

tetroxide-fixed lipids and discussed their interpretation. G. Schidlovsky described effects of stains and fixatives in various suspending media on the microscopic appearance of sections of two-layered systems: chloroplasts and artificial multilayers of fatty acids. With chloroplasts the results indicate that correlation between image density and specimen structure can be "normal," "intermediate," or "reversed," according to complex conditions present during fixation and dehydration steps. Lightness and darkness in the image can also be affected by the level of focus due to phase effects. The artificial multilayer experiments demonstrate fixative action of OsO_4 on saturated fatty acids without the production of noticeable contrast. They show bands which are double layers of fatty acid soap molecules and a 2- to 3-Å layer of barium atoms bound at the carboxyl groups within a double layer of fatty acid soap molecules. He concludes that band thicknesses of artificial multilayers, when measured statistically, relate well to chain length but that similar measurements on biological systems and the meaning of the lightness or darkness of the bands should be used with caution.

Experiments on the chemical reactions of OsO_4 and KMnO_4 (both widely used in preparing tissues) with amino acid peptides and proteins were reported by T. Hake. The results seem to prove that these reagents will render only a weak contrast in electron microscopy. They are often however used with $\text{Pb}(\text{OH})_2$, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and with glutar and adipindialdehydes. He believes OsO_4 is used with wide success because it preserves structure of tissues without the need of prefixation and because there are plenty of unsaturated compounds almost everywhere in the cell with which it can react. D. Peters showed the effects of a variety of fixatives on the appearances of virus particles in thin sections.

A brief session on an important aspect of electron microscopy, namely the characteristics of photographic materials and their use in recording electron images, was dealt with by E. Zeitler and R. Valentine.

A fundamental difference between the recording of light quanta and electrons is that in the latter case only one electron hit is required to render a photographic grain developable and one electron can hit several grains.

This means that as we examine smaller and smaller areas of an exposed and developed emulsion we reach a point where the number of electrons causing the photographic density within the area is sufficiently small that statistical fluctuations or "noise" will be observed which is unrelated to specimen structure. Significance cannot be attached to areas of less than a certain diameter which is given by probability theory; the corresponding limiting dimension in the specimen is simply this diameter divided by the linear magnification. Valentine estimates that for visual observation on a fluorescent screen we need a current density at the screen of about 4×10^{-11} amp/cm². If we are to record the image at this intensity in a reasonable exposure time, say 1 to 4 seconds, the number of electrons per unit area of the plate is fixed and the probability theory gives a dimension below which one is observing noise (or grain), not specimen structure. He examined a wide variety of photographic materials in a variety of developers and produced a table which gives the minimum magnification required to show prescribed specimen detail for each emulsion. The magnification depends to some extent on the nature of the specimen being about 3 times greater for arbitrary biological materials than for heavy metallic particles. For 10-Å resolution and plates commonly used, the magnification should be about 50,000 or more.

This symposium was sponsored by the Armed Forces Institute of Pathology and the Intersociety Committee for Research Potential in Pathology. The proceedings will be published in book form as soon as possible.

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Organic Photochemistry

The dynamic character of photochemistry was demonstrated by the International Symposium on Organic Photochemistry held in Strasbourg, 20–24 July 1964. The symposium was preceded by a 3-day course of lectures on the elements of photochemistry which was attended by a smaller number of students. The latter group included many young investigators who are initiating research in the field.

The meeting showed very clearly that photochemistry, despite its enormous

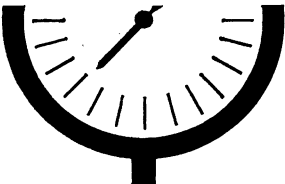
scope, is a field having genuine integrity. Participants known ordinarily as theoretical chemists, physical chemists, and organic chemists repeatedly found common ground for vigorous discussion. Exciting new information and understanding seemed to whet the appetites of the symposium members for more insight into remaining vast areas of confusion and ignorance.

The symposium program consisted of 15 principal lectures and two sessions devoted to presentation of brief communications. Since the latter programs were only organized after the meeting was convened, many of the brief reports dealt with work currently in progress in the laboratories of the investigators. George Hammond (California Institute of Technology) and Jacques Levisalles (Strasbourg) organized and directed the meeting.

Subjects of the lectures involved new photochemical reactions of both large and small molecules, direct study of excited states, various systematic schemes for visualization of the chemical reactions, and nonradiative decay of excited states. The impact of the concept of excitation transfer in photochemical reactions was illustrated by Paul de Mayo's (Western Ontario) classic remark, "So, wishing to know what was going on, we reached for a sensitizer." Even the inverse of photochemistry, chemiluminescence, was discussed (E. J. Bowen, Oxford).

The keynote of the conference was provided in the opening lecture by W. A. Noyes, Jr. (Texas) who discussed "The problem of energy dissipation by excited states," a matter to which he has personally given many years of study. The struggle of electronically excited molecules to divest themselves of excess energy is, of course, the real story of photochemistry. The chemical changes only represent special cases of radiationless decay processes. The subject of relaxation of excited molecules recurred repeatedly during the conference and was the principal subject of a paper by H. M. Frey (Southampton) who discussed the chemistry of "hot" products produced by reaction of methylenes (from photolysis of diaziranes) with various substrates.

Not surprisingly, the photochemistry of ketones and aldehydes was the main subject of no less than seven lectures and was mentioned frequently in other discussions. A considerable amount of order seemed to emerge. Apparently most carbonyl compounds undergo intersystem crossing very efficiently,



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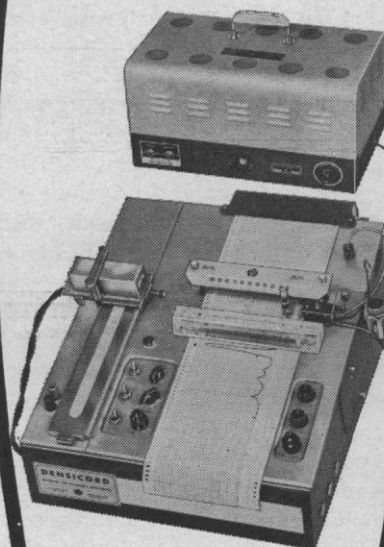
with consequent formation of triplet states in high yield. Much of the variation in behavior is understandable on the basis of the variation in the electronic structures of the lowest-lying triplet states of different molecules. The general picture was extended by George Porter (Sheffield) who added consideration of low-lying "charge transfer" states to the usual n, π^* and π, π^* states. Although it appears to the reviewer that charge-transfer states are π, π^* states having large dipole moments, the generalization will be of great value because compounds having such low-lying states are exceptionally unreactive and easily characterized by spectroscopy. However, the developing harmony of thought was jolted in the last lecture by N. C. Yang (Chicago) who presented strong evidence that 9-anthraldehyde (and perhaps other compounds) reacts by way of a triplet state that is not the lowest available to the molecule. Evidently solution photochemists will have to recognize the possibility, well known from vapor-phase studies, that decay to the lowest excited state of a given multiplicity will not always be fast compared with bimolecular reactions.

Howard Zimmerman (Wisconsin), Oskar Jeger (Zurich E. T. H.), and Gerhardt Quinkert (Braunschweig) also discussed rearrangement and fragmentation of ketones. No absolute mechanistic-type reaction has yet emerged. For example, reactions in which carbonyl groups are lost as carbon monoxide obviously involve free radicals in some instances, but in other cases show stereoselectivity which indicates that the lifetimes of any such intermediates must be vanishingly short. The well-known Zimmerman hypotheses concerning the rearrangements of unsaturated ketones were presented, discussed, expanded, and contracted. The writer is left with the feeling that he understands the various mechanisms but does not yet quite understand the compounds.

Discussions of photoaddition reactions by Richard Cookson (Southampton) and de Mayo served to remind participants that study of the mechanisms of photoreactions can often be blended with development of extraordinary new synthetic methods. One of the attractions of photochemistry is use of the reactions for synthesis of exotic compounds. Those who study reaction mechanisms seem to feel that they will shortly provide a systematic understanding to guide synthetic work. However, synthetic chemists feel such urg-

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ency that they forge ahead and develop spectacular synthetic procedures without waiting for the final word from chemical dynamics. Fortunately, the two approaches enjoy a symbiotic relationship, frequently within a single laboratory.

Various aspects of the chemistry of conjugated dienes and polyenes were expounded by Madame Mousseron (Montpellier), William Dauben (Berkeley), and Klaus Gollnick (Müllheim). These versatile molecules undergo ring-closure, ring-opening, rearrangement by hydrogen transfer, cyclodimerization, and internal cycloaddition to give fantastically distorted molecules and enter into a large number of reactions with other reactants—all under the influence of light. With this group of substrates there is often good evidence that triplet and singlet paths do not cross in many cases. Consequently, reactions effected by direct irradiation and by sensitization frequently give entirely different products.

Refreshing novelty was provided by Orville Chapman (Iowa State) and Mendel Cohen (Weizmann Institute). Chapman presented an entirely new group of photorearrangements of aromatic nitro compounds. Cohen discussed phototropism and photodimerization in crystals. The work complements studies of crystal structures by x-ray diffraction. At least within the two series of materials studied, it is possible to make unequivocal predictions concerning photochemical reactivity on the basis of intermolecular relationships within the crystals.

The symposium was sponsored by the Organic Division of the International Union of Pure and Applied Chemistry and the principal lectures will be published in a special issue of *Pure and Applied Chemistry*. The symposium and the accompanying course were supported by a grant from NATO. Financial aid from the latter organization was largely responsible for the presence of many young investigators.

GEORGE S. HAMMOND

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Surface Physics

Investigations of chemical and physical interactions occurring at solid surfaces were reported at the second annual Surface Physics Symposium held at Washington State University, Pull-



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