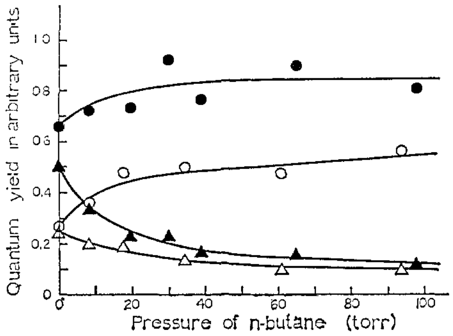

Figure 1. Variation of the quantum yield of isomerization of the *trans*-1-phenyl-2-butene with increasing pressure of *n*-butane. The circles correspond to *cis*-1-phenyl-2-butene and the triangles correspond to 1-phenyl-2-methyl cyclopropane. The open symbols denote runs with excitation at λ 252 nm while the closed symbols denote excitation at λ 266 nm.

methylcyclopropane showed the identity of these two compounds.

The effect of exciting wavelength upon the quantum yield of formation of the products is presented in Table I. The quantum yields of both II and III reach their maximum at the wavelength corresponding to the 0–0 absorption band of I, and the ratio Φ III:Φ II increases as the wavelength decreases.

Table I. Effect of Exciting Wavelength on Photolysis of *trans*-1-Phenyl-2-butene[a]

Wavelength[b] (nm)	Φ II	Φ III	Φ II/Φ III
	(in arbitrary units)		
247	0.090 ± 0.009	0.088 ± 0.009	1.02
252	0.27 ± 0.03	0.24 ± 0.025	1.13
261	0.57 ± 0.06	0.46 ± 0.05	1.24
266	0.66 ± 0.07	0.50 ± 0.05	1.32

[a] Temperature = 26 ± 1°, pressure = 0.8 Torr. [b] A Bausch and Lomb grating monochromator with linear reciprocal dispersion of 1.6 nm/mm was used with a slit width of 2 mm.

The observed decrease of the quantum yields at shorter wavelengths may be due to an isomerization of I to a benzvalene-type intermediate[7] which rapidly reverts to the starting material and thereby results in a decrease of the other photochemical processes. Such processes have been shown to occur in the photolysis of benzene and its alkyl derivatives.[8] In the case of the xylenes, where isomerization is thought to involve a benzvalene-type intermediate, the quantum yield of isomerization in the gas phase does increase at the shorter wavelengths.

When *n*-butane is added at pressure up to 100 Torr, the quantum yield of II increases while the quantum yield of III decreases as shown in Figure 1. Formation of III does not occur in the liquid phase, which can be expected from our result, since collisional deactivation is probably complete in the liquid phase.

The behavior of Φ II with respect to vibrational relaxation is quite normal in photochemical systems, but the contrasting effects of wavelength and pressure on Φ III are unusual.

While II may be formed by a conventional pathway, *i.e.*, *cis–trans* isomerization of a triplet, it is obvious that III is formed by a more complex mechanism. The effect of pressure on Φ III suggests that vibrational relaxation of an intermediate leading to III is important. This intermediate is not the initially excited singlet, but, nevertheless, must be derived from it. It is possible that this intermediate could be a hot triplet or a hot ground state but at this stage neither can be ruled out.

More quantitative results and a detailed discussion of this work will appear soon.

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On the Nature of the Oxygen Species Adsorbed on Oxide Surfaces

Sir:

We wish to report here some interesting results directly bearing on the formation of O^- and O_2^- ions on a zinc oxide surface. High-purity ZnO, prepared by the vapor-phase oxidation of zinc in gaseous oxygen,[1] vacuum outgassed at elevated temperatures (>450°), and subsequently exposed at 25° to pure hydrocarbons (*e.g.*, *n*-butane, isobutane), in the range 100–700 Torr, revealed a decrease in the intensity of the esr signal at $g = 1.96$ (attributed to either Zn^+ or oxygen vacancies[2]), and the formation of a 3-*g* valued signal shown in Figure 1a. An identical signal was also obtained on heating ZnO for 2 hr at 500° in a closed, static system, under a hydrogen or deuterium pressure of about 1 atm. While this signal is apparently similar to the triplet assigned in earlier studies[3,4] to an O_2^- species (Figure 1b), the formation of O_2^- ions on ZnO treated in a reducing atmosphere of either a hydrocarbon or hydrogen is extremely unlikely. We attribute this triplet (Figure 1a) to the formation of O^- species at the surface. A careful comparison of this signal with that obtained following low-pressure oxygen treatment of vacuum-heated ZnO (Figure 1b) reveals that the two are identical except for a slight difference between g_1 and g_1'. A statistical analysis of the g values following the different treatments established the fact that $g_1 = 2.042 \pm 0.001$ and $g_1' = 2.039 \pm 0.001$. It was also found that these two peaks are simultaneously and readily obtained (Figure 1c) upon oxygen treatment of a sample to which zinc dust has been added prior to the vacuum-heating treatment. That a slight shift in one of the three g values is all that makes the difference between

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[1] ZnO samples furnished by the courtesy of New Jersey Zinc Co., Palmerton, Pa.

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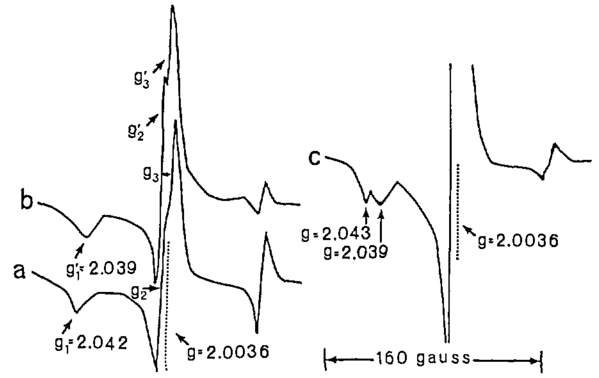

Figure 1. Esr spectra of zinc oxide (a) vacuum heated 2 hr at 500° and *n*-butane added; (b) vacuum heated 2 hr at 500°, oxygen added and evacuated; (c) 20% zinc dust added, vacuum heated 2 hr at 500°, oxygen added and evacuated. The field increases from left to right; spectra recorded at −196°.

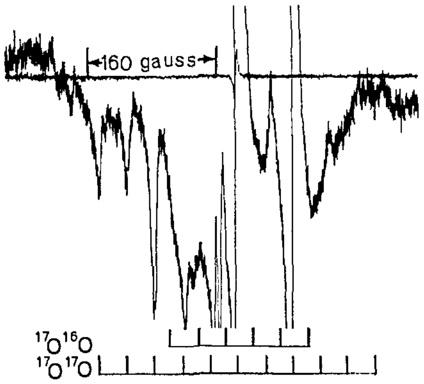

Figure 2. Esr spectrum of zinc oxide vacuum heated 17 hr at 500°, oxygen-17 added and evacuated. The hyperfine splitting constant in the direction of the $2p\pi_g$ orbital is 34.6 G. DPPH (upper spectrum) is used as a standard for the *g* value. Spectrum recorded at −196°.

O^- and O_2^- ions formed on TiO_2 has been shown recently by Micheikin, *et al.*[5]

While the mechanism of O^- formation is presently not very clear, it seems to us that in the presence of chemisorbed hydrogen (from a hydrocarbon), an electron transfer from the valence band (essentially O^{2-} electrons) to a Zn^+ species would be possible.

Using enriched oxygen (63.6% ^{17}O) a well-resolved spectrum of O_2^- (Figure 2), which shows the hyperfine lines due to the configurational interaction with the oxygen nuclei, has also been obtained for the first time on ZnO, which proves beyond doubt that molecular ions ($^{16}O^{17}O^-$, $^{17}O^{17}O^-$) are formed on its surface, following oxygen treatment of a sample which was previously heated *in vacuo* for 17 hr at 500°. However, it is obvious that such a study cannot give information on O^- species present, if any, since its esr spectrum would be similar to $^{16}O^{17}O^-$ or $^{18}O^{17}O^-$. Experiments with $Zn^{17}O$ (prepared by the oxidation of Zn dust in enriched oxygen) under conditions which lead to the exclusive formation of O^- ions at the surface are presently under way and could lead to an unambiguous identification of the species.

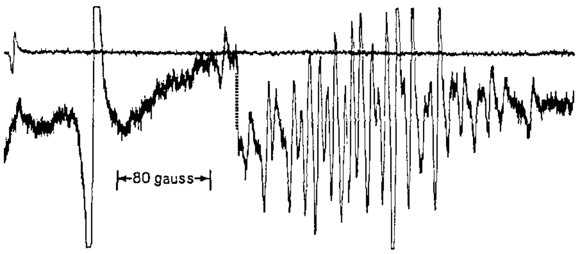

Figure 3. Esr spectrum of oxygen-17 at 15 mm, adsorbed on zinc oxide previously evacuated at room temperature. The center of the signal corresponds to a *g* value of 1.313. Spectrum recorded at −196°.

We also wish to report results on a series of experiments involving ZnO, TiO_2, MgO, and powdered porous glass, all outgassed at room temperature and treated with enriched oxygen at different pressures. A complex spectrum (Figure 3) was observed between 15 and 35 mm which was independent of the adsorbent used and appeared with identical *g* values in all cases. The spectrum was obtained at −196° but was not observable at room temperature. Its intensity increased slightly with microwave power in the range 20–200 mW. The characterization of the spectrum is not yet complete since it is obtained only with enriched oxygen. It seems that the spectrum arises from total spins of 5 and $^5/_2$ ($^{17}O^{17}O$ and $^{16}O^{17}O$). Further study of this phenomenon is presently in progress.

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Photochemistry of 5,8-Dihydro-5,8-bridged 1,4-Naphthalenediols. Structure of Photothebainehydroquinone

Sir:

As the dimeric structure suggested for photothebainehydroquinone (obtained by direct irradiation of thebainehydroquinone (**1**) with ultraviolet light[1]) did not account for its behavior with acid,[2] we examined crystals of photothebainehydroquinone hydrobromide (mp 255–257.5°. *Anal.* Calcd for $C_{25}H_{26}NO_5Br$: C, 60.01; H, 5.24; N, 2.80; Br, 15.97. Found: C, 59.81; H, 5.37; N, 2.81; Br, 16.16) by X-ray crystallography.

The crystals are orthorhombic, of space group $P2_12_12_1$, with cell dimensions $a = 10.67$, $b = 27.20$, and $c = 7.73$ Å. Since the crystal density is 1.46 g cm^{-3}, the alkaloid must be monomeric, and there are four molecules of $C_{25}H_{26}NO_5Br$ in the unit cell ($D_{calcd} = 1.48$ g cm^{-3}). The X-ray intensity data were collected by

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