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).

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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 pro-

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.

duced that was manifested by its ability to crack stressed rubber and to oxidize alkaline phenolphthalin reagent.

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.

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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

experiments (2) similar to those reported by Crozier and have observed effects that can cause the discrepancies noted.

The isopiestic method (3) involves the equilibration, in an enclosed space, of solutions of nonvolatile solutes in the same solvent. At equilibrium, the activity of the solvent is the same in all the solutions. The use, at a fixed temperature, of a large quantity of a suitable saturated solution in contact with excess solute provides a fixed, known vapor pressure within the enclosed space. If droplets of a second solution are in equilibrium with this vapor, their composition is determined by their temperature and by the vapor pressure. Crozier's microscopic droplets of sodium chloride were deposited on Dri-Film or Teflon slides and exposed in a closed box to atmospheres of several different water vapor pressures. Observed drop diameters were converted to drop volumes, assuming hemispherical particles. The relationships between these volumes were considerably different from those predicted from ICT vapor pressure and density data (Fig. 1).

Crozier assumed that his droplets were at the same temperature as the air and the saturated solutions within his small observation box. In similar studies, however, we found that a significant temperature differential existed between the droplets and the air to which they were exposed. We passed air that was conditioned to various water contents and maintained at 25.0°C through an observation cell containing upper and lower windows. A microscope lamp, equipped with a water cell, illuminated the substage mirror of a microscope, upon whose stage the observation cell was placed. Droplets of NaCl solution (in the same size range as those of Crozier) were deposited upon a glass cover-slip about 10^{-2} cm thick, and the cover slip was inverted to form the upper window of the observation cell. An oil immersion lens was used to observe the particles through the glass, and a fine thermocouple was placed in the oil in contact with the glass surface.

The thermal resistance of the glass being relatively slight, the temperature of the particles could be taken as nearly equal to that of the thermocouple. Other sensitive thermocouples were employed to measure the air temperature and humidity. The microscope and all the apparatus were installed in a constant-temperature room at 25°C. Under these circumstances, it was observed that the cover-slip temperature started to rise as soon as the (water-cell equipped) microscope illuminator was turned on, and that it continued to rise until there was more than 0.5°C difference in temperature between glass and air.

In previous work, even larger variations in the cover-slip temperature had been noticed when the apparatus was located in a room where the temperature was not closely controlled. On warm days, the junction in the immersion oil indicated temperatures considerably higher than 25°C, despite the large volume (about 8000 cm³) of 25.0°C air passing through the small cell (about 25 cm³) each minute.

As a result, NaCl crystals on the cover-slip sometimes did not pick up moisture until the relative humidity of the 25.0°C air passing through the cell was raised to more than 80 percent, whereas 75.5 percent should initiate particle growth. It seemed reasonable to believe that heat was being conducted to the oil and the cover-slip by the microscope.

It is apparent that, when relatively large plane surfaces are used for the support of droplets, heat transfer from surface to droplet can introduce serious error. As a matter of fact, the resistance to heat transfer that is offered by the air near the particles is so great that the thermal resistances of the droplets themselves are of negligible effect. The particles are essentially at the same temperature as the surface that supports them, even though the nearby air may be warmer or cooler.

We have recalculated the equilibrium relative humidities that would have existed at the surfaces of Crozier's NaCl droplets, if his Teflon and Dri-Film surfaces (and his droplets) were, for example, 0.8°C warmer than the saturated solutions contained in his box. With water at 25.0°C, assuming equilibrium in water concentrations, the slide surface at 25.8°C would be exposed to a relative humidity of 95.4 percent instead of 100 percent. Similarly, saturated
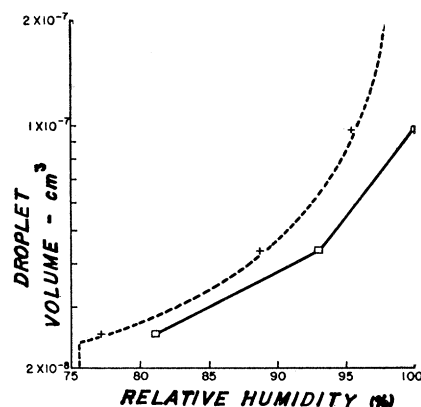

Fig. 1. Relationship of droplet volume to relative humidity. Solid line connects typical experimental points (□) obtained by Crozier (1). Broken lines are the calculated relationships based on vapor pressure and density of NaCl solutions; points marked (+) represent Crozier's data corrected as indicated in the text.

$(NH_4)H_2PO_4$ would yield a local relative humidity of 88.7 percent instead of 93.0 percent, and $(NH_4)_2SO_4$ would yield 77.4 percent instead of 81.1 percent. Employing these new relative humidity values, we have replotted a sample set of the droplet volumes recorded by Crozier, on Fig. 1. It will be observed that the revised plotting is in good agreement with the theoretical relationship between particle volume and relative humidity that is derived from ICT data. Similar treatment will yield similar results for the other droplets examined. The results obtained by Crozier could, therefore, be satisfactorily explained by the existence of a rather small temperature differential.

From Fig. 1, it is also apparent that the error that may be incurred by assuming, rather than determining, that isothermal conditions exist increases greatly as the relative humidity increases.

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Occurrence of Three Red Blood Cell Antigens in Rabbit as the Result of Interaction of Two Genes

In the course of the study of blood groups in the rabbit (1), isoimmunization techniques have been used to prepare specific antiserums that detect the presence of seven rabbit red blood cell antigens (labelled A, B, C, D, E, F, and H) (2). The mode of inheritance has been studied, and it has been shown that these antigens are controlled by five loci (3). A new isoantibody has been prepared that appears to identify an antigen resulting from the interaction of a pair of previously identified allelic genes.

The locus with which we are concerned has three alleles (Hg^A, Hg^D, and Hg^F), each of which gives rise to a detectable antigen. Thus, all rabbits must have antigen A, D, or F, or a combination of any two of these antigens. A new isoimmune serum appeared to contain three specific antibodies. One was identified as anti-D, and another as anti-H. The third antibody, called anti-I, was isolated by the absorption of the whole serum by cells of type D and by cells of type AFH. The resulting typing serum,