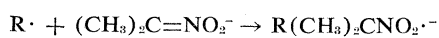
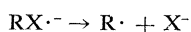


Free Radicals in the Liquid Phase: Structure and Reactivity

Free radical chemistry is rapidly expanding in a diverse manner. Electron spin resonance (ESR) in solution and the solid state, chemically induced spin selection, nuclear resonance of paramagnetic species, the triplet state, reaction of caged radicals, electron transfer, and chemiluminescence phenomena in both organic and inorganic systems are areas of intensive investigation as well as the study of classical free radical processes from a kinetic, thermodynamic, or synthetic point of view. From 31 August to 6 September 1970, a seminar on structure and reactivity of free radicals in the liquid phase was held at Hakone, Japan, under the sponsorship of the Japan Society for the Promotion of Science and the National Science Foundation. J. K. Kochi (University of Indiana) collaborating with P. Krusic (Central Research, E. I. DuPont de Nemours) discussed developments in the photochemical generation of alkyl radicals and their detection in solution by ESR. He demonstrated how ESR provides information on the conformational structure of species such as the cyclopropylcarbinyl radical (bisected conformation), the 7-bicyclo[2.2.1]heptyl radical (nonplanar), the *n*-propyl radical (nonequivalence of α -hydrogen atoms at low temperature), the *n*-butyl radical (nonequivalence of β -hydrogen atoms at low temperatures), and the β -mercaptoethyl radicals wherein an interaction between C-1 and the S atom favors a thiacyclopentane-like conformation. Such interactions are not seen for beta nitrogen or oxygen substituents.

Reagents for trapping free radicals were discussed. G. A. Russell (Iowa State University) described the intervention of a free radical chain reaction involving radical ions in a number of aliphatic substitution processes of aliphatic nitro compounds. A key step in this process involves the facile trapping of $R\cdot$ by the nitroalkane anion.



$RX =$ 2-chloro-2-nitropropane
2,2-dinitropropane
2-cyano-2-nitropropane
diethyl α -nitromalonate

F. Minisci (University of Parma) described the addition of radicals to protonated azabenzenes to yield radical cations of the dihydropyridinium type. G. Tsuchihashi (Sagami Chemical Research Center) demonstrated efficient trapping of radicals by thiobenzophenone. The $n-\pi^*$ photoexcitation of thiobenzophenone yields a species that is readily trapped (reversibly) by a variety of olefins. N. Inamoto (University of Tokyo) described the trapping of radicals by nitrones and nitrosobenzene. E. G. Janzen (University of Georgia) demonstrated the use of nitrones to trap highly reactive radicals and form a spin label easily detected by ESR spectroscopy. Both organic and inorganic [such as $(C_6H_5)_3Sn\cdot$] species can be trapped by this technique which is particularly easily adapted to studying the effects of radiation in the solid, liquid, or gas phase. The ESR work of Kochi supports a pyramidal structure for silyl radicals. The work of H. Sakurai (Tohoku University) supports this concept in that substitution reactions of an optically active naphthylphenylmethylsilane occur with retention of configuration. Cyclizations ($Ar_{2,7}$) or aryl migration processes were demonstrated by Sakurai for δ -aryltrialkylsilyl radicals. In the long kinetic chain reaction between trialkylsilanes and alkyl halides, described by Y. Nagai (Gunma University), alkyl bromides and chloride are much more reactive than alkyl iodides, and the benzyl halides are less reactive than the simple alkyl halides. Evidence was presented that the silyl radical is a slightly nucleophilic species. T. Migita (Gunma University) presented evidence that carbon-hydrogen bonds *alpha* to a tetravalent silicon atom had a reactivity toward free radicals similar to their carbon analogs.

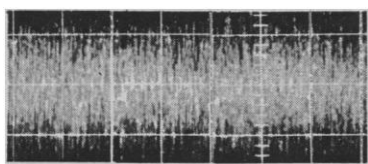
Electron transfer between anions (donors) and nitro compounds (acceptors) was demonstrated, by Russell, for a number of systems, for example, between *p*-nitrobenzyltrimethylsulfonium salts and its conjugate anion. R. Konaka (Shionogi Research Laboratory) demonstrated the use of this technique to spin label the nitro derivatives of a variety of benzobicyclo[2.2.1]heptane and benzo[2.2.2]octene derivatives. S. Nishida (Osaka University) demon-

strated electron transfer in the reaction between tetracyanoethylene (TCE) and tetracyclopentylethylene in which the TCE causes ring enlargement of one of the cyclopropyl group.

Solvation effects and ion pairing phenomena are easily investigated with paramagnetic ions (radical ions). K. Maruyama (Kyoto University) discussed results with the ketyls from aromatic ketones. K. Kuwata (Osaka University) discussed ion pairing in *o*-semiquinones, and showed that initial ESR signals in $Ti^{(IV)}$ -hydrogen peroxide reaction were complexes involving the $HOO\cdot$ radical and $Ti^{(IV)}$ species.

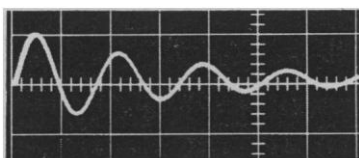
The stereochemistry of radical reaction was discussed by O. Simamura (University of Tokyo) and M. Poutsma (Union Carbide Research Laboratory). Simamura demonstrated that the 7-methylbenzo-7-norbornenyl radical is a pyramidal radical and can be trapped by oxygen before *cis-trans* isomerization is complete. This result was confirmed by the direct observation of the 7-norbornenyl radical (ESR) by Kochi. Evidence was presented that *cis*- and *trans*-1-phenylvinyl radicals had independent existence. Poutsma discussed the directive effects in homolytic addition reaction of vinylacetylenes. Initial radical attack usually occurs on the vinyl group (exception for tributylstannyl radical) to yield a propargyl radical which can yield either an acetylenic or allenic product. Propargyl radicals usually react to preserve the triple bond, but exceptions are known, such as thiophenol addition. Results emphasizing the bent character of allyl or allenecarbinyl ($C=C=C\cdot$) radical were presented. It was concluded that propargyl (linear) and allenecarbinyl (bent) resonance energies were similar.

The chemistry and magnetic resonance spectroscopy of the triplet state were discussed by G. Closs (University of Chicago), A. Rassat (Centre d'Etude Nucléaires de Grenoble), and I. Moritani (Osaka University). Closs described chemically induced spin selection arising from singlet-triplet intersystem crossing of radical pairs generated by photochemical or thermal processes. He deduced that, during the life of the diphenylmethylbenzyl caged radical pair of 2×10^{-10} second, 1 percent



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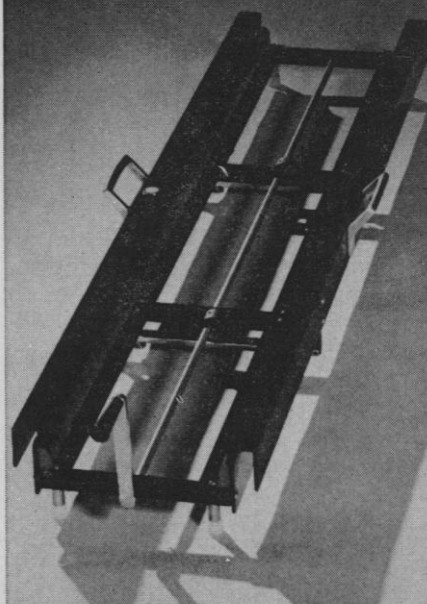
crossover from singlet to triplet state had occurred. This leads to a spin correlation time in this system of $\sim 10^{-8}$ second. A. Rassat discussed the ESR spectrum of bis-nitroxides in which the singlet-triplet energy separation varied between the extremes of much less and much greater than the electron-nuclear (nitrogen) hyperfine interaction. When the dipolar electron-electron coupling is small, solution ESR spectra can be observed for those molecules with population in the triplet state. In the solid state, measurement of the D and E dipolar splittings can be used to assign molecular geometry to the bis-nitroxide or to a diketone precursor. I. Moritani, head of the Japanese participants, described the stereospecific *cis* addition of di- or tri-benzocycloheptatrienylcarbene to the 2-butenes. Evidence was presented that the carbene existed in the triplet state. It was concluded that a stereospecific *cis* addition is not a diagnostic evidence for the ground state structure of a carbene. Closs emphasized that the rate of singlet-triplet intersystem crossing and the relative rates of singlet and triplet addition to the double bond must be considered carefully.

The decomposition of acyl and aroyl peroxide was considered by J. C. Martin (University of Illinois), K. Tokumaru (University of Tokyo), and M. Kobayashi (Tokyo Metropolitan University). Martin showed by ^{18}O labeling that the thermal decomposition of acetyl peroxide involves a caged pair of radicals in which statistical scrambling of the oxygen atoms occurs. Concerted 1,3 or 3,3 sigma-tropic rearrangements were excluded unequivocally. Tokumaru demonstrated that benzophenone-sensitized photodecomposition of benzoyl peroxide gave a triplet caged radical pair which diffused apart with $k_d \sim 10^{10} \text{ sec}^{-1}$. Since the lifetime of the cage is much less than the time needed for spin correlation ($k \sim 10^8 \text{ sec}^{-1}$), and since chemical reaction (bond breaking or formation) cannot occur with a change in multiplicity (singlet \rightleftharpoons triplet), geminate cage recombination to give phenyl benzoate is eliminated. Kobayashi discussed aromatic phenylation with the phenyl radical generated from a variety of sources including benzoyl peroxide, *N*-nitrosoacetanilide, phenyldiazonium hydroxide and tosylate, phenylazotriphenylmethane, and the novel system of phenyldiazonium salt plus sodium nitrite in dimethyl sulfide solution at 20°C. The reaction

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may proceed via the diazonium nitrite, $C_6H_5N=NONO$.

Photochemical generation of radicals from hydrated vicinal triketones was discussed by Y. Otsuji (Osaka Prefectural University). Alloxan or triketo dihydrophenalene gave products suggestive of loss of the hydroxy radical from the photoexcited state.

G. A. RUSSELL

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Forthcoming Events

October

1-2. Wisconsin Acad. of Sciences, Arts and Letters, Baraboo. (J. R. Batt, 5001 University Ave., Madison, Wis.)

1-5. American College of Apothecaries, Baltimore, Md. (R. A. Benedict, ACA, 7758 Wisconsin Ave., Washington, D.C. 20014)

3-6. American Ceramic Soc., Electronics Div., Kiamesha Lake, N.Y. (L. C. Hoffman, E. I. du Pont de Nemours & Co., Inc., Bldg. 336, Experimental Sta., Wilmington, Del. 19898)

3-6. American Oil Chemists' Soc., Atlantic City, N.J. (J. C. Lyon, 508 S. 6 St., Champaign, Ill. 61820)

3-8. Electrochemical Soc., Cleveland, Ohio. (E. G. Enck, ES, P.O. Box 2071, Princeton, N.J. 08540)

3-8. Water Pollution Control Federation, 44th annual, San Francisco, Calif. (WPCF, 3900 Wisconsin Ave., Washington, D.C. 20016)

4-6. Turbulence in Liquids, Rolla, Mo. (G. K. Patterson, Dept. of Chemical Engineering, Univ. of Missouri, Rolla 65401)

4-7. Instrument Soc. of America, 26th annual, Chicago, Ill. (ISA, 530 William Penn Pl., Pittsburgh, Pa. 15219)

4-8. American Dietetic Assoc., 54th annual, Philadelphia, Pa. (R. M. Yakel, 620 N. Michigan Ave., Chicago, Ill. 60611)

5-8. Optical Soc. of America, Ottawa, Ont., Canada. (J. W. Quinn, OSA, 2100 Pennsylvania Ave., NW, Washington, D.C.)

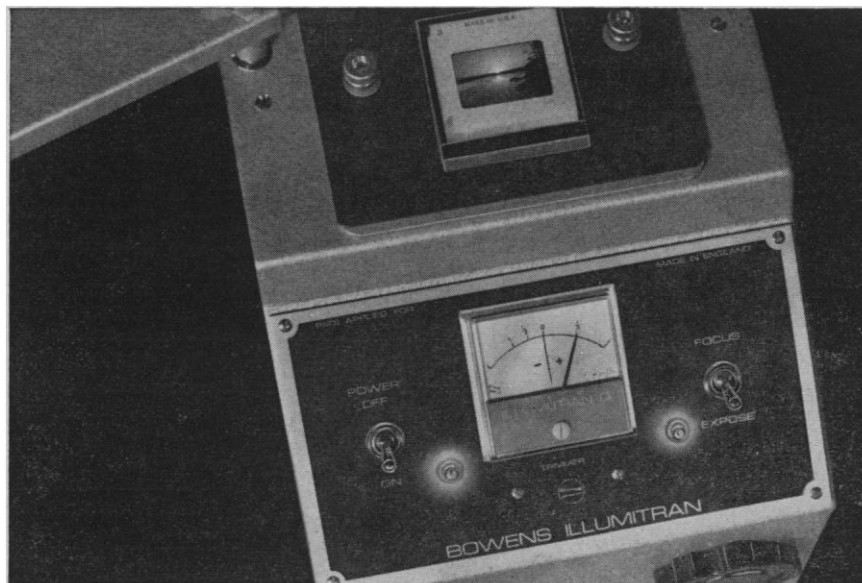
5-12. International Bureau of Weights and Measures, 14th general assembly, Paris, France. (J. Terrien, Pavillon de Breteuil, 92 Sevres, France)

8-10. Joint Conf. on Sensing of Environmental Pollutants (AIAA, ISA, ACS, IEEE, NASA, and NOAA), Palo Alto, Calif. (Instrument Soc. of America, 400 Stanwix St., Pittsburgh, Pa.)

9. Paleontological Research Institution, Ithaca, N.Y. (Mrs. K. V. W. Palmer, PRI, 1259 Trumansburg Rd., Ithaca, N.Y. 14850)

9-10. American College of Dentists, Atlantic City, N.J. (R. J. Nelsen, ACD, 7316 Wisconsin Ave., Bethesda, Md. 20014)

10-14. American Assoc. of Cereal Chemists, Dallas, Tex. (R. Tarleton, AACCC, 1821 University Ave., St. Paul, Minn. 55104)



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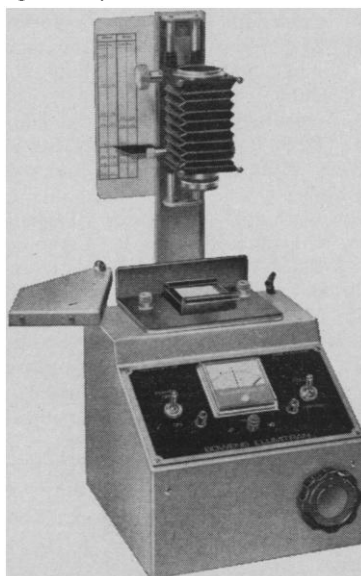
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