This shows that oxygen is mobile on an oxygenated tungsten surface at 70°K. The low temperature spreading thus consists of diffusion on top of the already covered regions of the surface, oxygen presumably becoming adsorbed on the clean tungsten at the edge of the layer, making it possible for other molecules to diffuse over the newly covered region.[3] The layer formed at 70°K. seems to have the high work function of a layer produced at ordinary temperatures and does not undergo detectable changes below 500°K. It would therefore seem that no appreciable activation is necessary even at 70°K. for the formation of a chemisorbed layer of oxygen on tungsten. Since the gas adsorbed directly on the tip comes from a source of at least 70°K. or higher, it is impossible at present to decide whether activation is necessary at 4°K.

We hope to obtain quantitative information on these phenomena by measurements on other gases and substrates.

(3) Diffusion with a sharp boundary is known to occur in cases where the diffusant is removed by reaction with the xarrier matrix (see H. Fujita, *J. Chem. Phys.*, **21**, 700 (1953)).

INSTITUTE FOR THE STUDY OF METALS
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILL.

ROBERT GOMER
JOHN K. HULM

RECEIVED JUNE 25, 1953

EVIDENCE FOR THE EXISTENCE OF RADICALS IN THE PRESENCE OF LEWIS ACIDS[1]

Sir:

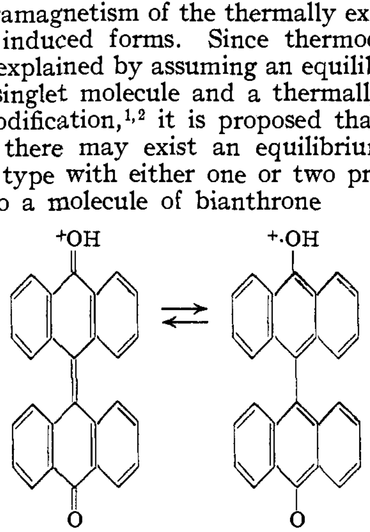
Paramagnetic resonance absorption spectroscopy has been used to detect radicals formed by several organic compounds in the presence of Lewis acids and, in some cases, the concentration of the paramagnetic species has been estimated.

Solutions of the following compounds in concentrated sulfuric acid, 96–98%, are deeply colored and were found to show paramagnetic resonance absorptions: (1) bianthrone, (2) fluorenone, (3) anthraquinone, (4) triphenylmethyl peroxide, (5) thiophenol, (6) *p*-thiocresol, (7) thio-β-naphthol), (8) diphenyl disulfide, (9) thianthrene (diphenylene disulfide).

The same compounds, when heated with anhydrous aluminum chloride to temperatures ranging from 60 to 180° and cooled to room temperature, yielded deeply colored solids which showed no paramagnetic absorptions. Bianthrone and fluorenone were also dissolved in anhydrous ether to which was added an ether solution of aluminum chloride. Both solutions were deep red and paramagnetic.

Neither the pure compounds nor their solutions in inert solvents (*e.g.*, ethanol, benzene, carbon disulfide, decalin) at room temperature showed any detectable paramagnetism. Rough preliminary estimates of the fraction of the dissolved material which exists in the radical form are: less than 5% for compounds (2), (3), and (4); 10% or more for the other compounds.

It is well known that bianthrone is thermochromic[2] and, when the deep red sulfuric acid solution is added to ice water, the bianthrone that precipitates is, for a short period of time, a dark green solid which is similar in color to the heated substance.[3] The thermally excited species is paramagnetic[4] and thus there may be a similarity in the paramagnetism of the thermally excited and the acid induced forms. Since thermochromism has been explained by assuming an equilibrium between a singlet molecule and a thermally excited triplet modification,[1,2] it is proposed that in acid solutions there may exist an equilibrium of the following type with either one or two protons attaching to a molecule of bianthrone



Herbert, Goren and Vernon[5] were unable to determine, by cryoscopic methods, whether one or two protons were taken up.

The intensity of the paramagnetic resonance spectrum of the sulfuric acid solution of bianthrone shows that about 10% of the dissolved material is in the paramagnetic form at room temperature. This is about ten times as large a fraction of excited molecules as that estimated to exist in inert solvents at room temperature.[2b] The triplet modification is thus a stronger base than the singlet form, and the acid lowers the difference in stability between the singlet and triplet species. Measurements are being made to determine accurately the equilibrium constant and the heat of reaction for this system.

Certain similarities in the colors and the paramagnetic spectra of all the thio compounds (5–9) indicate that similar species may be contributing to the paramagnetism in all these compounds. Fries and Volk[6] have reported that thiophenol in the presence of sulfuric acid, aluminum chloride, or stannic chloride yields thianthrene as a product. They also report analogous behaviors for thio-*p*-cresol and thio-α-naphthol. Stenhouse[7] reported that thiophenol is easily oxidized to diphenyl disulfide in sulfuric acid.

We are attempting to ascertain what molecular species are responsible for the unusual paramagnetic resonance spectra that are observed in the thio compounds.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

JACK M. HIRSHON
DONALD M. GARDNER
GEORGE K. FRAENKEL

RECEIVED JULY 13, 1953

---

(1) Supported in part by the Squier Signal Laboratory, U. S. Army Signal Corps.

(2) (a) W. T. Grubb and G. B. Kistiakowsky, THIS JOURNAL, **72**, 419 (1950); (b) W. Theilacker, G. Kortüm, G. Friedheim, *Ber.*, **83**, 508 (1950).

(3) G. Kortüm, W. Theilacker, H. Zeininger and H. Elliehausen, *ibid.*, **86**, 294 (1953).

(4) W. G. Nilsen and G. K. Fraenkel, submitted for publication.

(5) R. A. Herbert, M. B. Goren and A. A. Vernon, THIS JOURNAL, **74**, 5779 (1952).

(6) K. Fries and W. Volk, *Ber.*, **42**, 1170 (1909).

(7) J. Stenhouse, *Ann.*, **149**, 247 (1869).