

sites causing numerous diseases in fish. Finally, the method may be helpful in the control of schistosomiasis by destroying snails which act as intermediate hosts of human schistosomes.

We believe that we have now the basic principles of a method by means of which the age-old problem of protecting shellfish beds from predators can be solved. We realize, nevertheless, that our studies represent only the first steps toward achieving full control of these enemies and that many secondary problems have to be solved before the method can be recommended for general use. For example, it will be necessary to determine the effects of the chemicals on aquatic communities in general and ascertain if some of the substances used accumulate in the body tissues of mollusks, such as oysters, rendering them undesirable or dangerous as food (3).

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Sulfur Dioxide Sensitized Photochemical Oxidation of Hydrocarbons

Abstract. Near-ultraviolet sunlight is absorbed by sulfur dioxide to produce electronically excited molecules, which react with *n*-butane in the presence of wet or dry air to produce an aerosol and eventually a liquid precipitate. The product is a heavily oxidized, sulfur-containing, organic strong acid. The possible role of these reactions in photochemical air pollution is discussed.

The photodissociation of sulfur dioxide to SO and O occurs only at wavelengths below 2100 Å; at longer wavelengths an electronically excited molecule is produced (1), which is chemically much more active than ordinary sulfur dioxide. Irradiation of pure sulfur dioxide with a wavelength

Table 1. Formation of aerosol and liquid precipitate upon irradiation of sulfur dioxide and other substances in sunlight.

SO ₂	Partial pressure initially present (mm-Hg)		Aerosol formed	Liquid product formed
	<i>n</i> -butane	Air (dry)		
20	0	0	None	None
20	20	0	Light	Clear liquid
20	0	400	Light	None
0	20	400	None	None
20	20	400	Heavy	Yellow liquid
20	20	400	None in dark in 6 mo	None in dark in 6 mo
50	50	400 (dry)	Heavy within 2 min	At first yellow, later clear (all O ₂ consumed)
50	50	400 (wet)	Heavy within 2 min	

of 3130 Å produces sulfur and sulfur trioxide, with a quantum yield of about 10⁻² (2). At similar wavelengths, sulfur dioxide and oxygen yield only sulfur trioxide, again with a quantum yield of about 10⁻² (2). Gaseous solutions of sulfur dioxide and hydrocarbons, saturated or unsaturated, react photochemically with sulfur dioxide with a quantum yield of about 10⁻² to produce sulfinic acids, RSO₂H (3).

This more or less constant quantum yield for a wide variety of reactions, plus spectroscopic considerations, leads to the following interpretation: In about 99 percent of the cases sulfur dioxide absorbs near-ultraviolet radiation to form an excited singlet electronic state, which deactivates itself by fluorescence in about 10⁻⁸ sec. In about 1 percent of the cases a conversion to an excited triplet state occurs, for which fluorescence to the ground state is a forbidden process. The excited triplet state may survive for as long as 10⁻³ sec and thus may undergo up to 10⁶ collisions at ordinary pressures; however, if any of these collisions is with sulfur dioxide, or with oxygen, or with a hydrocarbon, reaction may occur. This study concerns itself with a preliminary survey of reactions of photoexcited sulfur dioxide molecules with oxygen and *n*-butane.

Two-liter Pyrex flasks were equipped with a small, easily sealed glass tube on the top and, on the bottom, with a closed-end glass tube which could be shielded from sunlight. The flask was filled with known amounts of sulfur dioxide, *n*-butane, and air, and it was sealed off. The flasks were placed in sunlight for various periods of time, from 2 minutes to 3 weeks. The bulbs were occasionally removed to a dark room and examined for aerosol by means of a Tyndall beam of light, and the nature of the liquid which settled out on the walls and into the bottom tubes was noted. Eventually these bottom tubes were broken off, and chemical, gas-phase chromatographic, or

spectroscopic studies were made of the liquid product.

The qualitative nature of the fog formation and liquid formation is given in Table 1. Whereas light fogs were formed with sulfur dioxide and butane or with sulfur dioxide and air, heavy fogs were formed only when all three components, sulfur dioxide, butane, and air, were present. No fog or liquid precipitate formed when the mixtures were kept in the dark, even after 6 months. The liquid which settled out at first was colorless (butane and sulfur dioxide, alone) or light yellow (with air), but where the liquid was struck by sunlight it turned dark brown. The half time for settling out of fog from the 2-liter flasks was about 2 hours.

The liquid products were sent through a gas-phase chromatography column at 115°C, packed with firebrick coated with *p*-tolyl cresyl phosphate. The products from a flask originally filled with sulfur dioxide, *n*-butane, and dry air at partial pressures of 20, 20, and 400 mm-Hg, respectively, showed eight major peaks and other broad minor ones; two were identified as dissolved sulfur dioxide and butane; the other peaks were not identified. Water was absent and sulfur trioxide was absent. The product from 20 mm of sulfur dioxide and 20 mm of butane showed 11 major peaks, including the two reactants. Aside from the reactants and two other, minor peaks, the products from the reaction without air and with air were all different.

The liquid products were pumped free of reactants and dissolved in alcohol, and the ultraviolet spectrum was taken. The liquid products absorb near-ultraviolet radiation much more strongly than the parent reactants; this spectrum lacks completely the vibrational structure shown by sulfur dioxide.

The liquid product was soluble in ethyl alcohol or in acetone to give a clear solution, and it was insoluble (at least in part) in carbon tetra-

Table 2. A comparison of nitrogen dioxide and sulfur dioxide as sensitizers for photooxidation of organic compounds (see Leighton and Perkins, 1).

Active wavelengths in sunlight	NO ₂ (2900 to 3900 Å)	SO ₂ (2900 to 3300 Å)
Active species	O atoms	SO ₂ * (triplet)
Quantum yield for producing active species	1	10 ⁻²
Absorption rate at 10 pphm (pphm/hr)	260	8
Principal product	Ozone and partially oxidized organic vapors and aerosols	Nonvolatile, highly oxidized organic strong acid as aerosol
Action on neutral KI	Oxidation to I ₂	No reaction
Secondary light absorption	Products absorb sunlight less strongly than do reactants	Products absorb sunlight much more strongly than do reactants

chloride, ethyl ether, or concentrated aqueous hydrochloric acid. The liquid formed a colloidal suspension in water with pH less than 2. The liquid was soluble in aqueous sodium bicarbonate solution, with strong evolution of gas. The mixed liquid products did not oxidize neutral potassium iodide solution to iodine, but it did reduce permanganate with an apparent equivalent weight of 1500 to 3000 (probably due to dissolved sulfur dioxide). The acid equivalent weight of the sample formed in the presence of air (wet or dry) was between 100 and 120. Elemental analysis of the mixed liquid product gave an average empirical formula of C₂H₄SO₅. Spot tests for organic peroxide were negative. These superficial chemical tests indicate that the mixed products are highly oxidized, sulfur-containing, organic strong acids.

These studies were made with a view toward determining the role of sulfur dioxide in air pollution. It is well established that the dominant chemical system in photochemical air pollution is that of nitrogen dioxide, sunlight, and hydrocarbons with intermediates and products including oxygen atoms, ozone, and partially oxidized hydrocarbons (4). There are many strong differences between the nitrogen dioxide sensitized photooxidation of organic materials and the sulfur dioxide sensitized photochemical system, as pointed out in Table 2. Nitrogen dioxide responds much more rapidly, and its photochemical products include easily monitored oxidants. As a corollary, nitrogen dioxide in the atmosphere is rapidly depleted by photochemical reaction, and its steady-state partial pressure is far less than 10 parts per hundred million (pphm). Sulfur dioxide responds relatively slowly to sunlight, and the principal product is a slowly settling aerosol with no easily monitored, specific chemical property. The slow photochemical reaction continues, however, throughout the day, and the concentration of sulfur diox-

ide may greatly exceed that of nitrogen dioxide. It is proposed that the slow, cumulative photoreactions of sulfur dioxide with organic material and air may add up to a significant contribution to air pollution, although its nature differs substantially from that produced by nitrogen dioxide (5).

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Connection between Archaeopteris and Callixylon

Abstract. Characters of two Upper Devonian genera, *Archaeopteris*, often considered to be a fern, and *Callixylon*, classified with the gymnosperms, have been recognized in a single specimen.

Archaeopteris Dawson (1) and *Callixylon* Zalesky (2) were among the most prominent genera of late Devonian times, similarly distributed over a wide area of the Northern Hemisphere. *Archaeopteris*, which commonly occurs as fragments of large, fernlike fronds, is known, primarily, from studies of compressions. Extensive information about the external morphology of its leaves and details of its fructifications has been accumulated. Except for the occasional observation of tracheid fragments isolated by maceration, its anatomical structure has remained, until

now, a complete blank in paleobotanical knowledge. *Callixylon*, on the other hand, is characterized, mainly, by the gymnospermous internal structure of petrified roots, stumps, logs, and branch fragments, but no knowledge of its foliage or fructifications has been previously acquired.

In North America, *Archaeopteris* is a common fossil of the continental beds of the East, having been collected in several localities from Gaspé Peninsula, Quebec, to southwestern Pennsylvania. Because of its great abundance, it is considered to have been one of the predominant elements in the vegetation during late Devonian times. It is usually thought of as a low, shrubby plant, and is so illustrated in restorations.

Petrifications of *Callixylon* are usually found in marine beds, well-known localities occurring in western New York, Kentucky, Indiana, Oklahoma, and southwestern Texas. A stump of *Callixylon* with a diameter of 5 feet has been discovered in the Woodford chert of Oklahoma, and logs 20 and 28 feet long have been uncovered in the New Albany shale of Kentucky and the Calballos chert of southwestern Texas, respectively. *Callixylon* was, therefore, a large tree, and the Oklahoma specimen has been estimated by Arnold (3) to be at least 60 feet tall.

Remains of *Callixylon* preserved in marine sediments are fragments of drift wood. The source of the western New York specimens was, undoubtedly, a land mass to the east, represented today, in part, by the continental beds of the Catskill region and adjacent areas of New Jersey and Pennsylvania. The discovery of foliage and fructifications of *Callixylon* in the richly fossiliferous beds of these areas has long been a recognized possibility, and a goal of several paleobotanists. Since the horizontal banding of groups of round-bordered pits on the radial walls of the secondary tracheids is a unique character of this genus, the recognition of this feature in even a small axis fragment of an identifiable foliage compression would be sufficient evidence for proof of common identity. Until now the searches of several paleobotanists have been fruitless, although *Callixylon* has been found occurring with *Archaeopteris* in the Oswayo sandstone in Pennsylvania by Arnold (4). However, while recently collecting (5) in beds of late Devonian age in the western part of the Catskill region, I had the good fortune to discover a large specimen (about 80 cm long) which consists of a partially compressed, pyritized stem with the internal primary and secondary structure of *Callixylon*, to which is attached fragments of several fronds of *Archaeop-*