AIP | The Journal of Chemical Physics

Paramagnetic Resonance Observations on the Condensed Products of Electric Discharges through Water Vapor and Related Substances

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Citation: The Journal of Chemical Physics **24**, 483 (1956); doi: 10.1063/1.1742520
View online: http://dx.doi.org/10.1063/1.1742520
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/24/2?ver=pdfcov
Published by the AIP Publishing

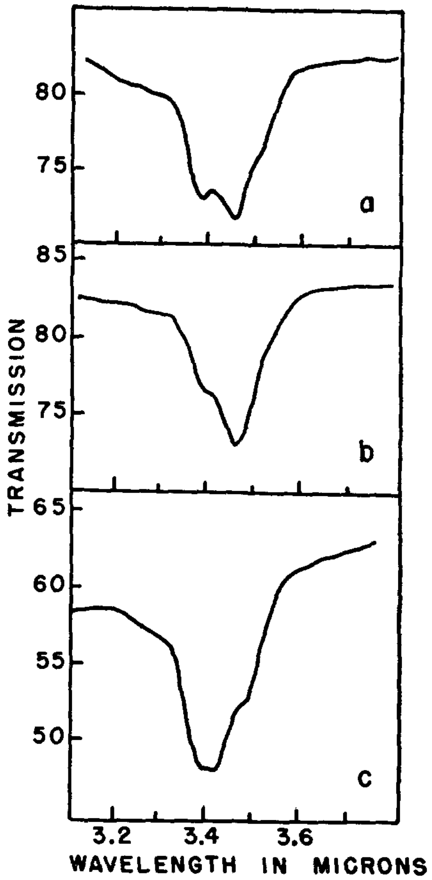
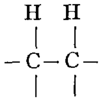


FIG. 1. Infrared spectra of (a) chemisorbed propylene, (b) chemisorbed ethylene, (c) chemisorbed acetylene.

found at less than 3.33μ. Hydrocarbons with an unsymmetric double bond as in propylene have a C=C stretching band near 6.1μ.

Chemisorbed propylene (spectrum *a* Fig. 1) has C—H stretching bands only in the paraffinic region. This, together with the absence of a band at 6.1μ, shows that there is no double bond in the adsorbed species.[2]

The paraffinic C—H stretching bands obtained from chemisorbed ethylene (spectrum *b*) could be due to either $-CH_2CH_2-$ or a saturated C_2H_2,  $-\underset{|}{\overset{\overset{H}{|}}{C}}-\underset{|}{\overset{\overset{H}{|}}{C}}-$. A band is also observed at 6.91μ which is attributed to CH_2 deformation. This band indicates that the $-CH_2CH_2-$ structure is present but does not preclude the presence of some saturated C_2H_2. Treatment with hydrogen shifts the absorption maximum from 3.46 to 3.41μ. The 6.91μ band is increased in intensity and shifted to 6.86μ. A sharp band is produced at 7.24μ. The 7.24μ band ls attributed to the symmetrical CH_3 deformation and the increase in the 6.9μ region to the superposition of the CH_3 asymmetrical deformation. These effects are evidence for the half-hydrogenated state, $-CH_2CH_3$.

The $-CH_2CH_2-$ and $-CH_2CH_3$ can be partially dehydrogenated by prolonged pumping (2 hr) at 27°C. This leaves a band at 3.43 and a weak band at 3.27μ. The 3.43μ band is attributed to saturated C_2H_2 and the 3.27μ band to olefinic C_2H_2. The saturated C_2H_2 appears to be predominant. The C_2H_2 is easily rehydrogenated to $-CH_2CH_3$. If ethylene is admitted in small doses, after a (350°C) H_2 pump-off, weak paraffinic C—H stretching bands are observed after the gas phase is pumped out. Subsequent hydrogen treatment produces intense bands indicating that this chemisorption procedure produces saturated C_2H_2 plus an easily hydrogenated carbidic species.

Spectrum *c* is obtained by chemisorption of acetylene. Its C—H stretching bands are similar in appearance to those of half-hydrogenated ethylene. Moreover, CH_2 and CH_3 deformation bands are also observed. Attempts were made to rule out effects due to residual surface hydrogen by using deuterated surfaces. However, the CH_2 and CH_3 groups are still formed indicating they are due to self-hydrogenation.

We are grateful to Dr. L. C. Roess and Dr. S. A. Francis for interesting discussions and to E. J. Bane and J. C. Webber for help with the experimental work.

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[2] See P. H. Emmett, *Catalysis* Vol. III for review articles pertaining to subjects discussed in this paper.

Paramagnetic Resonance Observations on the Condensed Products of Electric Discharges through Water Vapor and Related Substances*

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(Received December 5, 1955)

PARAMAGNETIC resonance absorption has been observed in the material formed by passing water vapor through an electric discharge and condensing the products on a liquid nitrogen cooled surface. A typical photograph of an absorption line at 23 000 Mc is shown in Fig. 1. An absorption line of the same appearance was obtained when the following modifications were made: (a) D_2O used instead of H_2O, (b) over 90% H_2O_2 used instead of water, (c) hydrogen passed through the discharge and then blended with oxygen, and (d) NH_3 used instead of hydrogen. In all cases the samples were examined at liquid nitrogen temperature. The discharge apparatus in most cases was similar to that described by Jones and Winkler.[1] Samples prepared in the above manner had a pale yellow color, and in a typical warming experiment the color bleached in the vicinity of −135°C accompanied by the disappearance of the paramagnetic absorption. At a higher temperature the samples evolved considerable oxygen and no hydrogen, essentially as reported[1] before for discharges through H_2O. No evidence could be found for the presence of atomic hydrogen[2] in any of the samples examined.

At 23 000 Mc the main peak appeared at $g=2.0085$ with the shoulder at about 2.027. The shoulder on the line was much less pronounced in observations made at 9000 Mc. The absorption line was at first considered to be two unresolved absorption lines, each, perhaps, being caused by different free radicals. The shape of the line remained the same, however, for materials prepared in greatly different manners and also in partially annealed materials where the line was very much weakened. Recently Sands[3] observed similarly shaped lines in glasses and clearly showed that lines of this appearance can result from a species having an anisotropic g value and being averaged over random orientations. The present results can be explained satisfactorily in this way. Possible free radicals that could give this behavior are OH and HO_2. In these cases there could be residual unquenched orbital angular momentum giving rise to an anisotropy. Hyperfine interactions with the hydrogen would be expected to be quite small and rather completely masked by the over-all envelope of the anisotropic line. This is consistent with the finding that preparations made from D_2O appeared to be no different from those made with H_2O.

An estimate has been made of the total number of unpaired electrons present by comparing integrated areas of the absorption line with areas of lines from known weights of hydrazyl radical. The assays were probably good to a factor of 2. Samples assayed in this manner were then warmed and the amount of H_2O_2 chemically

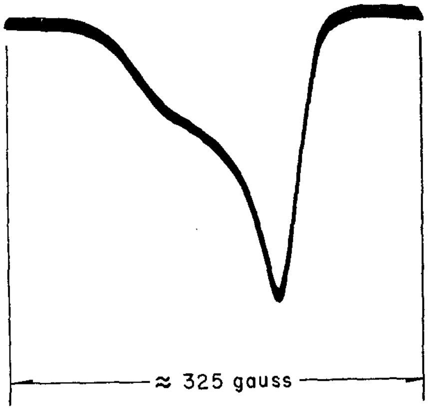

FIG. 1. The paramagnetic resonance absorption line observed at 23 000 Mc.

assayed. The ratio of molecules of H_2O_2 formed to unpaired electrons was found to be 154 in a sample prepared from water vapor. Somewhat similar ratios of 91 and 125 were found in material prepared from H_2O_2 and from hydrogen gas with subsequent addition of oxygen before condensing. Peroxide concentrations around 50% are found in the product made from H_2O[1]. On this basis the samples contained roughly 0.3% by weight of radical if HO_2 is assumed or 0.15% for OH. Giguère[4] has given infrared spectroscopic evidence for the presence of HO_2 in such materials. Foner and Hudson[5] have analyzed with a mass spectrometer the OH, HO_2, and H_2O_2 content in the gas phase from the reaction of H with O_2. Their results indicate that if HO_2 is present in the frozen, glassy deposit, it was formed on the surface. On the basis of this evidence it would then appear that HO_2 is a likely radical giving rise to the absorption line in Fig. 1 and that the approximate 0.3% by weight content was built up from radical formation at the surface as the material condensed.

* This work was performed for the U. S. Atomic Energy Commission.

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Hydration Effects in Chlorine-35 Nuclear Spin Resonance*

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(Received October 18, 1955)

STRIKING evidence for the infrequent exchange of hydrate water with solvent in aqueous solutions of some paramagnetic ions results from observations on Cl^{35} nuclear spin resonance. The 0.2 gauss line width[1] between points of maximum slope for Cl^- in aqueous NaCl is apparently the uncertainty-principle width owing to the short lifetime of the nuclear spin states (short thermal relaxation time). If this assumption is correct, addition of paramagnetic ions to NaCl solutions should broaden the Cl^- line because of the relaxation induced by the large fluctuating magnetic fields of the ions. Starting with 3 M NaCl, the line amplitude is diminished and its width increased by Mn^{++} or Cu^{++} in concentrations of 2×10^{-4} M. Beyond a 6×10^{-3} M concentration of either ion the line is so broad that it escapes detection. The reagent-grade NaCl probably contained enough such impurities to give the observed line width. At 0.1 M concentrations of the ions Ti^{+++}, Cr^{+++}, Fe^{+++}, Co^{++}, and Ni^{++} in 3 M NaCl the relative signal amplitudes compared to the reference solution (3 M NaCl) are 0.1, 1.3, 0.07, 1.1, and 0.6, respectively. The order Mn^{++}, Cu^{++}, Fe^{+++}, Ti^{+++}, Ni^{++}, Co^{++}, and Cr^{+++} is that of decreasing effectiveness in relaxation. Disregarding hydration, the order should be that of decreasing magnetic moment or (Fe^{+++}, Mn^{++}), Co^{++}, Cr^{+++}, Ni^{++}, Cu^{++}, and Ti^{+++}. For Co^{++}, Cr^{+++}, Nd^{+++}, and Sm^{+++} the relaxation effectiveness is low enough so that in dilute solutions of the pure salt the signal amplitude rises with concentration. Initial amplitude increases are found also in 3 M NaCl solutions dilute in Fe^{+++}, Ti^{+++}, Co^{++}, and Cr^{+++}. The line width for all ions studied increases from the lowest concentrations. The maximum amplitude for $CoCl_2$ occurs at 0.6 M, while it is at 1.4 M for $CrCl_3$. The latter compound shows a Cl^- signal even at 3 M. At 1.4 M, the signal amplitudes for $CrCl_3$ and $NdCl_3$ are, respectively, 0.6 and 1.4 times those of 3 M NaCl. On adding Cr^{+++} to 3 M NaCl, the maximum amplitude appears at 0.4 M $CrCl_3$. Thus, the maximum amplitude occurs at the same chloride ion concentration in the two cases.

The order of relaxation effectiveness is not the same as that for protons,[2,3] but there it is probably the closeness of approach of the hydrate protons which is significant. Even for proton relaxation, Co^{++} shows an apparently low value of effective magnetic moment.[2] The paramagnetic anion $Fe(CN)_6^{---}$ at concentrations up to 1 M had no effect on Cl^- line amplitude, width, or position in 3 M NaCl, indicating a surprising lack of relaxation effectiveness.

The exchange of hydrate water in $Cr(H_2O)_6^{+++}$ for solvent has a half-period of 40 hours, while for Co^{++} and Fe^{+++} the reaction appears to be complete in less than two minutes.[4] No corresponding rate information appears to be available for Ti^{+++}, Mn^{++}, Ni^{++}, and Cu^{++}. Mn^{++} and Cu^{++} probably exchange hydrate water with extreme rapidity and thus allow frequent close contacts with Cl^- ions. The activation energy for $Cr(H_2O)_6^{+++}$ water exchange has been given as 10 kcal per mole.[5] The order of increasing activation energies should be ascertained for comparison with the relaxation-effectiveness series.

The line in NaCl was shifted to weaker fields by Cr^{+++}, Co^{++}, Ni^{++}, and Cu^{++}, while for Sm^{+++} the reverse was true. Ti^{+++}, Mn^{++}, Fe^{+++}, and Nd^{+++} showed no shift.

A detailed account of chloride and perchlorate ion resonance will be published.

Thanks are due Fricis Dravnieks who operated the spectrometer and to my colleagues R. Lumry, W. Reynolds, and Z. Z. Hugus for helpful discussions. The research was made possible by grants-in-aid from the Graduate School of the University.

* This research was supported in part by the U. S. Air Force under Contract AF 18 (600)-479, monitored by the Office of Scientific Research, Air Research and Development Command.

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Abundance of Free Atoms in Solid Nitrogen Condensed at 4.2°K from a Gas Discharge*

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(Received December 8, 1955)

EVIDENCE for the presence of nitrogen atoms in the solid condensed at 4.2°K from a nitrogen gas discharge has been reported.[1] This evidence consists mainly of a glow observed during the operation of the discharge and an afterglow persisting for several minutes, followed by a blue afterglow which appears at some higher temperature during the warming of the apparatus. The present experiments show that the latter afterglow probably occurs between 28°K and 35°K. Partial interpretation of the spectra of these glows has been proposed by Herzfeld and Broida in terms of the interaction of nitrogen atoms and molecules with the solid.[2]