cans, it emphasizes the necessity of analyzing genetic similarities as near to the level of primary gene structure as possible. In practice, this amounts to analysis of the primary polypeptide structure. In that blood group systems probably reflect metabolic events, functional identity is often not the result of allelic identity and may be misleading.

The only other variant which achieves relatively high frequency is Tf D_{Chi}, present particularly in populations of Asia adjacent to the areas containing Tf D_1 (*9*). Although the electrophoretic mobilities of Tf D_{Chi} and Tf D_1 are similar and may be difficult to distinguish (*10*), Tf D_{Chi} has been observed to carry a different amino acid substitution (*11*).

AN-CHUAN WANG
H. ELDON SUTTON
Department of Zoology,
University of Texas, Austin 78712
IAN D. SCOTT
Human Genetics Unit, University of
Western Australia, Nedlands

References and Notes

1. E. R. Giblett, *Progr. Med. Genet.* **2**, 34 (1962); A. G. Bearn and H. Cleve, in *The Metabolic Basis of Inherited Disease*, J. B. Stanbury, J. B. Wyngaarden, D. S. Fredrickson, Eds. (McGraw-Hill, New York, ed. 2, 1966), p. 1321.
2. A.-C. Wang and H. E. Sutton, *Science* **149**, 435 (1965).
3. The original typing of transferrin variants was done in the Human Genetics Unit of the University of Western Australia. We thank Miss D. E. Halley for technical assistance, and A. Drummond, D. Corner, S. Denton, and the Western Australia Department of Native Welfare for the collection of blood. We also thank the subject, Dabadu.
4. H. E. Sutton and G. W. Karp, Jr., *Biochim. Biophys. Acta* **107**, 153 (1965).
5. Trypsin and α-chymotrypsin (three times crystallized) were obtained from Worthington Biochemical Corporation.
6. V. M. Ingram, *Biochim. Biophys. Acta* **28**, 539 (1958).
7. G. C. Ashton, *Genetics* **52**, 983 (1965).
8. L. L. Cavalli-Sforza, I. Barrai, A. W. F. Edwards, *Cold Spring Harbor Symp. Quant. Biol.* **29**, 9 (1964).
9. R. L. Kirk, W. C. Parker, A. G. Bearn, *Acta Genet. Statist. Med.* **14**, 41 (1964); R. L. Kirk, *Progr. Med. Genet.* **4**, 202 (1965).
10. W. C. Parker and A. G. Bearn, *Ann. Hum. Genet.* **25**, 227 (1961).
11. A.-C. Wang, H. E. Sutton, P. N. Howard, *Biochem. Genet.*, in press.
12. Supported in part by NIH grants GM 09326 and K3-GM-18,381. We thank Dr. R. L. Kirk for his advice and assistance in making arrangements for this study.

22 March 1967

■

Photooxidation of Hydrocarbons in the Presence of Aliphatic Aldehydes

Abstract. *A new group of gas-phase reactions have been shown to contribute to the photooxidation of hydrocarbons. The photooxidation of aliphatic aldehydes at wavelengths below 3400 angstroms produces intermediates that react with olefinic and aromatic hydrocarbons. Although the photooxidation rates are slower than those induced by nitrogen oxide, the rates are significant, considering the interest in urban atmospheric reactions. These results may indicate that the control of nitrogen oxides alone may not effectively reduce photochemical air pollution.*

The work of A. J. Haagen-Smit and co-workers (*1*) proved the importance of photooxidation of hydrocarbons in the presence of nitrogen oxides in photochemical air pollution. Subsequent studies have been concerned with more detailed measurements of such systems (*2, 3*). Leighton (*2*) has discussed a variety of substances of possible significance in primary photochemical processes. Aliphatic aldehydes were suggested as one of a number of substances possibly contributing to such processes. However, experimental work was insufficient to determine whether any primary process other than the photolysis of nitrogen dioxide was in fact significant in atmospheric photochemical reactions.

Several years ago, it was observed that the rates of photooxidation of mixtures of small amounts of aldehyde and nitrogen oxide (ppm) in air were higher than were the rates of the corresponding hydrocarbon and nitrogen oxide when radiation was below 3400 Å (*4*). Aliphatic aldehydes in air may react when irradiated with simulated solar radiation to form oxidants and phytotoxicants (*5*). The photooxidation of propionaldehyde in air (in the absence of nitrogen oxides) has been studied with simulated solar radiation and with sunlight (*6, 7*). Significant rates of reaction were obtained, with ethylhydroperoxide and carbon monoxide as major products. A free-radical mechanism was suggested to explain the results (*6*).

We have now shown that aliphatic aldehydes, when photooxidized in air with radiation at shorter wavelengths than 3400 Å, will produce intermediate species that react with olefinic and aromatic hydrocarbons. These reactions (even at very low concentrations, that is, parts per million) proceed at significant rates in the absence of nitrogen oxides. These reactions have been investigated both with sunlight-fluorescent lamps (maximum intensity at 3100 Å) and with sunlight.

The reaction mixtures were prepared in plastic containers fabricated from FEP (fluorinated ethylene-propylene copolymer) film. These containers were placed between two parallel banks, each usually having 14 sunlight fluorescent lamps with maximum intensity at 3100 Å, and the mixtures were irradiated for periods ranging from 1 to 3 hours. The reaction mixture was diluted with air so that the final volume was 150 liters, and the temperature was maintained at 23° ± 1°C. Experiments in sunlight were conducted by placing the FEP containers on the roof of the laboratory building for 5 or 6 hours around midday. Experiments were always done on clear, sunny days, but overcast occasionally developed later while the experiment was in progress.

The rates of consumption of aldehyde and of olefin were determined with a gas chromatograph (equipped with a flame ionization detector), on a bis-2(2-methoxyethyl)adipate column and a silicon fluid (SF-96) column, respectively. Formaldehyde was determined by a modification of the chromotropic acid method (*8*). Hydrogen peroxide was analyzed by the titanium-8 quinolinol method (*9*). Total oxidant was measured by a modification of the ferrous thiocyanate method (*10*); alkyl hydroperoxide was determined by kinetic colorimetry with catalyzed potassium iodide reagent (*11*).

The reactant consumptions for mixtures of one of the three aldehydes—formaldehyde, acetaldehyde, or propionaldehyde—with ethylene, *trans*-2-butene, 2-methylbutene-1, 2,3-dimethylbutene-2, or 1,3,5-trimethylbenzene are listed in Table 1 (for our experiments in the laboratory). Consumption of the olefin or aromatic hydrocarbons occurred in all these experiments. The order of increasing percentage consumption (Table 1) was as follows: 2,3-dimethylbutene-2 > 2-methylbutene-1 ~ 1,3,5-trimethylbenzene > ethylene. The rate of reaction of the olefins accelerated with increasing reaction time, an

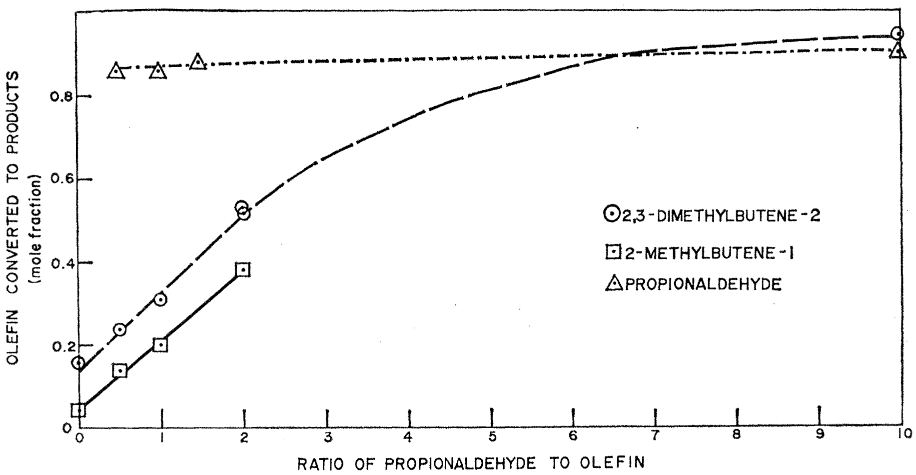


Fig. 1. Percentage conversion of olefins and propionaldehyde as a function of ratio of propionaldehyde to olefin in two different propionaldehyde-to-olefin systems after 3 hours of irradiation.

Table 1. Photooxidation of aldehyde-hydrocarbons in air mixtures by sunlight fluorescent lamps.

Aldehyde and hydrocarbon	Initial concentration (ppm by volume)	Percent reacted with irradiation by hour			Other products identified
		1	2	3	
Formaldehyde	13	66	70	79	Methyl ethyl ketone
2-Methylbutene-1	10	11	23	33	
Formaldehyde	30	57	71	74	Oxidant
2,3-Dimethylbutene-2	10	29	54	74	
Formaldehyde	10	50	62	71	
1,3,5-Trimethylbenzene	10	8	20	29	
Acetaldehyde	32	33	61	74	
2-Methylbutene-1	10	5	20	38	
Propionaldehyde	22	53	79		Acetaldehyde, ethyl hydroperoxide, hydrogen peroxide
Ethylene	10	2	6		
Propionaldehyde	22	53			Acetaldehyde, ethyl hydroperoxide, hydrogen peroxide
trans-2-Butene	11	9			
Propionaldehyde	20	49	76	89	Acetaldehyde, methyl ethyl ketone, ethyl hydroperoxide
2-Methylbutene-1	10	7	21	38	
Propionaldehyde	22	51	76	89	Acetone
2,3-Dimethylbutene-2	10	12	32	53	
Propionaldehyde	18	49	75	88	Acetone, methyl ethyl ketone, ethyl hydroperoxide, hydrogen peroxide
2-Methylbutene-1	10	1	8	15	
2,3-Dimethylbutene-2	10	8	21	36	
Propionaldehyde	18	50		88	Formaldehyde
1,3,5-Trimethylbenzene	10	8		34	

Table 2. Photooxidation of aldehyde-hydrocarbons in air mixtures by sunlight.

Aldehyde and hydrocarbon	Initial concentration (ppm by volume)	Percent reacted with irradiation by hour		Other products identified
		5	6	
Formaldehyde	15	61		Oxidant, hydrogen peroxide
2,3-Dimethylbutene-2	10	36		
Acetaldehyde	5	12		Oxidant
2-Methylbutene-1	10	4		
Propionaldehyde	19		25	Acetaldehyde, methyl ethyl ketone, oxidant, hydrogen peroxide
2-Methylbutene-1	10		10	

indication of the formation of a more reactive intermediate or product. Formaldehyde and propionaldehyde were more effective than acetaldehyde. These results provide further evidence that aldehyde photooxidation is associated with free-radical formation (*6*).

Slowly reacting oxidizing agents were consistently measured as products of these reactions (Table 1). No significant amounts of strong oxidizing agents, such as ozone or peroxy acids, could have been present. Based on rates of reaction with various colorimetric reaction systems (*9–11*), the oxidant included alkyl hydroperoxides and hydrogen peroxide. These oxidants have been identified as products of corresponding aldehyde photooxidations (*6, 7*). At this time it is not possible to determine which of these oxidants to ascribe to reactions involving hydrocarbons.

Carbonyl compounds, including formaldehyde, acetaldehyde, acetone, and methyl ethyl ketone, were identified as reaction products (Table 1). Acetaldehyde was an important product of the reactions involving propionaldehyde as a reactant. However, acetaldehyde in part formed by thermal decomposition of ethyl hydroperoxide was measured as a product of the propionaldehyde photooxidation in the absence of hydrocarbons (*6*). The acetone and methyl ethyl ketone produced (see Table 1) can reasonably be associated with attack on the double bond of the 2,3-dimethylbutene-2 and 2-methylbutene-1.

Our results show that more than 1 mole of aldehyde usually disappears per mole of hydrocarbon consumed. From 2 to 5 moles of aldehyde often are consumed per mole of hydrocarbon consumed. The ratio is even higher when ethylene is a reactant. When propionaldehyde or acetaldehyde are reactants, these ratios are only lower estimates, since the amount of the next lower aldehyde consumed in secondary processes is not included. However, after longer reaction times, mole-for-mole conversions of olefin to formaldehyde have been measured in several systems.

Whereas olefin conversions increase with increasing ratio, the propionaldehyde conversion is essentially constant (Fig. 1). The nonzero conversions when aldehyde is absent are real. The conversion is greater with irradiation than in the dark and increases with increasing irradiation time. The causes for this conversion are not clear. The sunlamp radiation does not extend into the olefin absorption region. Very low concentrations of nitrogen oxide (less than 0.01 ppm) were present in the dilution air. Despite these very small amounts and ratios of olefin to nitrogen oxide greater than 1000:1, at least part of the background conversions may arise from reactions induced by nitrogen oxide.

Although conversions of aldehyde and olfefin mixtures (Table 2) are slower in sunlight than in laboratory irradiations, the amounts consumed are significant. Comparisons of the rates of reactions in this new series of reactions with those under comparable conditions, but involving nitrogen oxides, are difficult. Laboratory irradiation sources do not reproduce accurately the ratio of total solar ultraviolet to the fraction of ultraviolet less than 3400 Å. Ultraviolet measurements in Los Angeles in October 1965 indicated that at that time of the year about 20 percent of the ultraviolet light was below 3400 Å (*12*). An initial comparison of laboratory results (Table 1) and sunlight irradiations (Table 2) of ethylene or 1-butene with aldehyde or nitric oxide indicates that the difference in rates of reaction is about an order of magnitude; that is, the rate of reaction of a hydrocarbon in the presence of optimum amounts of nitrogen oxides may be about ten times faster than for the same hydrocarbon in the presence of an aldehyde.

The relation of this class of reaction systems to the desirability of reducing atmospheric nitrogen oxides is of practical significance. Even the limited results now available suggest that the rates of reaction and product yields in atmospheric reactions may not approach zero as nitrogen oxides are reduced even to very low concentrations.

Aldehydes are emitted to the atmosphere directly by combustion processes. Furthermore, aldehyde yields in photooxidations of hydrocarbon in the presence of nitrogen oxide in the laboratory remain high even at low nitrogen oxide levels (*3*). The present results could have a direct bearing on efforts to determine the improvment in purity of the atmosphere attainable by control of nitrogen oxides from combustion sources.

A. P. ALTSHULLER
I. R. COHEN
T. C. PURCELL
National Center for Air Pollution Control, Cincinnati, Ohio 45226

References and Notes

1. A. J. Haagen-Smit, *Ind. Eng. Chem.* **44**, 1342 (1952); ——— and M. M. Fox, *ibid.* **48**, 1484 (1956).
2. P. A. Leighton, in *Physical Chemistry: Photochemical Aspects of Air Pollution* (Academic Press, New York, 1961), vol. 9.
3. A. P. Altshuller and J. J. Bufalini, *Photochem. Photobiol.* **4**, 97 (1965).
4. A. P. Altshuller and I. R. Cohen, *Int. J. Air Water Pollut.* **7**, 787 (1963).
5. I. J. Hindawi and A. P. Altshuller, *Science* **146**, 540 (1964); A. P. Altshuller, D. L. Klosterman, P. W. Leach, I. J. Hindawi, J. E. Sigsby, Jr., *Int. J. Air Water Pollut.* **10**, 81 (1966).
6. A. P. Altshuller, I. R. Cohen, T. C. Purcell, *Can. J. Chem.* **44**, 2973 (1966).
7. A. P. Altshuller and I. R. Cohen, *Int. J. Air Water Pollut.*, in press.
8. A. P. Altshuller and I. R. Cohen, *ibid.* **8**, 611 (1964).
9. I. R. Cohen and T. C. Purcell, *Anal. Chem.* **39**, 131 (1967).
10. I. R. Cohen, T. C. Purcell, A. P. Altshuller, *J. Environ. Sci. Technol.* **1**, 247 (1967).
11. T. C. Purcell and I. R. Cohen, *ibid.*, in press.
12. R. Stair, W. R. Waters, J. K. Jackson, *Photoelectric Filter Measurements of Solar Ultraviolet Irradiances at Los Angeles, California*, NBS Report 9034 (1965).

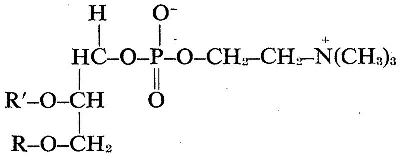
31 March 1967

Forces between Lecithin Bimolecular Leaflets Are Due to a Disordered Surface Layer

Abstract. *The long-range repulsion observed between bileaflets of lecithin cannot be explained either with the usual view that the polar groups are arrayed coplanar with the bileaflet surface or by the assumption that charges protrude straight into the aqueous environment. Statistical-thermodynamic analysis of experimental data suggests rather that structure of the leaflet surface is better described as a diffuse charge layer. Forces between leaflets are caused largely by entropy changes in the surface with leaflet separation.*

Recent x-ray diffraction studies on lamellar liquid-crystals of pure cell-membrane lecithin phospholipids in water (*1*) offer an unusual opportunity for quantitative study of their bimolecular leaflet properties (Fig. 1). These data have been interpreted as showing (*2*) that there is a long-range potential field around the electrically neutral leaflet that has a strength comparable to forces within the leaflet. This field, acting to repel the leaflets, causes an increase in the thickness of the lipid aggregates as the water fraction decreases. The x-ray data can be accounted for by applying a statistical-thermodynamic theory previously developed (*3*) to explain phase transitions between liquid-crystalline states of fatty acid salts and water. This analysis indicates that the lecithin molecules tend to aggregate in bilayers with maximum disorder, and this disorder itself acts as a thermodynamic force when perturbed.

The lecithin molecules,



$$\begin{array}{ll} \mathrm{H} & \mathrm{O^-} \\ | & | \\ \mathrm{HC{-}O{-}} & \mathrm{P{-}O{-}CH_2{-}CH_2{-}\overset{+}{N}(CH_3)_3} \\ | & \| \\ \mathrm{R'{-}O{-}CH} & \mathrm{O} \\ | & \\ \mathrm{R{-}O{-}CH_2} & \end{array}$$

each have two hydrocarbon chains (16 to 22 carbons long) esterified to the glycerol backbone which merge to form a nonpolar region (Fig. 1a). The zwitterionic polar group is part of the boundary region between hydrocarbon and water. In the one-phase liquid-crystal system (*1*), planar lipid lamellae alternate with layers of water. For each lipid concentration set in the experiment, the system assumes a measurable repeat distance or long spacing d to minimize its free energy. Measured densities and molecular weights of components allow one to calculate a volume fraction ϕ = (volume hydrocarbon)/(total volume) from the weight concentration. Mean thickness of the hydrocarbon of the bilayer, then, is $d_{\mathrm{hc}} = \phi d$ and of the water layer, plus any polar parts of the lipid molecule, is $d_{\mathrm{aq}} = (1 - \phi)\, d$. The interfacial area S allotted per molecule can also be calculated from the spacing d, since $S \cdot d_{\mathrm{hc}} = 2\, V_{\mathrm{hc}}$, where V_{hc} is the volume of hydrocarbon per molecule (*3, 4*).

The generally assumed picture (*5*) of the bileaflet surface has been that the zwitterionic polar groups are coplanar with the hydrocarbon-water interface. A cardinal feature of this model is that all stabilizing interactions are confined to the individual lipid leaflets; there is only a weak force field outside the leaflets (*5*). The fact that lamellar thickness changes with concentration is strong evidence against this. If all stabilizing interactions were confined to the same leaflet its size would not be changed by the approach of other structures. Instead, when water is removed from the one-phase system (that is, ϕ is increased) interaction between leaflets causes them to thicken (d_{hc} increases). Water layer thickness d_{aq}