both salts show an absorption maximum near 3200 cm.$^{-1}$ as part of the broad absorption region which extends to frequencies above 3500 cm.$^{-1}$. Very little of the observed spectrum can be attributed to ice, whose intense bands[1] at 812 cm.$^{-1}$ and 3150 cm.$^{-1}$,[2] do not appear. Except for the peaks at 2770 cm.$^{-1}$ in OH_3Cl and 2410 cm.$^{-1}$ in OH_3Br, the halides cannot be responsible either since the same bands occur in both salts.

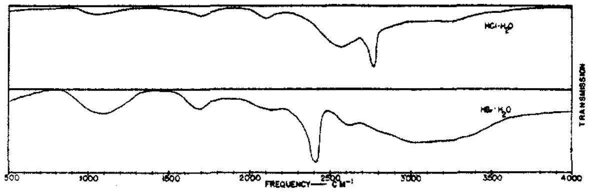

Fig. 1.—The infrared absorption spectrum of oxonium chloride and oxonium bromide at −195°.

To confirm these conclusions we have, in addition to the equimolar compounds, condensed five gas mixtures with composition ranging from 90% HCl-10% H_2O to 20% HCl-80% H_2O, and these showed the expected HCl or ice spectrum superimposed on that of the OH_3^+ ions. The compositions containing excess HCl showed two peaks very close to those reported for pure crystalline HCl at 2704 cm.$^{-1}$ and 2746 cm.$^{-1}$.[3,4] Therefore the HCl responsible for the 2770 cm.$^{-1}$ peak in the OH_3Cl sample must be in a different environment, *e.g.*, as HCl molecules in the OH_3Cl lattice. In this case they may be produced by the equilibrium

$$OH_3Cl \rightleftarrows H_2O + HCl$$

but we have not yet investigated this possibility. Altogether, the general outlines of the experimental situation seem clear, but some details still need clarification. A number of films have been prepared and the spectra were not completely reproducible, differing chiefly in two respects: (a) the shape of the diffuse absorption region between 2350 cm.$^{-1}$ and 3500 cm.$^{-1}$ and (b) the height of the peak we have ascribed to free HX molecules. Further studies are continuing.

Whereas the observed spectrum is different from either ice or the hydrogen halides, it is closely parallel to that of ammonia. The hydrogen stretching frequencies are lower and the bands broader but both of these features may be attributed to strong hydrogen bonds. It may therefore be concluded that the OH_3^+ ion which is isoelectronic with NH_3, also exists in a symmetrical pyramidal configuration. This conclusion agrees with that derived from proton resonance measurements.[5-6]

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A METHOD FOR STUDYING THE MOBILITY OF CHEMISORBED FILMS: OXYGEN ON TUNGSTEN[1]

Sir:

Field emission microscopy has been applied to the above named problem as follows: A small sealed-off field emission tube is immersed in liquid helium kept in an unsilvered Dewar vessel.[2] The tip is cleaned off by electric heating. The resultant clean single crystal emission pattern is stable indefinitely if the tube contains no helium. It is now possible to liberate gas from an auxiliary filament (also heated electrically). If the gas emitter is so placed that it is seen by only a part of the field emitter tip, only that region of the latter will become contaminated with gas. This results from the sufficiently high accommodation coefficient of the internal surface of the tube at 4°K. It is then possible to heat the field emitter electrically and thus to determine how and at what temperature mobility sets in. Field emitter temperature is determinable from its electrical resistance.

Experiments with oxygen on tungsten were carried out with three oxygen sources: A CuO, covered Pt wire, a BaO_2 covered Pt wire, and a rope consisting of ~20 strands of 0.00045 mil W wire on which oxygen condensed on cooling to helium temperatures if the tube contained oxygen at a pressure of 10 mm. The results agree for these sources and are as follows. If small amounts of oxygen are evaporated onto the tip, mobility does not become appreciable below 350°K., and increases with increasing temperature. The phenomenon is definitely not a two-dimensional melting but a gradual, activation-energy-limited diffusion process. Certain regions of the crystal, particularly those in the zone connecting (211) with (211) via (110) hold oxygen most tenaciously. On these regions (the first to show oxygen contamination in this experiment) the oxygen is bound so firmly that desorption seems to precede mobility, setting in at about 1800°K. On other planes mobility seems quite fast at temperatures where these regions cannot retain oxygen for periods of time longer than those required for diffusion to the firmly bonding regions. This is shown by the fact that it is impossible to contaminate regions other than those mentioned above if oxygen is evaporated onto a clean tip kept at 1000°K. or higher. If a previously contaminated tip is heated to these temperatures, however, very complicated patterns result, indicating that desorption is slow and may proceed via the formation of metastable surface oxides.

If oxygen is evaporated in larger amounts onto a tip kept at 4°K. totally different behavior occurs. Under these conditions spreading sets in at 70°K. It is possible to watch the film cover the tip like the unrolling of a carpet. However, the layer thus formed is not itself mobile; if the amount of oxygen initially evaporated is only enough to "unroll the carpet" part way, the sharp boundary thus formed will not change until the tip temperature is 300°K. unless more oxygen is evaporated onto the tip.

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(1) Work supported in part by Contract AF 33(038)-6534 with the U. S. Air Force.

(2) Apparatus very similar to that used is described by R. Gomer and J. K. Hulm, *J. Chem. Phys.*, **20**, 1500 (1952).

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)).

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

Sir:

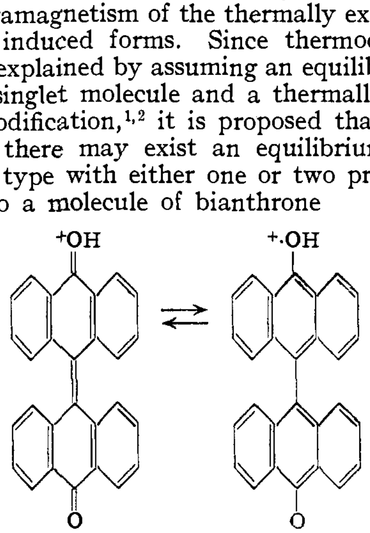
Paramagnetic resonance absorption spectroscopy has been used to detect radicals formed by several organic compounds in the presence of Lewis acids and, in some cases, the concentration of the paramagnetic species has been estimated.

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.

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[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).