Meetings

Transient Free Radicals

In the environs of one of the world's oldest universities, the 7th International Symposium on Free Radicals was held 5 to 10 September 1965 at the University of Padua (founded in 1222). A large part of the six-session program, which was organized by G. Giacometti (Padua), was devoted to discussion of transient free radicals. The symposium was opened by the Magnifico Rettore of the University, Guido Ferri. After a greeting by G. Semerano (Bologna), president of the symposium, G. Porter (Sheffield) gave the keynote address on the aims, techniques, and difficulties of studies involving free radicals.

At the first session, on the quantum theory of open-shell molecular states, M. Simonetta (Milan) reviewed the theory by summarizing the several methods of computing approximate wave functions for molecular radicals and excited states. J. Serré (Paris) described her work with G. Berthier (l'Ecole Normale Supérieure, Paris) in which they used Löwdin orthogonalized atomic orbitals to compute spin densities for the vinyl radical. S. Fraga (Alberta) continued by giving a schematic development of the self-consistent-field (SCF) formalism. F. Gerson (Technische Hochschule, Zurich) introduced his well-resolved electron-spin-resonance (ESR) spectra for radical anions and radical cations of several nonalternant hydrocarbons. He showed that Huckel pi-electron spin densities give a satisfactory semiquantitative explanation of the spectra. L. C. Snyder (Bell Laboratories) summarized his work with T. Amos (Nottingham) on the computation spin densities for alternant hydrocarbon pi radicals from unrestricted Hartree-Fock wave functions after annihilation of higher spin multiplets. He noted that annihilation is very nearly equivalent to projection in these cases. G. Giacometti (Padua) showed that the unrestricted Hartree-Fock wave functions for pi-electron radicals have the usual simple relation to proton hyperfine splittings, if one uses a corrected definition of the pi-electron spin density for the unprojected determinant with the usual definition of spin density. M. Rossi (Padua) proposed that LCAO–MO (linear combination of atomic orbital–molecular orbitals) wave functions of minimum energy be found by iterative two-by-two rotations of the molecular orbitals. He applied this new method to obtain spin densities for the benzyl radical.

V. Voevodsky (Novosibirsk) introduced the session on the detection of gas-phase free radicals, emphasizing the present importance and, even more, the future promise of ESR methods. Most of the remaining papers were concerned with recent advances in technique toward the resolution of shorter time intervals. C. W. Hand and R. M. Hexter (Mellon Institute) described an infrared spectrometer capable of 10,000 scans per second. The rapid-scan infrared spectrometer of K. C. Herr and G. C. Pimentel (Berkeley) can detect CF_3 in the gas phase.

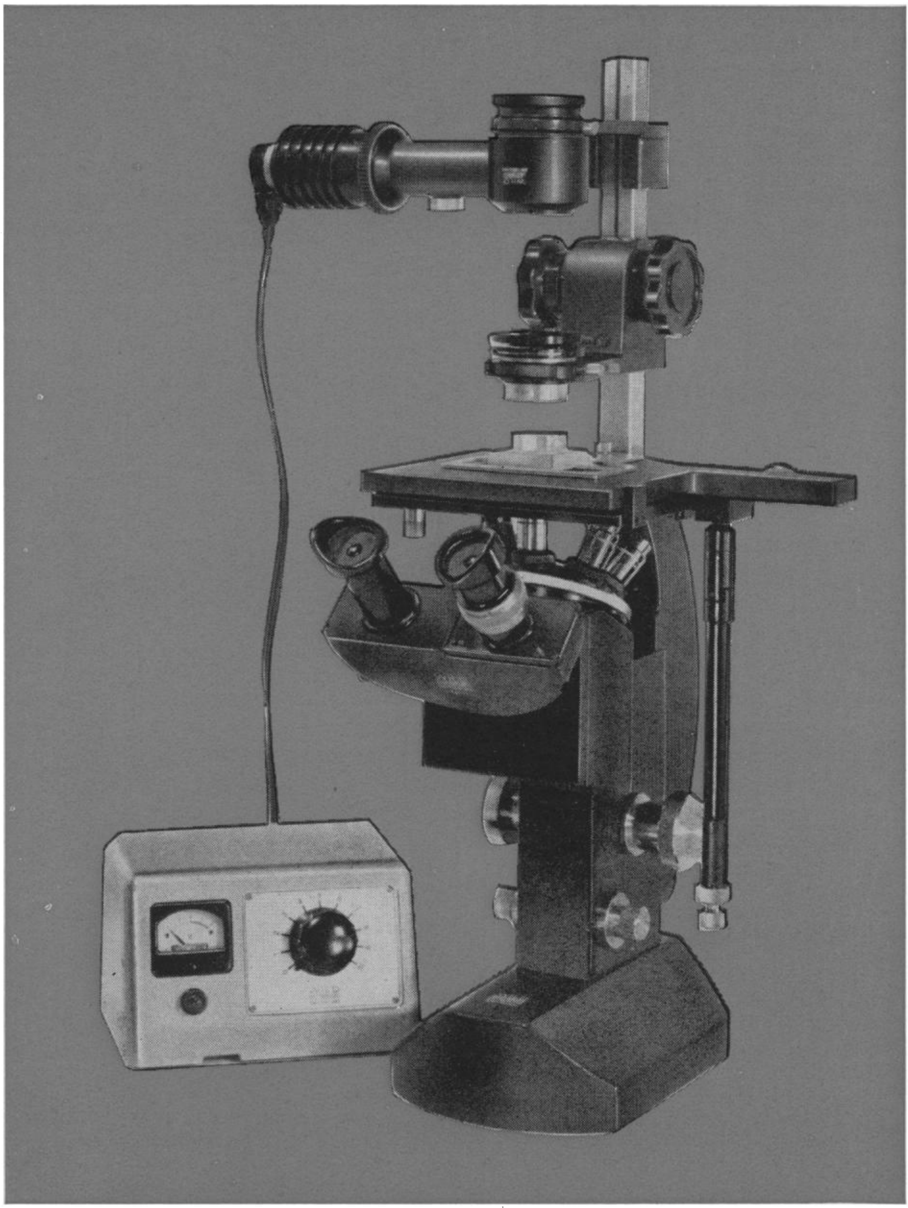
D. R. Lide and F. X. Powell (National Bureau of Standards) have examined the microwave spectra of gaseous SO and OH in a cell coated to retard recombination of the radicals. R. C. Smith (Southampton) described an ESR spectrometer capable of recording the spectra of photolytic free radicals with lifetimes of 5 μsec. P. Goldfinger and G. Huybrechts (Brussels) discussed the oxygen effect in the photochlorinations of ethane and trichloroethylene, which allowed them to determine the rate constants for the reaction of C_2H_5 and C_2HCl_4 with oxygen. Z. R. Grabowski (Warsaw) described an ultraviolet and visible spectrometer capable of a scan within 100 μsec. R. Marx (Orsay) has used a beam of low-energy electrons to produce radicals in the gas phase, which are then trapped on a cold finger for ESR examination.

F. Lossing (Ottawa) opened the session on mass spectrometry of free radicals with a general review. P. LeGoff, A. Cassuto, and A. Pentenero (Nancy) considered the choice of optimum conditions for measuring a reaction rate with the greatest precision and for obtaining the highest concentration of free radicals in a mass spectrometer. S. N. Foner and R. L. Hudson (Applied Physics Laboratory, Silver Spring, Maryland) have determined the ionization potential of methylene by mass spectrometry and obtained a value in agreement with the "vacuum-ultraviolet" result. G. G. Volpi and F. Zocchi (Rome), investigating the reaction of ethylene and hydrogen, found that at low pressures the ethyl radicals react with hydrogen atoms to form ethylene and molecular hydrogen, while at high pressures the radicals are stabilized and can yield methyl radicals on further reaction with atomic hydrogen. B. Pascat, J. M. Berthou, and H. Guenebaut (Rheims) have assigned the visible emission band in the atomic flame of PH_3 to PH_2. S. Leach, M. Horani, and J. Rostas (Orsay) have observed emission spectra from CS_2, CSO, and H_2S on excitation by a crossed beam of slow electrons. D. A. Ramsay (National Research Council, Ottawa) has observed the allyl and vinoxy radicals in absorption in the near-ultraviolet under high resolution.

The fourth session dealt with the use of far-ultraviolet photochemistry in free radical studies. J. R. McNesby (National Bureau of Standards) reviewed the photochemistry of simple hydrocarbons and the photolysis of nitric oxide. The flash photolysis of methane (with light of wavelength greater than 1100 Å) yielded ethane as the major product indicating that, as expected under flash conditions, radical-radical reactions are involved. The isothermal flash photolysis of CSe_2 was discussed by A. B. Callear (Cambridge). Atomic selenium is produced in the ($4^3P_{2,1,0}$) states, and its rate of addition to olefins was measured. Differences in reactivity of the olefins were shown to correlate with ionization potential. S. Leach (Paris) photolyzed methanol vapor with irradiation at 1850 and 1236 Å. The products were accounted for by primary processes: (i) $CH_2O + H_2$; (ii) $CH_3O + H$; (iii) $CH_2OH + H$; and (iv) $CH_3 + OH$. A. Terenin (Leningrad) presented the photoionization and disruption patterns of a variety of organic molecules irradiated with ultraviolet light while in a vacuum. By means of deuterated compounds it was shown that, in these ionization-photolysis processes, the stronger bond is frequently broken instead of the weaker ones.

The fifth session began with a talk by J. Baxendale (United Kingdom) who outlined the development of the idea of the solvated electron. S. Gordon (Argonne) continued with a description of his optical studies of transients formed in the pulsed radiolysis of aqueous solutions of phthalate ions. He obtained a second-order rate constant for the reaction of a hydrated electron with *p*-phthalate ion to form the transient. J. Simons (Birmingham), in discussing the formation of color centers by trapping electrons on polyhaloalkanes in rigid organic glasses, concluded that this light-induced process does not necessarily require the addition of an efficient electron donor. J. Bennett described his work with B. Mile and A. Thomas (all of Shell Research, Chester, England); they obtained optical and ESR spectra of solvated electrons produced by the deposition of potassium atoms on ice and solid alcohols in a rotating cryostat. They postulated mechanisms for the transformations which occur when these samples are warmed. D. Smith (Chalk River, Canada) described the results of ESR studies with a "dual" cavity (TE_{104}) which permits measurements of ESR difference spectra and thus microwave saturation properties of the solvated electron. A. Maclachlan (DuPont, Wilmington) discussed his use of pulse radiolysis to form peroxy radicals, which are then studied by transient spectroscopy during their interaction with inhibitors. Short contributions were also made by M. Haissinsky (Institute du Radium, Paris) and by M. Donodetti.

The sixth and last session of the symposium was concerned with diradicals, triplet, and unstable singlet molecules. There was some brisk discussion, moderated by the chairman, J. van der Waals (Royal Dutch Shell, Amsterdam). P. S. Skell (Pennsylvania State University) reviewed the chemical criteria for distinguishing singlet and triplet methylene molecules; he applied these criteria to a variety of novel reactions involving carbon atoms and C_3 molecules. R. Wolfgang (Yale University) also described some reactions of free carbon atoms produced in the form of C^{11} by the nuclear-recoil technique. With hydrocarbons two major mechanisms were established: (i) insertion into the C-H bond



and (ii) addition to a double bond. A. M. Trozzolo, E. Wasserman, and W. A. Yager (Bell Laboratories) had applied electron spin resonance to the study of the structure and isomerism of ground-state triplet methylenes. Geometric isomerism was detected in the naphthylmethylenes. Studies of methylenes by electron absorption spectroscopy were presented also. J. W. Johns (National Research Council, Ottawa) observed the methylenes HFC and HCCl, obtained in the flash photolysis of dibromofluoromethane and dibromochloromethane. G. L. Closs (Universtiy of Chicago) had studied the electron absorption spectrum of diphenylmethylene oriented in single crystals of diphenylethylene. By an elegant combination with ESR results, it was possible to obtain the polarized spectrum. Narrow-line vibrational structure also was observed. Evidence for the formation of carbenes in the reaction of hydrogen atoms with polyhalomethanes was given by J. M. Tedder (St. Andrews). A vibrationally excited polyhalomethane was postulated as an intermediate that undergoes unimolecular decomposition to yield the dihalocarbene and hydrogen halide.

Other contributions to the discussion included descriptions of studies of bisnitroxides, thermochromic molecules, reactions of carbon suboxide, sulfur monoxide, and production of triplet states by pulse radiolysis.

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Forthcoming Events

December

1–2. **UNESCO**, 75th executive board session, Paris, France. (Pl. de Fontenoy, Paris 7)

1–3. **Medicine and Sociology**, intern. symp., East Berlin, Germany. (K. Winter, Hygiene-Institut Humboldt-Universität, Otto-Grotewohl-str. 1, 108 Berlin, East Germany)

1–8. **Heads of National Research Insts.**, mtg., Bangkok, Thailand. (U.N. Economic Commission for Asia and the Far East, Sala Santitham, Rajadamnern Ave., Bangkok)

2. American **Industrial Hygiene** Assoc., mtg., Metropolitan New York, New Jersey, Delaware sections, Sterling Forest, N.Y. (O. M. Banks, Shell Chemical Co., 110 W. 51 St., New York 10020)

2–3. Perspectives in **Leukemia**, symp., New Orleans, La. (W. Dameshek, Leukemia Society, 211 E. 43 St., New York 10017)

2–3. **Nuclear Power Stations Operation**, conf., Bern, Switzerland. (Swiss Assoc. for Atomic Energy, P.O. Box 2613, 3001 Bern)

3–4. **Space Flight**, conf., Bremen, Germany. (Secretariat, Hermann Oberth Soc., Fritz-Beindorff-allee 9, 3000 Hanover, West Germany)

3–8. American Acad. of **Dermatology and Syphilology**, 25th annual mtg., Miami Beach, Fla. (The Academy, 636 Church St., Evanston, Ill.)

3–11. **Aviation and Aerospace**, intern. exposition, New York, N.Y. (F. S. Doman, Aviation and Aerospace Exposition, Inc., 500 Fifth Ave., New York 10036)

4–7. American Inst. of **Chemical Engineers**, 59th annual mtg., Detroit, Mich. (E. B. Chriswell, California Research Corp., Room 807, 200 Bush St., San Francisco, Calif.)

4–8. American Inst. of **Chemical Engineers**, 59th annual mtg., Detroit, Mich. (R. E. Greenhaigh, Dow Corning Corp., Midland, Mich.)

5–7. **Antennas and Propagation**, intern. symp., Palo Alto, Calif. (R. L. Deadabrand, Radio Physics Laboratory, Stanford Research Inst., Menlo Park, Calif.)

7. **American Institute of the City of New York**, mtg., New York. (Mrs. G. E. Peterson, American Institute of the City of New York, 2 E. 63 St., New York 10021)

5–7. Theory and Application of **Gas**