6. Rapid observation of the absorption spectrum is possible because we use the pulsed-Fourier-transform method of spectroscopy. See R. R. Ernst and W. A. Anderson, *Rev. Sci. Instr.* **37**, 93 (1966). We used a Jeolco 100-Mhz spectrometer converted to pulsed operation; a detailed report describing this instrument is available from us on request. In principle, the same experiment could be performed on a conventional swept spectrometer by steady-state double irradiation.
7. Transfer of energy from one methyl group to a neighboring group in the same protein ("cross relaxation") would produce a similar effect. The cross bleaching due to cross relaxation and exchange can, however, be distinguished by a comparison of the results on mixed and unmixed samples.
8. A. Kowalsky [*Biochemistry* **4**, 2382 (1965)] reports a broadening of the NMR lines in a mixed oxidized and reduced sample. He attributes this broadening to electron interchange as in the present experiment.
9. W. H. Caughey, J. L. York, P. K. Iber, in *Magnetic Resonances in Biological Systems*, A. Ehrenberg, B. G. Malmstrom, T. Vanngard, Eds. (Pergamon, New York, 1967), p. 26.
10. Such a group, isolated by an extra C-C single bond from the porphyrin ring, might have a contact shift of about 0.05 times that of a ring methyl, or around ±1 ppm. See, for example, M. K. Carter and G. Vincow, *J. Chem. Phys.* **47**, 302 (1967).
11. The dipolar interaction produces a "pseudocontact" shift if the electron's *g*-tensor is anisotropic; see G. N. LaMar, *J. Chem. Phys.* **43**, 1085 (1965). The principal *g*-values have been found to be 1.24, 2.24, and 3.06 at 4°K by I. Salmeen and G. Palmer, *J. Chem. Phys.* **48**, 2049 (1968). If the $g = 3.06$ principal axis is roughly perpendicular to the heme plane, then a spin at the distance of a ring methyl group is pseudocontact-shifted zero to +5 ppm, depending on the orientation of the other two *g*-tensor axes. In myoglobin azide the largest *g* axis is perpendicular to the heme plane; see D. J. E. Ingram, *Biological and Biochemical Applications of E.S.R.* (Hilger, London, 1969), p. 255.
12. R. J. P. Williams in *Chemistry of Hemes and Heme Proteins*, B. Chance, R. W. Estabrook, T. Yonetani, Eds. (Academic Press, New York, 1966), p. 585.
13. We thank Mrs. H. Shlank for preparing our samples, and Dr. T. Fabry for suggesting the study of half-reduced mixtures to us.

4 May 1970; revised 1 July 1970 ■

Oxidation of a Polymer Surface with Gas-Phase Singlet ($^1\Delta_g$) Oxygen

Abstract. *Singlet molecular oxygen ($^1\Delta_g$) produced by the microwave discharge of ground state oxygen in a flow system was passed over a film of* cis-*polybutadiene. This treatment resulted in the formation, at the surface, of hydroperoxides which were detected by internal reflection infrared spectroscopy.*

Electronically excited molecular oxygen in its singlet state ($^1\Delta_g$) has been frequently discussed as an agent that in polluted air may be responsible for the oxidative degradation of various naturally occurring and synthetic substances (*1*). There has also been speculation on the role of singlet oxygen in producing cancer on the skins of irradiated animals treated with photosensitizing substances (*2*) and in promoting the photooxidation of polyethylene (*3*) and a variety of other substances (*4*). An important question that must be answered before one invokes a singlet oxygen mechanism to account for such surface effects is whether metastable singlet oxygen ($^1\Delta_g$) molecules can indeed survive long enough to chemically react with an environmental surface. Our results show conclusively that gaseous singlet oxygen impinges on the surface of *cis*-polybutadiene films causing the formation of the expected hydroperoxides.

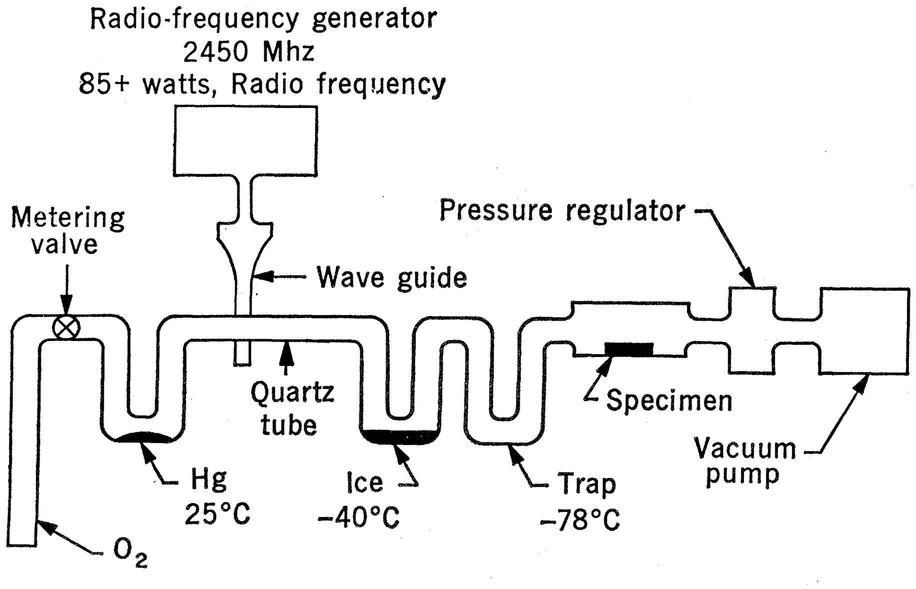

Fig. 1. Diagrammatic representation of the flow system used for polymer oxidation.

The electrodeless discharge of oxygen either by radio-frequency or microwave energy is known to produce a variety of active species including atomic oxygen, excited molecular oxygen ($^1\Delta_g$ and $^1\Sigma_g$), ozone, and some ionic components (*5*). The reaction of such a complex plasma with a large number of bulk polymers has been used to improve adhesion and alter other surface-related properties (*6*). The primary effects in those cases were attributed to atomic oxygen. Similar experiments were performed on thin films of methyl linoleate with the observation of an increase in the absorbance at 234 nm, which was interpreted as indicating the formation of conjugated hydroperoxides [R–C=C–C=C–C(OOH)R] from the attack of singlet oxygen on the 1,4-diene structure (*7*). Although singlet ($^1\Delta_g$) oxygen was produced by photosensitization and not electrodeless discharge, the mean diffusion path for excited molecular oxygen through stearate films has been determined to be 115 Å (*8*). It was estimated that in traversing that distance in the film one-half of the diffusing molecules had been deactivated.

The flow system used in our work (Fig. 1) has the advantage that all active species except singlet oxygen ($^1\Delta_g$) are removed from the gas stream before contact with the polymer surface. Tank oxygen is passed over mercury (25°C) and into a quartz tube. A wave guide focuses microwave power (2450 Mhz) so that energy couples with the gas at the center of the quartz tube. The pumping speed based on the capacity of the vacuum pump is 33.4 liter/min. The mercury vapor in the stream is oxidized, forming a mercuric oxide ring both upstream and downstream from the plasma glow. This mercuric oxide is effective in removing oxygen atoms and ozone and in enhancing the singlet oxygen ($^1\Delta_g$) concentration (*9*). Ionic species deactivate a few millimeters from the glow region (*5*). The stream is then passed over ice at −40°C to quench the singlet oxygen in its $^1\Sigma_g$ state (*10*) and then through a −78°C trap to remove water and mercury vapor carried over by the gas flow. The distance traveled by the excited molecular oxygen before it reaches the sample chamber is about 100 cm. We estimate that flow rates over this distance are of the order of 1 second. Typical oxidations are performed at an oxygen pressure of 5 torr for 5 hours. The *cis*-polybutadiene was purified by two precipitations and then cast on aluminum surfaces or sodium chloride crystals from methylene chloride solution. Films formed in this way were ~ 0.1 mm thick. The salt crystals or aluminum surfaces containing the films were analyzed by infrared transmission and internal reflection infrared spectroscopy, a technique that permits the examination of chemical changes occurring on or near the surfaces of different materials at depths of approximately one wavelength (*11*). Spectra were recorded on a spectrophotometer (Perkin-Elmer model 21).

We obtained internal reflection spectra with KRS-5 crystals and a Wilks model 12 attachment as a single beam unit. The spectra of oxidized *cis*-polybutadiene films recorded in this way (Fig. 2a) show clearly the presence of the –OOH band at 3 μ. The formation of allylic hydroperoxides from olefins is often used as a specific diagnostic reaction indicating the presence of singlet oxygen (*2*), and the oxidized *cis*-polybutadiene probably contains such a functional group. The presence of hydroperoxides was also deduced from the liberation of iodine by the reaction between *cis*-polybutadiene treated with singlet oxygen (${}^1\Delta_g$) and a saturated solution of potassium iodide in acetone. The yellow iodine color was monitored spectroscopically (maximum wavelength, 362 nm). No iodine production was observed when unoxidized films were treated in the same manner. Subsequent heating of the oxidized films at 125°C for 30 minutes in air resulted in the formation of carbonyl compounds (films were analyzed by transmission and internal reflection infrared spectroscopy) (Fig. 2b), as would be expected upon thermal decomposition of hydroperoxides. Surface effects were much greater. Films that were unoxidized and subsequently heated show essentially no spectral changes either on the surface or internally. This behavior strongly suggests that the initial surface oxidation (with singlet oxygen) of polymer films, and probably of other substances as well, tends to overcome the well-known induction period observed in thermal autoxidations.

Gas-phase reactions of singlet oxygen (*12–16*) and energy transfer from gaseous singlet oxygen to solutions of appropriate acceptors (*17*), which results in luminescent species, have been reported. In fact, singlet oxygen (${}^1\Delta_g$) can survive 3.5×10^4 collisions with the walls and more than 10^8 collisions in the vapor phase (*13*). Our results now supply firm evidence that gaseous singlet oxygen (${}^1\Delta_g$) has a long enough lifetime to cause the oxidation of a solid polymer surface some distance from the site of formation of the active agent. This effect must continue to be given serious consideration in air pollution studies since gas-phase photolysis of known air contaminants, such as aromatic substances (*18*) and ozone (*19*), results in the production of singlet oxygen, as do the exothermic reactions of several pollutants with ozone, for example, phosphite esters (*15*), ethers, and alcohols (*20*).

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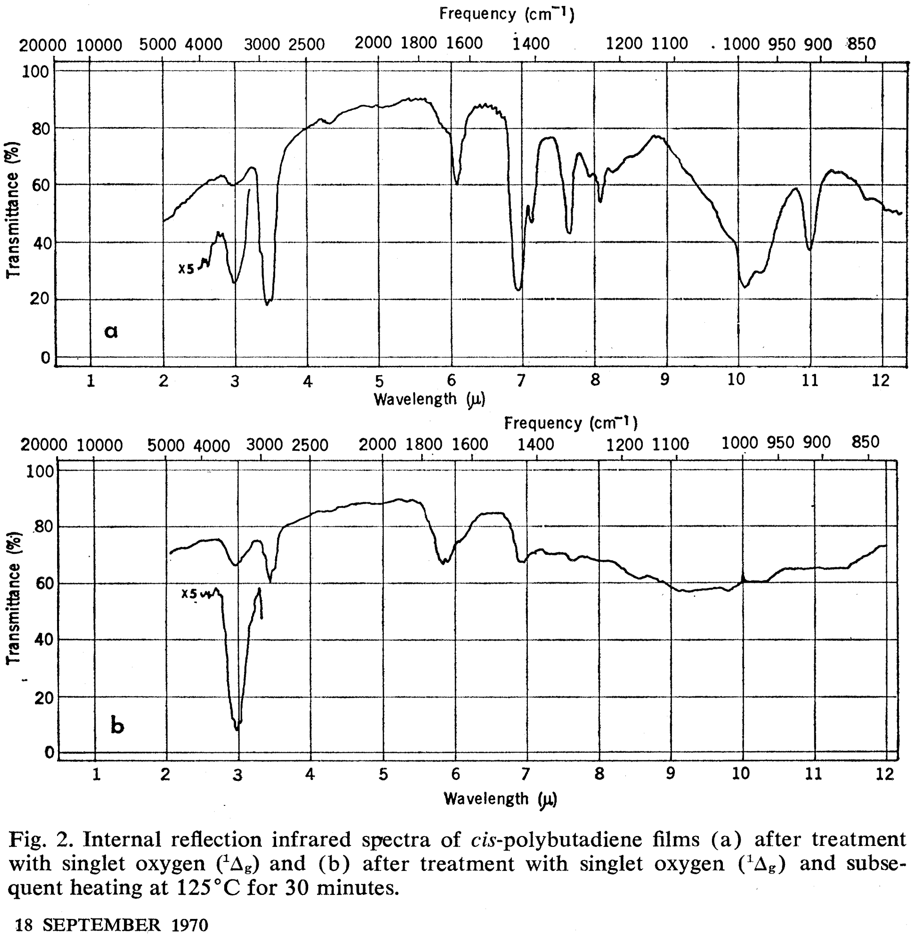

Fig. 2. Internal reflection infrared spectra of *cis*-polybutadiene films (a) after treatment with singlet oxygen (${}^1\Delta_g$) and (b) after treatment with singlet oxygen (${}^1\Delta_g$) and subsequent heating at 125°C for 30 minutes.

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21. We thank Dr. E. A. Chandross for his valuable comments concerning this manuscript.

12 June 1970