts were often observed in the transmission electron microscopic image of β_1 regions of Cu-40 wt % Zn alloy. In addition, in the electron diffraction

patterns many additional spots with streaks were obtained corresponding to this fine structure. In the present work, a detailed analysis of various E. D. patterns was made to determine the crystal structure of the fine product in the matrix. The structure obtained is an orthorhombic with $\mathbf{A}=(2a/3) [1\bar{1}2]_{\beta 1}$, $\mathbf{B}=(a/2) [1\bar{1}\bar{1}]_{\beta 1}$ and $\mathbf{C}=a [110]_{\beta 1}$, which is also considered as a distorted hcp structure. The relation between the product and the martensite or bainite was examined respectively by cooling or heating of the quenched specimen, under an electron microscope. The $(110) [\bar{1}10]$ shears play an important role in producing the product. The products may be considered to be the embryos of close-packed structure, which are transformed by a mechanism similar to that of Burgers for the martensite transformation from bcc to hcp.

International Discussion Meeting on
Studies of Lattice Distortion and Local
Atomic Arrangements by X-ray, Neu-
tron and Electron Diffraction. 29 April-
3 May, 1974, Jülich, Federal Republic
of Germany

A Study on the Recovery of Heavily Faulted Cu-Ge Single Crystals by X-ray Diffraction

T. TAKAMA, N. YOKOTA and S. SATO

X-ray diffraction profiles have previously been examined on individual crystals in deformed Cu-11 wt % Ge alloy. Diffuse streaks with broad peaks were diffracted from "heavily faulted regions" in the specimen. The work was extended to study the changes in the arrangement of stacking fault in heavily faulted regions following annealing. At temperatures higher than 300°C, remarkable redistributions of peak intensities on the streak were observed in addition to the decrease in the total diffuse intensity. It was revealed that the following changes in stacking order occur during annealing:

- | | |
|--|---|
| | ABA random stacking in ABC regular stacking (fcc) |
| | ABAC random stacking in ABCA regular stacking (fcc) |
| | ABAC regular (d. hcp), AB regular (hcp) and CBA (twin, fcc) |

The first change corresponds to the reaction where the intrinsic stacking faults accumulate in successive layers to form the extrinsic stacking fault. It was noted that the monotonic decrease in random fault density was not observed.

ICEC 5 (Fifth International Cryogenic Engineering Conference) on May 7-10, 1974, at Kyoto International Conference Hall

Heat Transfer from Horizontal Cylinder to Subcooled Liquid Helium

Hideo TSURUGA and Kazuo ENDOH

Experiments were made on the heat transfer in subcooled liquid helium I and II from a horizontal copper cylinder of 2.5 cm in diameter and 5 cm in length. The results for helium I indicated some difference between subcooled and saturated helium. The heat flux in subcooled helium was larger than that of saturated helium in the nucleate-boiling region. In the free-convection region, the heat flux of subcooled helium was smaller than that of saturated helium. In the experiments for helium II, it was found that the difference of heat transfer rate between subcooled and saturated helium did not appear significantly.

OSA/SPIE International Seminar on Image Assessment and Specification, Rochester, U.S.A., May 20-22, 1974

Two-dimensional Measurement of Optical Transfer Function by Holographic Techniques

Kazumi MURATA, Hirofumi FUJIWARA
and Ryuichi SATO*

Department of Applied Physics

A new method for measuring the optical transfer function of an optical system by means of holographic matched filtering was studied by the present authors. In this method, the modulus and phase of the transfer function can be obtained two-dimensionally. Compared with the traditional methods for measuring the optical transfer function, this holographic method is quite simple with regard to the construction of the apparatus and its operation. Since the matched filter is made by recording the complex conjugate of the pupil function of the optical system on the photographic plate, the nonlinear relation between the exposure and the amplitude transmittance has considerable influence on the results.

In the present paper, we have studied the nonlinear effect of the exposure vs amplitude transmittance curve of the photographic materials from its theoretical and

* Present address: Canon Inc., Tokyo.

experimental aspects and have attempted to lessen the nonlinear effect by modulating the pupil function by use of a Ronchi grating. Under certain conditions for the contrast of the grating the influence of the nonlinearity is reduced.

Furthermore, some techniques for practical applications of our method to the testing of optical systems are proposed.

OSA/SPIE International Seminar on
Image Assessment and Specification,
Rochester, U.S.A., May 20-22, 1974

Standard of Optical Transfer Function in Japan

Kazumi MURATA

Department of Applied Physics, Faculty of Engineering

and

Teruji OSE

Institute of Industrial Science, University of Tokyo

In order to set forth the standard of optical transfer function (OTF), it is necessary to confirm the accuracy of measured OTF and that of the calculated OTF.

Several new OTF measuring instruments have been constructed and are now in practical use. In order to check the accuracies of these instruments, three kinds of test lenses are produced as the standard lenses. The measuring processes using these standard lenses will be established in 1974 as the standard testing method.

Because the calculated OTF is regarded as a true OTF, whether the error depends on calculation methods or not has been checked by comparison tests of calculation methods. The results show that several problems exist in the case where the lenses have a large aperture or a large amount of aberrations. A new correction method has thus been developed.

The standard representation of OTF has already been adopted over a widerange. From a view point of practical lens assessment, however, this representation involves too many parameters. Thus, a simple representation, worthy of OTF standard, was discussed.

5th International Congress of Radiation Research (July 14-20, 1974, Seattle, U.S.A.)

Benzyl Radical Formed by Dissociative Electron Attachment in Ragid Matrices

Hiroshi YOSHIDA, Masaoiro IRIE
and Masaaki SHIMIZU

Benzyl radical was formed by electron attachment to benzyl derivatives such as benzyl chloride or their direct photolysis in several organic glasses. It was found by means of a fluorescence spectrophotometer that the electronic transitions of benzyl are different depending on the formation method, radiolysis or photolysis, in non-polar glass. This indicates an interaction between benzyl and the fragment anion such as Cl^- formed in the case of radiolysis as the counterpart. The adjacent anion causes red-shift of all spectra, broadening of the spectral lines, and the appearance of a new band. These features are not observed in polar glass. In soft non-polar glass, the effect of anions becomes increasingly lesser even at 77 K, until the spectra are identical with those of benzyl formed by photolysis. These results give an indication of the intermediate state of the dissociative electron attachment to the formation of benzyl in organic glasses.

Fifth International Congress of Radiation Research, Seattle, Washington, U.S.A. July 14-20, 1974

The Mechanism of Radiation-Induced Ionic Polymerization of Styrenes

Meiseki KATAYAMA and Sadashi SAWAMURA

The radiation-induced polymerization of styrene and α -methylstyrene has been studied by means of pulsed conductivity measurements and also by Hittorf type conductivity measurements. It is well known that in these compounds, the more thoroughly the monomers are dry, the larger the $G(-\text{monomer})$ becomes. The pulsed conductivity measurements for α -methylstyrene showed that when it is dry, the mobility of anionic species became smaller than that of cationic ones, indicating the relative importance of anionic polymerization under such conditions, although the relationship is reversed for moderately dry samples. The Hittorf type conductivity measurements also showed the importance of anionic polymerization under extremely dry conditions.

The conclusions from these measurements are as follows:

- (1) the anionic polymerization is at least as important as the cationic polymerization,
- (2) the main mechanism of termination for both anionic and cationic polymerizations

is the chain transfer to monomers since the number of chain transfers is estimated to be some ten thousands, and (3) the main charge carrying species are electrons which move freely in dry liquid styrenes.