humidity under which leaves develop in Florida.

From the evidence obtained, it appears conclusive that the unique chlorotic leaf pattern on citrus that appears in association with triple-superphosphate manufacturing plants is the result of the fluorine evolved in the process of manufacture (*6*).

I. W. Wander
J. J. McBride, Jr.
Citrus Experiment Station,
Lake Alfred, Florida

References and Notes

1. O. C. Bryan, *Florida Dept. Agr. Bull. No. 93* (1940); A. F. Camp and B. R. Fudge, *Univ. Florida Agr. Expt. Sta. Bull. No. 335* (1939).
2. V. Sauchelli, *Manual on Phosphates* (Davidson Chemical Corp., 1942), p. 35.
3. J. C. Kaudy *et al., Citrus Leaves* 34, 8 (1954).
4. L. McCabe, *Air Pollution* (McGraw-Hill, New York, 1952), p. 104.
5. M. Katz, *Chem. Eng. News* 33, 2496 (1955).
6. Florida Agricultural Experiment Station Journal Series No. 406.

18 November 1955

Photochemical Reactions of Nitrogen Dioxide and Hydrocarbons in Air

The principal chemical characteristic of Los Angeles smog is the presence of relatively high oxidant concentrations. The nature and genesis of the oxidant have been the subject of intense study during the past several years. Haagen-Smit and coworkers (*1, 2*) have investigated the photochemical reactions of a series of synthetic mixtures of nitrogen dioxide and hydrocarbons in both oxygen and air carriers. Concentrations of the reactants were in the range of parts per million. On irradiation from polychromatic sources, such as the sun or blue fluorescent lamps, oxidant was produced that was manifested by its ability to crack stressed rubber and to oxidize alkaline phenolphthalin reagent.

Table 1. Photolysis results with full mercury arc (Hanovia Type A).

Time (hr)	Concentrations (ppm)			
	3-methyl heptane	NO_2 initial	Ozone	NO_2 recovered
3	13.2	1.36	0.89	0.08
1	14.7	1.47	0.33	1.44
1	8.9	0.76	0.38	1.07
3	20.4	0.93	0.86	0.24
17	10.0	0.48	0.53	0.18
3	3.5	0.65	0.97	0.05
3	0.97	0.50	0.59	0.20
5	0.00	1.11	0.0	1.47
3	3.9	0.72	0.2*	0.51
3	2.3	0.72	0.44	
3	1.35	0.48	0.39	0.51
3	0.04	0.50	0.0	0.76
3	3.3	0.00	0.00	0.00

* Corning -7380 glass filter 2 mm thick cut out 3130 A radiation but passed 60 percent of 3660 A.

A verification of Haagen-Smit's findings was carried out in the course of our study of the photochemical reactions of trace constituents in the atmosphere (*3*). The purpose of this communication is to report the nature of the verifications obtained.

A series of experiments was run by one of us (A. M.) at California Institute of Technology laboratory of Haagen-Smit (*4*). A number of 5-lit flasks containing heptene-2 at 3 ppm and nitrogen dioxide at 0.1, 0.4, 1.0, and 3.0 ppm in humidified air were irradiated for 10 hours with a bank of Westinghouse 40-w fluorescent lamps. The flasks contained suspended strips of stressed rubber as oxidant traps (*5*). The degree of rubber cracking rose from zero to high values as a function of NO_2 concentration.

To determine the reproducibility of the quenching effect reported (*2*) at elevated hydrocarbon concentration, several runs were made in the same system using NO_2 at 1 ppm and 3-methyl heptane at 1 and 700 ppm. After 10 hours of irradiation, cracking of rubber was confirmed at the 1-ppm hydrocarbon level, with no cracking found at the 700-ppm concentration level.

Investigation of the photochemistry of the NO_2-3-methyl heptane system continued in our laboratory. A 2-lit Vycor photolysis flask was wrapped in aluminum foil except for an opening to admit the collimated radiation from a Hanovia Type A mercury arc that was filtered with a Pyrex filter to cut out radiations at wavelengths below 3000 A. The use of the reflective lining on the flask to form a multiple reflection system was necessary to achieve sufficient light intensity with this system. A relatively uniform radiation flux was thereby obtained. The radiation intensity, as determined with a photoelectric probe, was approximately the same as that of noon sunlight in the ultraviolet region but considerably less in the visible region.

At the conclusion of photolysis, the reaction mixture was passed through liquid-oxygen-cooled traps packed with glass beads and then through a train of three bubblers containing alkaline phenolphthalin reagent. Oxidant values were obtained by spectrophotometric measurement of the partially oxidized reagent mixture. Controlled experiments revealed that NO_2 was efficiently trapped in the freeze-out traps and did not contribute to oxidation of the reagent. Presumably, oxidants less volatile than NO_2 (peroxides, and so on) would also be trapped. The physical evidence therefore points strongly to ozone as the principal oxidant product of the photochemical reaction.

Typical results of irradiation of NO_2 and 3-methyl heptane in oxygen are given in Table 1. No ozone was obtained when either the NO_2 or the hydrocarbon was omitted. Recovery of NO_2 from the freeze-out traps was checked by analysis with the Saltzman reagent (*6*). A tendency toward high recovery by this method has not been completely resolved, but the results consistently show low recovery (or none) in photolyses in which an appreciable quantity of ozone was found.

These experiments support the finding of Haagen-Smit that traces of NO_2 and hydrocarbon in air undergo a photochemical reaction to produce ozone. Furthermore, NO_2 is consumed in the course of the reaction, indicating that NO_2 is more than a radiation absorber. Work is in progress to determine the stoichiometric relation between ozone formed and NO_2 consumed. A paper presented late last year by Hanst and coworkers (*7*) confirms the oxidant as ozone by infrared spectroscopy and also shows disappearance of NO_2 as the reaction proceeds.

Arnold Miller
Callaway Brown
Karl D. Franson
Armour Research Foundation, Illinois Institute of Technology, Chicago

References and Notes

1. A. J. Haagen-Smit, *Ind. Eng. Chem.* 44, 1342 (1952) and 45, 2068 (1953); A. J. Haagen-Smit and M. Fox, *Air Repair* 4, 105 (1954).
2. A. J. Haagen-Smit, C. E. Bradley, M. Fox, *Proc. 2nd Natl. Air Pollution Symposium, Pasadena, Calif.* (1952).
3. This work was supported and suggested by the Air Pollution Foundation, Los Angeles, Calif.
4. We are pleased to acknowledge the cooperation and assistance given to us by A. J. Haagen-Smit in our initial study at California Institute of Technology.
5. C. E. Bradley and A. J. Haagen-Smit, *Rubber Chem. and Technol.* 24, 750 (1951).
6. B. E. Saltzman, *Anal. Chem.* 26, 1949 (1954).
7. P. L. Hanst *et al.*, fall 1955 meeting of the American Chemical Society, Minneapolis, Minn.

14 November 1955

Temperature Control in the Measurement of Particle Volumes by the Isopiestic Method

Crozier has recently reported (*1*) some observations on the relative volumes of small droplets (diameter about 10^{-3} cm) of sodium chloride solutions equilibrated in atmospheres of varying water vapor pressure. Rather large discrepancies were noted between observed volumes and those calculated from ICT values for the vapor pressures of NaCl solutions at the temperature employed (25°C), which the author was unable to explain. The particle sizes were in the range where the Thompson-Gibbs effect is slight, and this effect was, in any case, allowed for. We have been performing