Preprints of papers read at

The Fifth International Symposium on Free Radicals July 6 -7, 1961

Institute of Physical Chemistry,
University of Uppsala, Sweden

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PREFACE

The previous Symposia in this series were held each year from 1956 to 1959. The meetings were initiated by Prof. Giguère who arranged the First Symposium in Quebec City. The Second was held in Washington and the Third in Sheffield (as a Faraday Society Discussion). On the latter occasion an informal international committee considered the question of future meetings. The committee was then strongly in favour of a new meeting the following year in Washington to permit scientists to learn about the extensive programme on Free Radicals at the National Bureau of Standards which had been initiated in 1957 and should terminate in 1959. At the Fourth Symposium in Washington in September 1959, the informal international committee met again. The committee members were: A.M. Bass (U.S.A.), H.P. Broida (U.S.A.), S. Claesson (Sweden), P.A. Giguère (Canada), S. Leach (France), P. Le Goff (France), V.D.J. Mathot (Belgium), G. Porter (England), D.A. Ramsay (Canada), and G. Stein (Israel). The committee was again strongly in favour of a continuation of these meetings because of the rapidly growing interest in the field of free radical research, but it was felt that a two year interval between the meetings would be more appropriate. Different places for the next meeting were also considered and the committee felt that Uppsala would be a suitable place for a two day meeting in 1961.

As a consequence of these discussions, arrangements were made for the present meeting, "The Fifth International Symposium on Free Radicals".

It is a pleasure to thank all those who have contributed generously to make this meeting possible. Our thanks are primarily due to the Swedish Ministry of Education, which included the Symposium among the Government supported meetings in 1961/62. The U.S. Air Force, Office of Aerospace Research, and the U.S. Army have provided travel assistance for scientists not living close to Sweden. Without their generous support the meeting could not have become as truly international as it is.

This book contains both the plenary lectures and the submitted contributions. In order to have a very late deadline for the contributions it was decided to reproduce the manuscripts

exactly as they were sent in by the authors. Sincere thanks are due to all the authors who have collaborated so helpfully in this matter. However, the latest papers, which were submitted in the middle of June, could not have been included in this volume without the most generous co-operation from the printers, Messrs. Almqvist and Wiksells Boktryckeri AB.

There has been a widespread demand that at this meeting more attention should be paid to chemical problems. As seen from the content of this volume, this is the case, but has forced us to run the meeting in two parallel sections. Inconvenient as this is, it was nevertheless felt better to allow the participants to make their own choice of listening to the many excellent contributions, instead of having to refuse almost one half of the submitted papers. To save time, the work in progress at the Institute of Physical Chemistry will be presented at a tour of the laboratories in the evening of Thursday, July 6. A short description of the tour is therefore also included in this book.

In line with the established tradition, this meeting is planned more for work than pleasure, but even so, or perhaps rather, because of that, we hope that you will enjoy your stay in Uppsala.

Uppsala, June 21, 1961

Stig Claesson
Symposium Chairman

GENERAL INFORMATION

All lectures will be held in the Main University Building.

The official opening of the Symposium will take place on Thursday, July 6, at 9.00 in Room X. The Symposium is then run in two parallel sections, sessions A and B. The A sessions will be in Room X and the B sessions in Room IX.

The detailed programme is given on pages VIII to XV.

All contributions will be taken as read and the speaker will be allowed 10 minutes to point out the main features of his work, followed by 5 minutes discussion.

A conducted tour of the Institute of Physical Chemistry will start at 19.30 on Thursday, when most of the photochemical research and also part of the macromolecular work will be shown. Those who desire to look at a few specific instruments at more leisure, will be given the opportunity to do so on Saturday morning.

The Congress Bureau in the Entrance Hall of the Main University Building will be open as follows: July 5 between 12.00 and 22.00, and July 6 and 7 between 8.30 and 18.00. It also has banking and travel agency facilities, and will take care of telegrams.

Telephones are available in Room IV, ground floor.

Buses will convey the participants from the conducted tour of the Institute to an informal reception in the Linnéan Gardens 21.00 - 23.00 where light refreshments will be served.

The banquet at Uppsala Castle on Friday, July 7, will start at 19.00. Tickets may be obtained at the Congress Bureau

Luncheons on July 6 and 7 and dinner on July 6 will be served at "Galejan", S:t Larsgatan 7, at a moderate price.

Additional information may be obtained at the Congress Bureau.

PROGRAMME

Thursday, July 6, at 9.00, in Room X
OPENING OF THE SYMPOSIUM

Chairman: Dr. F.O. Rice, Georgetown University, Washington, D.C., U.S.A.

Dr. H.P. Broida, National Bureau of Standards, Washington, D.C., U.S.A.: Present status of free radical research, introductory remarks

Thursday, July 6, at 9.30, in Room X. Session A1.
LOW TEMPERATURE STABILIZATION OF FREE RADICALS

Chairman: Dr. A.M. Bass, National Bureau of Standards, Washington, D.C., U.S.A.

9.30 Plenary lecture by V.V. Voevodsky: Formation, stabilization and subsequent reactions of hydrogen atoms in solids and their importance in radiolysis (Plenary lecture A1)

10.15 Th. Baurer: The storage of energy in low-temperature condensates of excited gases (Paper No. 7)

10.30 G.B. Sergeev, V.S. Gourman, V.I. Papissova, and E.I. Yakovenko: Some principles governing free radical stabilization in condensed systems (Paper No. 63)

Chairman: Dr. P.A. Giguère, Laval University, Québec City, Canada

11.00 A.M. Pilon: Temperature effect in the phosphorescence of solid nitrogen (Paper No. 50)

11.15 G.J. King and F.F. Carlson: Production and trapping of N in sodium azide at low temperatures (Paper No. 32)

11.30 D.E. Mann and A.M. Bass: The absorption spectrum of CF_2 trapped in an argon matrix (Paper No. 40)

11.45 M.W. Windsor: Studies of trapped radicals at liquid helium temperatures by carbon resistance thermometry (Paper No. 73)

12.00 R.W. Nicholls: Spectroscopic study of luminosities produced in X-radiolysis of frozen simple gases at 4° K - 20° K. (No preprint)

Thursday, July 6, at 9.30, in Room IX. Session B1.
STUDIES OF FREE RADICALS TRAPPED IN MACROMOLECULAR SYSTEMS

Chairman: Dr. C.H. Bamford, Courtaulds Research Laboratory, Maidenhead, Berkshire, England

9.30 Plenary lecture by M. Szwarc: Studies on "cage" reactions. (Co-authors L. Herk and M. Feld) (Plenary lecture B1)

10.15 A. Ťkáč and Z. Frait: Zur Stabilisierung der bei erhöhter Temperatur in der festen Phase von Makromolekülen generierten freien Radikale (Paper No. 71)

10.30 T.T. Jones: The influence of medium rigidity on the termination of trapped polymeric radicals (Paper No. 27)

Chairman: Dr. A. Charlesby, Royal Military College of Science, Swindon, Wiltshire, England

11.00 R.B. Ingalls and L.A. Wall: ESR observations of the rates of formation and reaction of free radicals produced by hydrogen atom bombardment of polystyrene (Paper No. 25)

11.15 A. Kelen and W. Dick: On property changes in high polymers irradiated by low-energy electrons or exposed to electrical discharges (Paper No. 31)

11.30 E.L. Powers, B. Smaller, C.A. Tobias, and J. Lyman: Factors controlling radiation-induced free radicals in a biological system (Paper No. 54)

11.45 M. Sangster: A rapid freezing technique for the study of radical intermediates in the photosynthetic process (Paper No. 59)

X

Thursday, July 6, at 14.00, in Room X. Session A2.
FREE RADICAL REACTIONS AT LOW TEMPERATURES

Chairman: Dr. S. Leach, Laboratoire de Chimie-physique, Paris, France

14.00 Plenary lecture by H.A. McGee, Jr.: Trapped species and chemical synthesis at cryogenic temperatures (Plenary lecture A2)

14.45 V.J. DeCarlo and F.O. Rice: Reaction of atomic hydrogen with solids at -195° C (Paper No. 15)

15.00 R. Klein and M. Scheer: Cross dimerization in the hydrogen atom addition to mixtures of solid olefins at 77° K (Paper No. 34)

15.15 A. Thomas: Chemical reactions at very low temperatures A rotating cryostat for mixing reactants at 4.2° K (Paper No. 70)

15.30 G. Stein: Reactivity of atomic hydrogen in aqueous solutions (Paper No. 67)

Chairman: Dr. G. Stein, The Hebrew University, Jerusalem, Israel

16.00 B. Smaller and J. McMillan: Free radical species produced by radiation in H_2O and H_2O_2 (Paper No. 65)

16.15 H. Engelhard, G. Breuer, and F.-W. Froben: Reactions of H atoms and OH radicals in aqueous systems (Paper No. 17)

16.30 R.C. Smith and S.J. Wyard: Electron spin resonance of free radicals produced by irradiation of hydrogen peroxide-water solutions at 90° K (Paper No. 66)

16.45 J.M. Flournoy and S. Siegel: Radical formation and trapping in tritium-enriched ice (Paper No. 19)

17.00 C. MacKay and R. Wolfgang: Reactions of atomic carbon with simple hydrocarbons: Evidence for C-H bond insertion (Paper No. 39)

17.15 A. Ponomarev and V. Talrose: Interaction of gaseous atomic hydrogen with solid olefines at low temperatures (No preprint)

Thursday, July 6, at 14.00, in Room IX. Session B2.
SPECTROSCOPIC STUDIES ON FREE RADICALS

Chairman: Dr. P.S. Skell, The Pennsylvania State University, University Park, U.S.A.

14.00 Plenary lecture by D.A. Ramsay: The spectra of free radicals (Plenary lecture B2)

14.45 B.deB, Darwent, R.L. Wadlinger and R.P. Borkowski: The lifetimes of vibrationally excited species (Paper No. 14)

15.00 D.E. Milligan: Infrared spectroscopic study of intermediates in the photolysis of several azides (Paper No. 45)

15.15 L.J. Schoen: Spectra produced by electron bombardment of hydrocarbon-rare gas solids; a new transition of the C_2 molecule (Paper No. 61)

15.30 L.S. Nelson and N.A. Kuebler: Kinetic spectroscopy of free radicals produced by heterogeneous flash heating (Paper No. 47)

Chairman: Dr. M. Magat, Laboratoire de Chimie Physique de la Faculté des Sciences, Orsay (Seine-et-Oise) France

16.00 G. Dixon-Lewis and A. Williams: Methods for investigating free radical reactions in a hydrogen-oxygen flame in the region of 1000° K (Paper No. 16)

16.15 R.L. Strong: Transient charge-transfer complexes of halogen atoms in aromatic solutions (Paper No. 68)

16.30 D.B. Harrington: Experimental methods for studying free radicals using the time-of-flight mass spectrometer (Paper No. 24)

16.45 R. Pointeau and J. Favède: Etude des radicaux libres qui se forment au cours de la reduction cathodique des hydrocarbures cycliques (Paper No. 52)

17.00 H. Schüler: Entstehung von Biradikalen in der Glimmentladung (Paper No. 62)

17.15 H.P. Broida and L.J. Schoen: Double wall glass dewars for optical and other studies at liquid helium temperatures (Paper No. 10)

Friday, July 7, at 9.00, in Room X. Session A3.
E S R STUDIES ON FREE RADICALS

Chairman: Dr. V.V. Voevodsky, Institute of Chemical Physics, Academy of Sciences, Moscow, U.S.S.R.

9.00 Plenary lecture by C.K. Jen: A survey of E S R studies of radicals trapped at low temperatures (Plenary lecture A3)

9.45 F. Martinez, J.A. Wojtowicz, and J.A. Zaslowsky: The characterization of hydrogen superoxides in frozen matrices (Paper No. 42)

10.00 R.E. Florin, D.W. Brown, and L.A. Wall: Electron spin resonance studies of γ-irradiated small molecules at 4° K and 77° K (Paper No. 18)

10.15 E.L. Cochran and F.J. Adrian: E S R studies of radicals formed by secondary processes in photolytic systems at 4.2° K (Paper No. 12)

Chairman: Dr. V.D.J. Mathot, Centre d'Etude de l'énergie nucléaire, Mol-Donk, Belgium

10.45 Ya. S. Lebedev, V.K. Ermolayev, Yu. D. Tzvetkov, Yu.N. Molin, N.Ya. Buben, and V.V. Voevodsky: On the recombination of radicals in the condensed phase (Paper No. 37)

11.00 N.Ya. Buben, I.I. Chkheidze, A.T. Koritzky, Yu.N. Molin, V.N. Shamshev, and V.V. Voevodsky: E S R investigations on energy transfer in radiolysis of organic substances (Paper No. 46)

11.15 J.B. Farmer, D.A. Hutchinson, and C.A. McDowell: Electron spin resonance studies of nitrogen dioxide trapped in inert matrices at liquid helium temperature (Paper No. 44)

11.30 V.A. Bowers, E.L. Cochran, S.N. Foner and C.K. Jen: Spin resonance of alkali atoms in inert-gas matrices (Paper No. 26)

11.45 P.I. Abell and L.H. Piette: Low temperature EPR studies of free radicals in the ultraviolet catalyzed addition of HBr to olefins (Paper No. 1)

12.00 H. Fischer and K.-H. Hellwege: ESR-Untersuchungen an bestrahltem orientiertem Polypropylen (Paper No. 23)

Friday, July 7, at 9.00, in Room IX. Session B3.
PROPERTIES AND REACTIONS OF RADICALS PRODUCED BY HIGH ENERGY RADIATION

Chairman: Dr. M.S. Matheson, Argonne National Laboratory, Argonne, Ill.. U.S.A.

9.00 Plenary lecture by G.O. Schenck: Mehrzentren-Termination (Plenary lecture B3)

9.45 R.L. McCarthy and A. MacLachlan: Transient kinetics of free radicals produced by high energy radiation (Paper No. 43)

10.00 Ya.A. Zarifyanz, V.F. Kisselev, and G.G. Fedorov: Investigations on the adsorption of free radicals formed on solid surfaces by cleavage and by ionizing radiation (Paper No. 33)

10.15 V.I. Goldanskii: The action of unpaired electron on positron annihilation in the condensed phase (Paper No. 21)

Chairman: Dr. R.L. McCarthy, E.I. du Pont de Nemours and Co., Wilmington, Del., U.S.A.

10.45 Z.P. Zagórski: Free radicals in the chain reaction of γ-radiation induced reduction of oxygen (Paper No. 75)

11.00 A. Charlesby and M.G. Ormerod: Low temperature reactions of radicals in irradiated polymers (Paper No. 11)

11.15 A. Orszagh, H. Czarnodola, Z. Górska, and J. Zurakowska-Orszagh: Influence du rayonnement γ sur les polyesters aliphatiques (Paper No. 49)

11.30 G. Löfroth, L. Ehrenberg, and A. Ehrenberg: Radiation induced free radicals in carbohydrates and an estimation of their concentration (Paper No. 38)

11.45 D.S. Ballantine and Y. Shinohara: A study of the free radicals in irradiated nylon (Paper No. 5)

12.00 F.S. Rowland: Free radicals formed in gaseous and condensed phases by reactions of high kinetic energy tritium atoms (No preprint)

Friday, July 7, at 14.00, in Room X. Session A4.
E S R STUDIES ON FREE RADICALS

Chairman: Dr. C.A. McDowell, University of British Columbia, Vancouver, B.C., Canada

14.00 Plenary lecture by D.H. Whiffen: Electron spin resonance studies on the geometry of trapped radicals (Plenary lecture A4)

14.45 R.S. Anderson and Th.S. Jaseja: Electron resonance examination of trapped radicals resulting from radiation damage to organic single crystals: urea compounds (Paper No. 2)

15.00 C.H. Bamford and J.C. Ward: The properties of radicals produced in organic crystals by the high-frequency discharge (Paper No. 6)

15.15 H.C. Box, H.G. Freund, and K. Lilga: Paramagnetic resonance line widths in some irradiated organic crystals (Paper No. 9)

15.30 J. Cunningham: Radical species detected in γ-irradiated nitrate crystals by E.P.R. and U-V spectral studies (Paper No. 13)

Chairman: Dr. R. Klein, Melpar Inc., Falls Church, Va., U.S.A.

16.00 M. Fujimoto: Electron spin resonance studies of radicals formed by X-irradiation of α-amino isobutyric acid (Paper No. 20)

16.15 H. Kallmann, N. Wotherspoon, and J. Gallagher: Paramagnetic resonance of trapped electrons in zinc sulfide phosphors (Paper No. 28)

16.30 H. Kallmann, W. Riedel, and N. Wotherspoon: High energy induced free radical formation in benzene-carbon tetrachloride mixtures (Paper No. 29)

16.45 J.A. Weil: Electron spin resonance of stable organic free radicals: The dissociation of hexaphenyl-ethane (Paper No. 72)

17.00 J. Zanchetta, A. Marchand, and A. Pacault: Technique d'etude des radicaux libres dans les carbones pré-graphitiques: Choix d'un etalon en resonance paramagnetique electronique - conditionnement des echantillons pulverulents (Paper No. 76)

17.15 P.B. Ayscough, K.J. Ivin, J.M. O'Donnell, and C. Thomson: Reactions in γ-irradiated alkyl halides and sulphones (Paper No. 4)

Friday, July 7, at 14,00, in Room IX. Session B4.
PHOTOCHEMICAL STUDIES ON FREE RADICALS

Chairman: Dr. V.N. Kondratiev, Institute of Chemical Physics, Academy of Sciences, Moscow, U.S.S.R.

14.00 Plenary lecture by G. Porter: Benzyl, anilino, phenoxyl and related free radicals (Co-author E.J. Land) (Plenary lecture B4)

14.45 H. Berg: Radikalbestimmung durch photopolarographie (Paper No. 8)

15.00 Z.R. Grabowski and M.K. Kalinowski: Electrochemical study of free ketyl radicals (Paper No. 22)

15.15 J.N. Pitts, Jr., Th. Kuwana, and A. Marchetti: Photochemical and electrochemical studies of organic free radicals I. Photopotentials in ketone-alcohol systems (Paper No. 51)

15.30 S. Leach and L. Grajcar: The photolysis of toluene, dibenzyl and benzyl chloride in rigid media: Studies by absorption and luminescence spectroscopy (Paper No. 36)

Chairman: Dr. H. Schüler, Forschungsstelle für Spektroskopie in der Max-Planck-Gesellschaft, Göttingen, Germany

16.00 J.P. Simons and A.J. Yarwood: The decomposition of hot radicals (Paper No. 64)

16.15 F. Ramirez, N. McKelvie, and N.B. Desai: The phosphoranyl free radical $/R_3\dot{P}X/$ (Paper No. 57)

16.30 R.E. Rebbert and P. Ausloos: Photochemical decomposition of organic compounds in the solid state (Paper No. 3)

16.45 J. Wojtczak: Process of blackening of photosensitive cuprous compounds in the medium of some gels (Paper No. 74)

17.00 R.J. Marcus: A source of concentrated free radicals in the liquid phase (no preprint)

17.15 J. Kasarnowsky: A new chemical source of free hydroxyl radicals (No preprint)

PRESENT WORK AT THE INSTITUTE OF PHYSICAL CHEMISTRY, UNIVERSITY OF UPPSALA, UPPSALA, SWEDEN

The activities at the Institute can be grouped into two main fields, macromolecular physical chemistry and photochemistry. The macromolecular research originated with the development of the ultracentrifuge by The Svedberg, the first head of the Institute, and has since been continued and developed. During the last decade, a considerable amount of work in photochemistry has also been done. Much work has been carried out on the photochemistry of macromolecular systems using conventional techniques, but at present most of the photochemical studies is done by flash photolysis. The Institute has now some of the most powerful and fastest flash sources in the world. The studies on pyrolysis are closely connected with the photochemical work.

In the following presentation, which serves as an introduction to the tour of the Institute, on the evening of Thursday, July 6, the emphasis is on the photochemical and pyrolysis equipment, including some of the advanced analytical tools used (a highly sensitive gas chromatograph, and a time-of-flight mass-spectrometer). Some of the instruments on the macromolecular side are also included, as well as a section on the mechanical workshop, where most of the equipment has been built.

A plan of the Chemistry Institutes in Uppsala is given in Fig. 1.

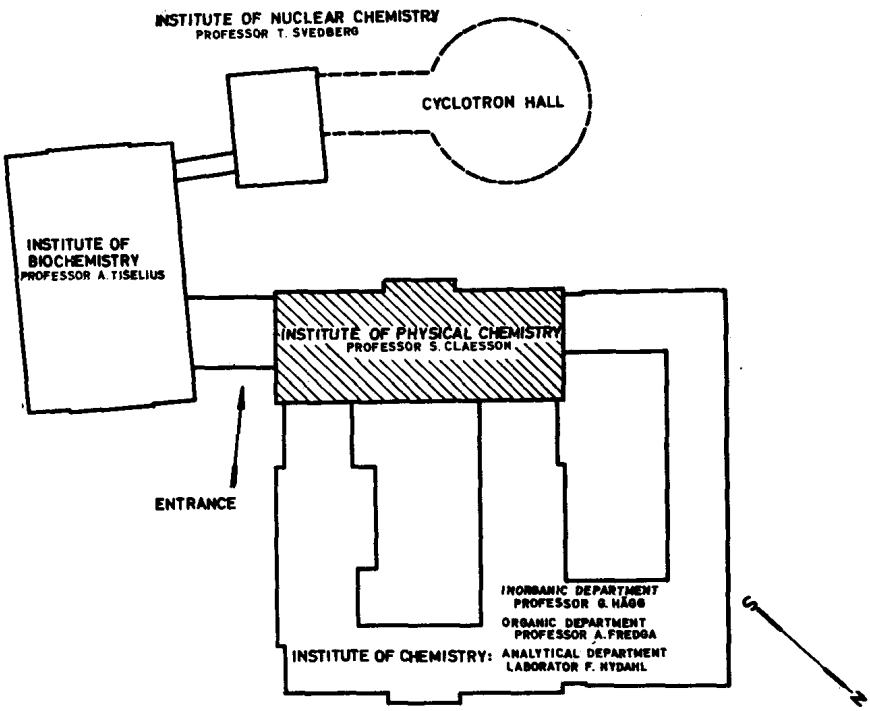

Fig. 1. Plan of the Chemistry Institutes in Uppsala

A. Photochemistry and Pyrolysis

Flash Apparatus I

Flash apparatus I was built during the years 1953-56 (1). In the present version, the condensor bank (max. 1400 μF, 7 kV) is mounted in two symmetrical halves, where one half is charged to a positive and the other half to a negative potential. The condensors (AB Liljeholmens Kabelfabrik, Stockholm) are discharged through two straight quartz lamps of 60 cm length, placed on each side of the reaction vessel. The lamps are fitted with tungsten electrodes and oxygen-filled to a pressure of 20-40 mm Hg. At maximum energy, absorbed intensities of about 500 Einstein/litre sec are obtained with a flash duration of 150 μsec.

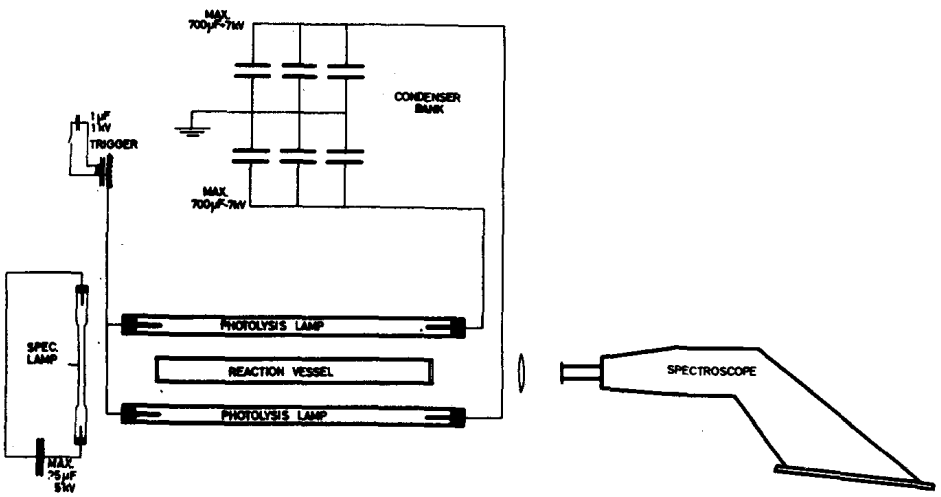

Fig. 2. Schematic diagram of Apparatus I (max. 1400 μF, 7 kV), when used for flash spectrography

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(1) S. Claesson and L. Lindqvist, Arkiv Kemi 11, 535 (1957)

The reactions taking place in the reaction vessel after the flash are followed by the two usual techniques, flash spectroscopy (depicted in Fig. 2, using a Hilger Medium Quartz or the corresponding glass instrument), and kinetic spectrometry (using an Osram XBO 300 xenon arc lamp, a Zeiss MM 12 monochromator, EMI or DuMont end-on type photomultipliers, and a Tektronix 535 oscilloscope).

Apparatus I has been employed for a great variety of problems especially for studies on the intermediate photoproducts of dyes. Thorough studies have been made on chlorophyll and the determination of its triplet spectrum and the decay reactions of the triplet (2). Similar studies have also been made on fluorescein, revealing the existence of two new metastable species, in addition to the triplet, viz. a semi-reduced and a semi-oxidized form of fluorescein (3).

Flash Apparatus II

To obtain higher intensities than those employed in apparatus I, it is desirable to decrease the flash time while retaining a rather high capacity C. As the flash time is proportional to $\sqrt{LC}$, this means that the inductance L of the circuit has to be decreased as much as possible; apparatus II was constructed with this in mind (4). The twelve condensors, each of 12 μF (giving 7200 J at 10 kV) have been specially designed by AB Liljeholmens Kabelfabrik, Stockholm, to have a low inductance. In order to make the circuit as coaxial as possible, the condensors are mounted approximately in a circle on a vertical copper plate, which also serves as the earth plate (Fig. 3). The lamp is placed at the centre of this circle, and has a new coaxial design. The discharge takes place in the annular compartment between two concentric tubes, with an outer metal tube serving as the return lead. The reaction vessel is placed inside the transparent silica inner tube, where it is efficiently illuminated. The outer tube, where the shock from the discharge is most severe, is made of sintered silica and reinforced with a bakelite tube. The total inductance of this apparatus is

(2) S. Claesson, L. Lindqvist and B. Holmström, Nature 183, 661 (1959)

(3) L. Lindqvist, Arkiv Kemi 16, 79 (1960)

(4) S. Claesson and L. Lindqvist, Arkiv Kemi 12, 1 (1957)

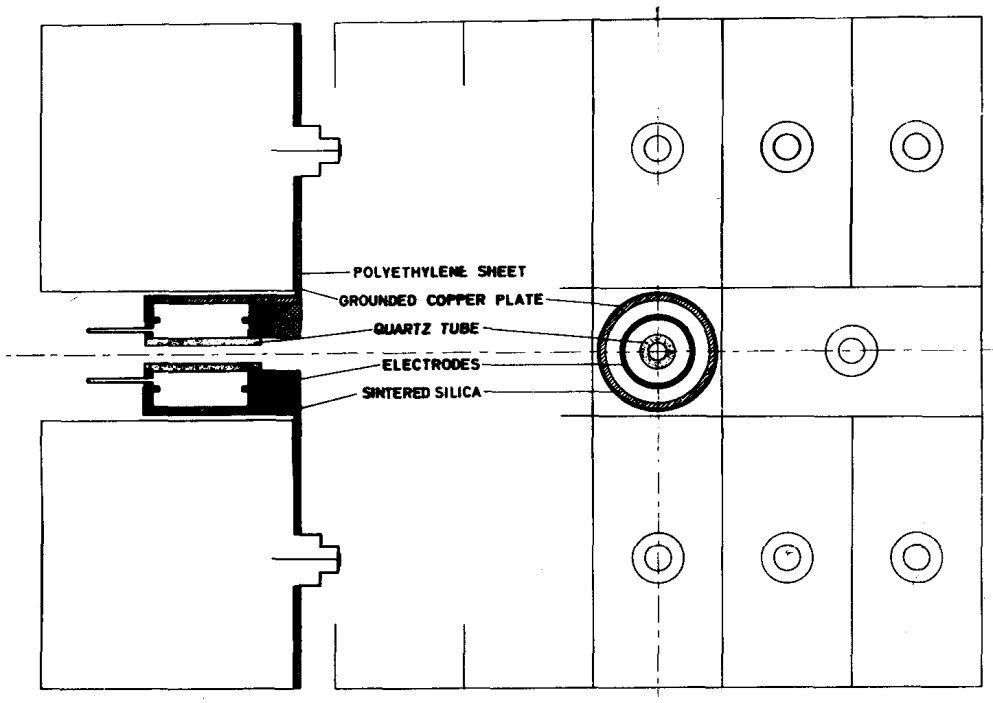

Fig. 3. Schematic diagram of Apparatus II (max. 144 μF, 10 kV). The condensors are mounted around a coaxial lamp, which gives a low inductance to the discharge circuit (0.006 μH).

about 0.006 μH. The discharge time is proportional to the energy used and varies from 5 to 25 μsec.

With this apparatus, the number of quanta emitted from one flash causes enough photochemical change in a system to make possible the quantitative analysis of the stable products formed. Such studies, where the stable products formed from a single flash are being quantitatively measured, have now proceeded at the Institute for several years and have yielded information, for example about the decomposition reactions of simple organic molecules and the reactions between the radicals formed. The results from photolysis of acetone and some aliphatic aldehydes have recently been published (5).

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(5) G. Wettermark, Arkiv Kemi 18, 1 (1961)