Meeting

Air Pollution: Photochemical Aspects

The type of atmospheric pollution originally associated with the Los Angeles Basin area came under scientific investigation about 15 years ago. Early studies by A. J. Haagen-Smit and others demonstrated that the adverse effects observed could be reproduced in the laboratory by irradiating mixtures of certain organic substances and nitric oxide or nitrogen dioxide with energy in the 3000- to 4000-Å region. Sulfur dioxide also is important in some reactions in producing aerosols. These processes occur in the atmosphere when the reactants are present at concentrations well below 1 part per million. The complexity of the primary steps, and particularly of the secondary reactions, has made it difficult to understand the underlying mechanisms. The physical-chemical complexities are aggravated by the analytical problems associated with measurement in the part-per-million range.

A symposium on the photochemical aspects of air pollution was held at the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, 20–22 April 1965, to discuss the status of research in this field. Topics ranged from the measurement of solar radiation in the ultraviolet region and investigations of chemical, physical, and biological aspects of irradiation of model systems in the laboratory to the relation between meteorological parameters and chemical effects in polluted atmospheres.

Introductory remarks by J. H. Ludwig (Public Health Service) emphasized (i) the desirability of relating laboratory investigations to aerometric studies, (ii) the meteorological aspects of the atmospheric pollution problem, and (iii) the availability of improved techniques for the measurement of ultraviolet intensities. He pointed out important relationships between photochemical studies in air pollution and the technical aspects of control of hydrocarbons and other pollutants.

The problems involved in accurately measuring the ultraviolet portion of solar radiation were discussed by R. Stair (Bureau of Standards). Improved standards of spectral irradiance have been developed to resolve some of the variations reported. Surface characteristics of the detector have recently been shown to be critical in applications with spectroradiometers. Lack of concern about these difficulties can account for much of the lack of correlation in data obtained by different observers. Improvements in sources of spectral irradiance, in use of detectors, and in general instrument design have yielded improved spectroradiometers. Among these, filter spectroradiometers should prove very useful in field measurements. An experimental program is being designed to measure ultraviolet radiation at several urban and nonurban locations.

D. F. Dever (Bureau of Mines) discussed recent experimental work carried out at the Bartlesville Petroleum Research Center on the photooxidation of aldehydes in the presence of nitrogen oxides. Particular attention was given to product identification by three methods—infrared, gas-liquid partition chromatography, and mass spectrometry. Products of such reactions included aldehydes of lower molecular weight, alcohols, alkyl nitrates, peroxyacyl nitrates, and paraffinic and olefinic hydrocarbons and oxidants of lower molecular weights. The relative rates of reaction were determined and compared. The dark reactions of aldehyde-ozone also were investigated; these reactions account for the major oxygenated products (excluding nitrogen-containing compounds).

The role of reactions between oxygen atoms and ozone in air pollution was considered by E. R. Stephens (University of California). He discussed the factors controlling such reactions and reviewed the reactions of these species with nitrogen oxides. Available data on rates of reaction of ozone with olefins indicate serious disagreement on the stoichiometry of these reactions. The observed rates of reaction of atomic oxygen and ozone with hydrocarbons are appreciably less than the observed rate of hydrocarbon consumption in photooxidation in the presence of nitrogen oxides. Although free-radical attack has been postulated regarding the discrepancies in rate, this approach presents difficulties. The presentation elicited considerable discussion on the validity of free-radical concept and of the chain-lengths in such reactions.

C. S. Tuesday (General Motors) reviewed the chemical results obtained through photooxidation of various pure organic substances with nitrogen oxides. The available data on reactant concentration, reactant ratio, light intensity, temperature, pressure, and oxygen concentration were considered. Considerable differences are found in the rates of reaction reported by various investigators. Tuesday proposed reaction mechanisms to explain the experimental results of olefin-nitrogen oxide photooxidations.

The attempts to duplicate smog effects in the laboratory by ultraviolet irradiation of automobile exhaust were discussed by M. W. Korth (Public Health Service). He reviewed various earlier studies and compared these with studies performed in the Public Health Service laboratory in Cincinnati. He considered in detail the influence of reactant ratio on chemical measurements, plant damage, and responses by an eye-irritation panel.

A. Goetz (California Institute of Technology and National Center for Atmospheric Research) discussed recent experimental work on photochemical formation of aerosols. He reported on a study of aerosol formation in the system 1-octene–nitrogen dioxide in air as a function of sulfur dioxide concentration, humidity, presence or absence of nucleating material, and the order of addition of reactant. Goetz emphasized the great importance of nucleating material, both before irradiation as a site for concentration of reactants and during irradiation as centers for aerosol formation. In the absence of sulfur dioxide, contact between nitrogen dioxide and the nucleating surfaces before irradiation increased the stability of the aerosol system formed with irradiation. Also in the absence of sulfur dioxide, increasing humidity resulted in decreasing light scattering. In the presence of sulfur dioxide, initial contact of the sulfur

dioxide with nucleating material resulted in more light scattering upon irradiation than is caused by adding nitrogen dioxide first. In the absence of nucleating material, whether or not sulfur dioxide is present, initial addition of nitrogen dioxide is most effective in promoting autonucleation. The autonucleates appear to be more thermally stable in the presence of sulfur dioxide. Discussion concerned the relative role of sulfur dioxide in aerosol formation and the importance of various photochemically produced aerosols in visibility reduction.

R. H. Daines (Rutgers University) considered plants as indicators of air pollution, reviewing the responses of many plant varieties to various pollutants. Among the substances associated with photochemical air pollution, ethylene, ozone, peroxyacyl nitrates, and possibly aldehydes have been observed to cause injury to ornamentals and field crops. Although plant variety is important, leaf age, nutritional status, water relationships, and light intensity can markedly alter the sensitivity of plants to pollutants. Daines suggested that the patterns of plant injury observed during a pollution episode also may serve as indicators of meteorological conditions during the episode.

L. G. Wayne (University of Southern California) reviewed the function of eye-irritation panels as biological indicators of photochemical reactions. The uses and limitations of the intensity, threshold, and response-delay methods were discussed. Wayne pointed out the need to minimize the suggestibility of subjects while maximizing consistency in their responses. Results of several investigations have suggested the presence of lachrymators other than formaldehyde, acrolein, and peroxyacetyl nitrate. Conflicting interpretations of eye-irritation data from studies of irradiated automobile exhaust were reviewed. Wayne suggested that the evidence does not favor basing prediction of eye irritation on rates of reaction of the hydrocarbons, since such a measurement does not properly reflect the intensity of eye irritation developed.

A. P. Altshuller (Public Health Service) discussed "reactivity" or "photochemical reactivity," defined as the tendency of various types of organic substances to participate in the reactions leading to the adverse effects associated with the photochemical type of air pollution. He showed that the same relative order of reactivities of organic substances could be obtained from various studies of rates of hydrocarbon consumption and nitrogen dioxide formation. The contributions of various organic substances to the reactions producing oxidant, aldehydes, and peroxyacyl nitrates were reviewed. Chemical and biological effects may not be simply related, and care is needed in any attempts to relate them quantitatively. The available measurements of aerosol formation, plant damage, and eye irritation were related to the type of organic substances involved in the experiments. Atmospheric levels were estimated for various types of organic substances studied in laboratory investigations. The magnitudes of effects observed in the atmosphere and the laboratory were compared. Altshuller emphasized the need for removal of all types of reactive substances including olefins, most aromatic hydrocarbons, and aldehydes from emissions. He also suggested several simplified approaches for analysis of emissions and polluted atmosphere for reactive substances.

E. A. Schuck (University of California) discussed a study of the relationships between meteorological factors and photochemical air pollution in the Los Angeles Basin. In this study the atmospheric levels of hydrocarbons were shown to correlate satisfactorily with the atmospheric levels of nitrogen oxide and carbon monoxide. The effect of day of the week on levels of oxidant and eye irritation at various monitoring stations was analyzed for several periods in 1962 to 1964. Weekend oxidant levels and temperatures associated closely with the patterns of human activity and time of the year. Oxidant levels can be quantitatively related to inversion height, wind speed, and light intensity. Smog incidence increases as average daily temperature increases up to 70°F (20°C). The study indicates that certain smog symptoms and emissions are proportional over large areas of the Los Angeles Basin. The laboratory and atmospheric levels of oxidant and eye irritation were compared as functions of hydrocarbon and nitrogen oxides. Calculations based on the atmospheric data indicate that smog incidence is reduced as reactive hydrocarbons are reduced. Similar calculations indicate that if a significant decrease in smog incidence is to be achieved by nitrogen oxide reduction alone, a high degree of control of nitrogen oxide emissions will be necessary.

An informal discussion of research problems comprised the final session. Difficulties in obtaining properly purified air for some of the large irradiation chambers were discussed. Various methods for removal of pollutants in dilution air were considered. Surface effects from adsorbed pollutants also cause difficulties, and procedures were discussed for reducing surface contamination. These problems make it difficult to do satisfactory experiments at very low concentrations of reactants or with systems of low reactivity.

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Forthcoming Events

March

10–11. **Heat Transfer** to Non-Newtonian Fluids, 12th annual heat transfer conf., Oklahoma State Univ., Stillwater. (J. D. Parker, Dept. of Mechanical Engineering, Oklahoma State Univ., Stillwater 74075)

11–13. National Council of **Teachers of Mathematics**, San Diego, Calif. (J. D. Gates, 1201 16th St., NW, Washington, D.C. 20036)

11–13. National **Wildlife** Federation, annual mtg., Pittsburgh, Pa. (T. L. Kimball, 1412 16th St., NW, Washington, D.C. 20036)

12–13. **Linguistics**, 11th natl. conf., Linguistic Circle of New York, N.Y. (L. Pap, State Univ. College, New Paltz, N.Y. 12561)

14–16. Society of **Toxicology**, annual scientific mtg., Williamsburg, Va. (C. S. Weil, Mellon Inst., 4400 Fifth Ave., Pittsburgh, Pa. 15213)

14–16. **Wildlife and Natural Resources**, 31st North American conf., Pittsburgh, Pa. (C. R. Gutermuth, Wildlife Management Inst., Wire Bldg., Washington, D.C.)

14–20. **Obstetrics and Gynecology**, 8th Australian congr., Hobart. (J. F. Correy, 173 Macquaire St., Hobart)

14–6 May. Extraordinary Administrative **Aeronautical Radio** Conf., 2nd session, Geneva, Switzerland. (Intern. Telecommunication Union, Place des Nations, Geneva)

15–16. **Flame Resistant Polymers**, conf., London, England. (Secretary, Plastics Inst., 6 Mandeville Pl., London, W.1)

15–18. **Optical Soc.** of America, spring mtg., Washington, D.C. (M. E. Warga, 1155 16th St., NW, Washington, D.C. 20006)

17–19. **Isobaric Spin in Nuclear Physics**, intern. conf., Florida State Univ., Tallahassee. (D. Robson, Dept. of Physics, Florida State Univ., Tallahassee)