

In view of these observations it seems likely that peptide deuterium-hydrogen exchange rates reflect more the state and configuration of acidic and basic side chains in the local environment than the percentage of hydrogen-bonded peptide groups in proteins (3).

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References and Notes

1. I. M. Klotz and J. S. Franzen, *J. Am. Chem. Soc.* **84**, 3461 (1962).
2. S. O. Nielsen, *Biochim. Biophys. Acta* **37**, 146 (1960).
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Schistosoma mansoni: Natural Infection of Cattle in Brazil

Abstract. In an area in Brazil where schistosomiasis has long been endemic, examination of cattle which were slaughtered for food disclosed the presence of adult *Schistosoma mansoni* in the mesenteric veins of four animals. Eggs of *S. mansoni* were found in the feces and rectal mucosa of one animal.

Knowledge of possible animal hosts of a human parasite is important for the control of the infection in endemic areas. Several animal hosts naturally infected with *Schistosoma mansoni* in Africa and South America have been found since 1952. These infections have been reported frequently in South America in small mammals, such as domestic and wild rodents, and the opossum. In Africa, besides rodents, baboons have also recently been found to be infected with *S. mansoni*.

Paulista, State of Pernambuco, a small town near Recife is well known as an important endemic area for schistosomiasis caused by *S. mansoni*. In the abattoir at Paulista, 29 animals, among the cattle killed for food during the months from April to July 1962, were examined and their mesenteric veins were carefully searched for worms. All the animals had been raised in the endemic area. Four animals out of the total at autopsy were infected with adult schistosomes morphologically indistinguishable from *S. mansoni*. Although a thorough search was made no eggs could be found in the feces of three of the infected animals; however, in the fourth infected animal laterally spined eggs were discovered when the mucosa of the animal's rectum was scraped. A total of 67 eggs were seen. All of them

had become degenerated and showed a granular interior structure. Eggs were also present in the mucus and in the feces adherent to the mucosa of the animal's rectum. This is the first record of natural infection with *S. mansoni* in cattle. Until the present time no other large quadruped has been found to be a natural host of *S. mansoni*.

The possibility that the schistosome reported here and found in cattle could be a member of the *S. mansoni* complex, an animal instead of a human schistosome, was considered. However, no schistosome species, other than *S. mansoni*, has ever been reported in any mammal in Brazil. The presence of subterminal spines in the eggs of the African species, *Schistosoma rodhaini*, easily distinguishes it from *S. mansoni*, whose eggs have lateral spines.

Although *S. mansoni* could be considered a trematode that lives in several mammals besides man, the significance of the role that animal hosts may play in the maintenance of *S. mansoni* in nature is not understood. (1).

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Note

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Atmospheric Photochemical Reactions Inhibited by Iodine

Abstract. The inhibition by iodine of the atmosphere photochemical reaction of olefin with nitrogen dioxide has been confirmed. The presence of iodine in concentrations comparable to those of the reactants retards the formation of aldehyde, peroxyacetyl nitrate, and aerosol as well as the disappearance of olefin. The reaction of iodine with atomic oxygen may account for this inhibition. A number of other potential inhibitors were found to be ineffective.

Photochemical reactions in the atmosphere play a crucial part in the development of several of the symptoms of smog. The oxidation of hydrocarbons initiated by the photolysis of nitrogen dioxide, with the participation of both nitric oxide and nitrogen dioxide, accounts for many of the observed facts, of which one is the formation of ozone. The addition of sulfur dioxide enhances aerosol formation. Free radi-

Table 1. Photolysis of cis-2-butene and nitrogen dioxide in air (5 ppm each) with increasing concentrations of iodine.

Iodine (ppm, vol./vol.)	Initial rate of aldehyde formation (ppm/min)
0	0.30
0.22	0.23
0.32	0.075
3.8	0.046
5.6	0.024

cals may be involved although there is doubt that chains of any length could develop in the presence of oxides of nitrogen. There have been unpublished reports that molecular iodine inhibits the formation of ozone in systems of irradiated hydrocarbon and nitrogen oxides (1). In addition to possible practical use in controlling atmospheric conditions, inhibition studies may reveal the mechanism of these reactions.

Olefins have been found to be the most active of the hydrocarbons. During photolysis of mixtures of olefin and nitrogen oxide at low concentrations in air, the olefin disappears rapidly and yields an approximately stoichiometric amount of a carbonyl compound, along with alkyl nitrate, peroxyacetyl nitrate, ozone, and small amounts of other products. The techniques of long-path infrared spectroscopy have proved particularly valuable for the study of these very dilute reactions (2, 3). Accordingly, a short series of experiments were undertaken to investigate the reported inhibition by iodine of atmospheric photochemical reactions.

As a test mixture, concentrations of 5 parts per million (ppm) each of nitrogen dioxide and cis-2-butene in normal air were used. First experiments showed that the formation of the phytotoxic compound peroxyacetyl nitrate was suppressed by the addition of iodine. A further series of experiments showed that the formation of aldehyde was also inhibited.

Instead of dosing the long-path cell with a measured amount of elemental iodine, which is corrosive to many of the metal parts, a few crystals were allowed to vaporize in the circulation system. The amount in the vapor was measured by bubbling a measured volume of the air through potassium iodide solution and estimating the resulting iodine colorimetrically. The values obtained are given in Table 1.

At these concentrations the only cis-2-butene absorption strong enough to measure was the C-H band at 3.4 microns. The products of the reaction collectively absorbed much less at this

wavelength than did the starting olefin, so that absorption decreased in the uninhibited reaction. This decrease in absorption was also inhibited by the presence of the iodine, which indicates that even the disappearance of olefin was inhibited. Since attack by oxygen atoms appears to be a major cause of olefin disappearance, the iodine may react preferentially with oxygen atoms.

The following compounds were not inhibitors of the photolytic cis-2-butene nitrogen dioxide reaction: carbonyl sulfide, ammonia, pyridine, ethylamine, ethyl iodide, trimethyl phosphite, carbon tetrachloride, dimethyl disulfide, and a series of boron compounds. Diphenylpicrilhydrazyl, a stable free radical, was not an inhibitor but it is not certain what concentration of this nonvolatile solid reached the gas phase.

In a separate but related series of experiments formation of aerosol was studied in a stirred dynamic reactor under the following specific conditions, which are believed to represent a normal daylight atmospheric condition: a 34-minute residence time, filtered laboratory air of ambient temperature and 20 percent humidity, and irradiation with black-light fluorescent lights through Pyrex glass. Aerosol formation was monitored with a forward-scattering Sinclair-Phoenix smoke photometer.

At parts per million concentrations of simple olefins, such as pentene-2 and butene-2, nitrogen dioxide, and sulfur dioxide, aerosol is formed on irradiation (4). Without the sulfur dioxide no aerosol is detected. If sulfur trioxide is substituted aerosol is not formed in the dark but is formed upon irradiation very much as it is with sulfur dioxide. Thus the photochemical oxidation of sulfur dioxide to trioxide is only one step in the aerosol formation reactions.

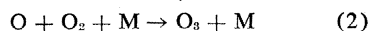
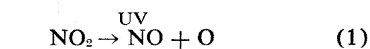
Iodine inhibition studies were performed with a system containing 2 ppm pentene-2, 1 ppm nitrogen dioxide, and 0.5 ppm sulfur dioxide in filtered air at ambient temperatures and about 20 percent relative humidity. When the iodine was 0.1, 0.25, 0.50, and 1.0 ppm, respectively, the reduction in aerosol

was 17, 46, 57, and 70 percent, respectively.

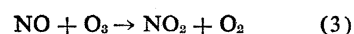
Among several inhibitors which were tried in the same photochemical system, pyrrolidine enhanced aerosol formation and produced aerosol alone in air in the dark. Phenol and 4-*n*-hexylresorcinol slightly depressed aerosol formation at concentrations of a few parts per million; 2,6-ditertiary butyl, 4-methylphenol increased aerosol somewhat. Pyrogallol, morpholine, and 2,6-ditertiary butyl, 4-methoxyphenol did not effect aerosol formation. At 0.5 and 5.0 ppm, aniline increased aerosol formation; at 5.0 ppm aniline formed aerosol without sulfur dioxide, but pentene-2, nitrogen dioxide, and irradiation were required. *N*-Methylaniline slightly depressed aerosol formation at 0.5 ppm. At 5.0 ppm it increased aerosol formation; when sulfur dioxide was eliminated aerosol was still formed provided that pentene-2, nitrogen dioxide, and irradiation were present. *N,N*-Dimethylaniline increased aerosol at both 0.5 ppm and 5.0 ppm; at 5.0 ppm aerosol was formed without sulfur dioxide and pentene-2, but aerosol was enhanced when pentene-2 was added. Addition of 100 ppm nitric oxide strongly inhibited aerosol formation.

Phenolic and amine inhibitors function as antioxidants in fats and oils by trapping radicals involved in long-chain mechanisms (5). Thus the lack of large effect on our photochemical system is further evidence that we are not dealing with long chains. Some of the amines studied could serve as nuclei in forming aerosol, but we cannot state at this time that this is via a free radical mechanism.

It might seem that the iodine-oxygen atom reaction should be fast compared to the O-atom olefin reaction in order to inhibit the latter reaction. According to present views of the mechanism (2), however, this is not true. Most oxygen atoms arising from the photolysis of nitrogen dioxide react with molecular oxygen:



The back reaction of ozone with nitric oxide:



regenerates the reactants and leads to quasi-steady state concentrations of all the individual species including oxygen atoms.

The concentration of atomic oxygen is determined by the balance between its rate of formation and its rate of reaction with molecular oxygen (Eq. 2). The rate of destruction of oxygen atoms by inhibitor must be at least comparable to the rate of reaction (Eq. 2) in order for the concentration of the atomic species to be reduced significantly. Although the inhibitor has the disadvantage of being present at a concentration six orders of magnitude smaller than that of the molecular oxygen it has the advantage that the reaction of atomic oxygen with molecular oxygen is third order.

The iodine concentrations used, while they represent traces as compared to the air, are comparable to the concentrations of the reactants. This alone would discourage practical use of this substance to inhibit the smog reaction (6).

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References and Notes

1. W. H. Hamilton, private communication from Lockheed Aircraft Corporation.
2. E. R. Stephens, in *Chemical Reactions in the Lower and Upper Atmosphere* (Interscience, New York, 1961), p. 51; P. A. Leighton, *ibid.* p. 1; C. S. Tuesday, *ibid.* p. 15.
3. E. R. Stephens, E. F. Darley, O. C. Taylor, W. E. Scott, *Proc. Amer. Petrol. Inst. Sect. III* **40**, 325 (1960); ———, *Intern. J. Air Water Pollution* **4**, 79 (1961); E. A. Schuck, G. J. Doyle, N. Endow, *Air Pollution Foundation, San Marino Calif. Rept. No. 31* (1960).
4. M. J. Prager, E. R. Stephens, W. E. Scott, *Ind. Eng. Chem.* **52**, 421 (1960).
5. C. Walling, *Free Radicals in Solution* (Wiley, New York, 1957), p. 397.
6. Sponsored by the Air and Water Conservation Committee of the American Petroleum Institute as part of a program on photochemical air pollution. The aerosol experiments were done at Perkasie, Pa., the long-path cell studies in cooperation with the University of California at Riverside.

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