

Electron Spin Resonance Absorption of Perylene in Sulfuric Acid Solution

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Vibrational Spectra for Oxalate Ion in Coordination Compounds

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RAMAN displacements and infrared wave numbers have been obtained for oxalate ions in $K_3[Al(Ox)_3] \cdot 3H_2O$. The observed infrared and Raman bands are given in Table I. Since there are

TABLE I. Comparison of observed and calculated fundamental frequencies for *cis* $(COO)_2^{2-}$.

Raman (aqueous solution)	$\Delta\nu$	I	Infrared (solid)	I	ν_{calc}		Assignment
					Set I	Set II	
357	m	a	315	322	$\nu_5(a_1)$
442	w		436	458	$\nu_4(a_1)$
570	m		562	573	$\nu_{11}(b_1)$
799	w	805	s		774	782	$\nu_{10}(b_1)$
910	m	908	s		879	870	$\nu_3(a_1)$
1346	w	1305	s		1293	1305	$\nu_9(b_1)$
1417	s	1406	s		1340	1402	$\nu_2(a_1)$
1670	s	1658	s		1665	1664	$\nu_1(a_1)$
1737	s	1724	s		1795	1790	$\nu_8(b_1)$

* Not investigated below 700 cm^{-1} .

bands that occur both in the Raman and in the infrared spectrum, it is to be expected that oxalate ions in this complex have not the plane symmetrical form (point group V_h) but perhaps *cis* form

TABLE II. Potential constants for *cis* $(COO)_2^{2-}$ (10^8 dynes/cm).

Type	Set I*	Set II
K(C—C)	2.10	2.94
K(C—O ₁)	6.20	5.68
K(C=O ₂)	9.10	9.10
H(O ₁ —C=O ₂)	0.60	0.77
H(C—C—O ₁)	0.45	0.42
H(C—C=O ₂)	0.55	0.70
F(C...O ₁)	0.40	0.40
F(C...O ₂)	0.60	0.50
F(O ₁ ...O ₂)	1.00	0.83

* See reference 1.

(point group C_{2v}). The equilibrium values of the bond distances and bond angles used are the same as those for oxalic acid¹ and the potential constants are given in Table II. The calculated wave numbers are compared with the observed values in Table I.

¹ H. Murata and K. Kawai, *J. Chem. Phys.* **25**, 589 (1956).

Electron Spin Resonance Absorption of Perylene in Sulfuric Acid Solution

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IT has been reported that electron spin resonance absorption was detected in sulfuric acid solutions of certain organic molecules containing oxygen or sulfur atom, e.g., dianthrone, thianthrone.^{1,2} In the present work using the same solvent spin resonance absorption ten times stronger than that of dianthrone was observed at room temperature for perylene which is a pure hydrocarbon, and it was found that the strength of this absorption decreased with decreasing temperature, suggesting that it was due to an excited triplet state.

The measurements were carried out at a frequency of about 9000 mc/sec covering the range from room temperature to liquid air temperature. The absorption intensity of perylene solution was determined comparing with diphenyl picryl hydrazyl and its spectroscopic splitting factor was found almost the same with that of D.P.P.H. No detectable absorption was observed in perylene itself and in any of its solutions in benzene or in pyridine.

The ratio of absorption intensity of perylene to that of D.P.P.H., which should represent the relative concentration of unpaired spins, is determined in the range of temperature studied (Fig. 1).

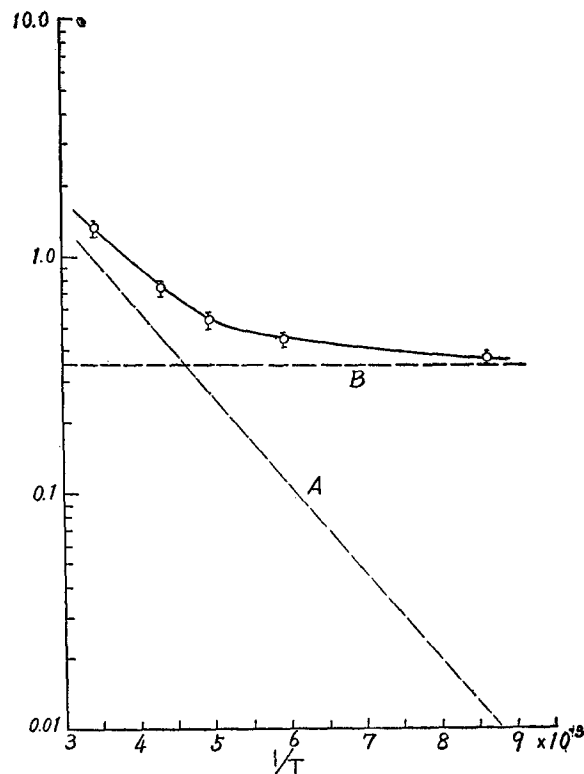


FIG. 1. Temperature dependence of spin resonance absorption intensity of sulfuric acid solution of perylene. Ordinate: the ratio of the absorption intensity of sulfuric acid solution of 8 mg perylene to that of 0.7 mg D.P.P.H. Abscissa: the reciprocal of absolute temperature.

At a glance at Fig. 1, it is seen that the absorption curve consists of two parts which are denoted by dotted lines A and B. Judging by their temperature dependencies, it may be considered that A represents the absorption coming from a triplet state while B arises from free radicals.* From the slope of line A, the energy separation ΔE between the triplet and ground levels is evaluated as 1.7 kcal. The ratio of the susceptibility of perylene solution to that of D.P.P.H. at room temperature is calculated from the population of the excited triplet state including the free radical component, resulting in the value of 48 mole %, which is in good agreement with the ratio of susceptibilities of 41 mole % determined from comparison of the observed intensities of perylene solution and D.P.P.H. at room temperature.

The spin resonance absorption is also observed in the precipitates obtained by throwing the sulfuric acid solution of perylene into ice water. Its intensity becomes small compared to that of the sulfuric acid solution and the ratio of this intensity to D.P.P.H. is constant in the range of measured temperatures. This fact seems to indicate that there exist some free radicals within. Further, it supports the above view that there are two origins in the absorption of acid solution of perylene.

The spin resonance absorption of the sulfuric acid solution of dianthrone and its precipitates similarly obtained are also studied,

These intensities are inversely proportional to the absolute temperature, that is, the numbers of unpaired spins remain constant. Very likely therefore, these absorptions are due to free radicals and not to triplet state.¹

A more detailed description of this work will be published elsewhere.

We wish to present our sincere thanks to Professor K. Higasi for his kind interest and to Professor Y. Nagai and his collaborators, University of Tokyo for the gift of perylene which was specially prepared for the present experiment.

¹ Hirshon, Gardner, and Fraenkel, *J. Am. Chem. Soc.* **75**, 4115 (1953).

² J. E. Wertz and J. L. Vivo, *J. Chem. Phys.* **23**, 2193 (1955).

* We refer "the free radicals" only to the ground state of $S = \frac{1}{2}$.

Spectroscopic Observations on Pentaborane-Air Flames and Explosions*

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NO spectroscopic studies have been reported previously for the combustion of boron hydrides. These compounds are of particular interest owing to their unusually high flame speeds in their reactions with oxygen. This letter describes some recent work on pentaborane (B_5H_9) diffusion flames in air and on premixed pentaborane-air explosions at atmospheric pressure.

Gaseous pentaborane¹ was diluted with nitrogen in a storage tank. The resulting mixture was burned as a diffusion flame above a porous metal disk in air. For high nitrogen dilution the blue reaction zone was surrounded by a white mantle. Thermocouple traverses showed that the maximum temperature of these diffusion flames is about 500°K.

Oxygen was added to the nitrogen-diluted B_5H_9 in a flow system to prepare pentaborane-air mixtures. These mixtures were ignited by an electric spark giving rise to a rapidly expanding flame kernel. The duration of such explosions is of the order of a millisecond.

Spectra were taken with a F/4 Hilger spectrograph giving a resolution of about 4 Å at 5200 Å (glass) and 0.8 Å at 2600 Å (quartz). Eastman 103a-O, 1N, and 1F plates were used, permitting a survey of the spectral region from 2200 to 8500 Å.

Figure 1(a) shows the spectrum obtained from the inner cone of a diffusion flame in air of pentaborane diluted with nitrogen in the ratio of 1 to 69.5. The main spectral feature observed were the α bands of BO between 3370 and 6200 Å due to the transition from the $A^2\Pi_1$ state to the $X^2\Sigma^+$ ground state. In addition, a weak system of diffuse bands was observed in the same region and found to be identical with the so-called "boric acid fluctuation band."² No emission was observed at wavelengths shorter than 3350 Å or longer than 6400 Å. These spectra were obtained under conditions in which the white mantle covered the entire inner cone. In the absence of this mantle the exposure time had to be increased by a factor of six to obtain spectra of comparable intensity.

Figure 1(b) shows the spectrum obtained from 12 consecutive explosions of a lean pentaborane-air mixture (equivalence ratio = 0.78). The only spectral feature observed were the diffuse "boric acid fluctuation bands" in the spectral region from 3850 to 6350 Å. In agreement with Singh² we find that some of the bands have heads and are degraded to longer wavelengths. In addition, there is a band with a head near 4080 Å which is degraded to the violet. The α bands of BO observed in the diffusion flame were not found in the explosion spectra.

Singh³ expressed the opinion that the diffuse bands in the region from 3850 to 6350 Å are due to a transition of BO with the upper state about 64 000 cm^{-1} above the $X^2\Sigma^+$ ground state. There is now, however, quite conclusive evidence that the emitter of the "boric acid fluctuation bands" is B_2O_3 and not BO.⁴ This was

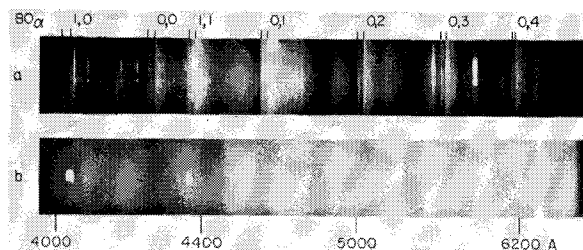


FIG. 1. (a) Spectrum of a pentaborane-nitrogen diffusion flame ($B_5H_9/N_2 = 1/69.5$). Eastman 1F Plate, 18 minute exposure, F/4 glass spectrograph. The Hg comparison spectrum is at the center. (b) Spectrum of pentaborane-air explosions. Equivalence ratio = 0.78. Eastman 1F Plate, 12 exposures, F/4 glass spectrograph.

established by a photometric study of the vapor over liquid B_2O_3 which showed that the spectral intensity of these bands varied with temperature in the same manner as the equilibrium vapor pressure of B_2O_3 . It is interesting to note that a penta-atomic species such as B_2O_3 is stable at the high temperature reached in the pentaborane-air explosions ($\sim 2500^\circ K$).

No bands of BH, BN, or OH were observed in either the diffusion flame or the explosions. Furthermore, no BO bands were observed in the explosions and only the α system of BO was found in the diffusion flames. It is possible that the observed emission from the high-temperature explosions is thermal. However, the appearance of BO- α bands and B_2O_3 bands in the low-temperature ($\sim 500^\circ K$) diffusion flame strongly indicates a chemiluminescent origin of the radiation in this flame.

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¹ The pentaborane was obtained through the courtesy of the Olin Mathieson Company.

² N. L. Singh, *Proc. Indian Acad. Sci.* **29A**, 424 (1949).

³ N. L. Singh, *J. Sci. Research Banaras Hindu Univ.* **2**, 147 (1951).

⁴ Soulen, Sthapitanonda, and Margrave, *J. Phys. Chem.* **59**, 132 (1955).

Nitryl Fluoride: A New Method of Preparation, Nuclear Magnetic Spectrum and Structure

RICHARD A. OGG, JR., AND JAMES D. RAY

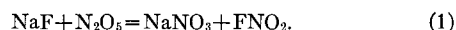
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THE nitryl halides present an important example of the type of error incumbent in choice of molecular structure based on classical methods of chemical reactivity. Thus in the case of nitryl chloride, Schmeisser's¹ data lead to the conclusion that the chlorine atom is attached to oxygen. Yet, the conclusion of Ryason and Wilson² based on the infrared spectrum of nitryl chloride as confirmed by the microwave spectrum observed by Smith and Magnuson,³ and the completely parallel infrared spectrum of nitryl fluoride of Dodd, Rolfe, and Woodward⁴ is that the halogen atoms are attached to nitrogen.

This paper gives nuclear magnetic resonance data which corroborates existing spectral data in a completely unambiguous fashion.

Nitryl fluoride was prepared by a new method not dependent on the use of elemental fluorine. Equation (1) represents the stoichiometry of the new reaction.



The reaction was carried out in the apparatus of Fig. 1, which was attached to a vacuum system equipped with a glass Bourdon gauge. All joints and stopcocks were lubricated with Halocarbon grease.

Nitrogen pentoxide was prepared by the reaction of dry ozone with dry nitrogen dioxide.

Sodium fluoride was placed in the bottom of tube B and a small amount at D. While the system was open to a high vacuum pump,