field produced by the oxygen of the oxovanadium(IV) radical overshadows any minor changes in spin-orbit interaction produced by the adsorbent. The hyperfine structure intervals, however, do vary from one adsorbent to another. The interval is largest in the two sulfonic acid-type cation exchangers, slightly smaller on charcoal, and much smaller when bonding to nitrogens on the anion exchanger occurs.

The magnitude of the hyperfine structure interaction (about 0.018 cm.$^{-1}$ for $|A|$) indicates that the promoted s-electron hypothesis of Abragam and Pryce[3] may also be required for oxovanadium(IV). The decrease of the splitting with increase of covalent character in the bonding suggests a shift of the magnetic electron toward the ligand. The molecular orbital theory developed by Stevens and Owen[4] predicts such an effect.

It would also be interesting to know the signs of A and B for oxovanadium(IV) in order to permit comparison with possible theory. Only the absolute values of the hyperfine structure constants are obtained by measuring the splittings, however. Consequently, recourse must be made to indirect arguments. In certain cases, at least, the signs may be inferred from an examination of the variation of the absolute values of A and B as the amount of covalent bonding is varied. For example, inspection of equations 7 and 8 for the hyperfine structure constants of Cu(II) reveals that increase of covalent bonding corresponds to larger values of κ and the more negative values of A and B. This means that the absolute value of the splitting constant will increase if the sign is negative and decrease if the sign is positive. Table II illustrates the application of this fact to the Cu(II) samples examined in this research. The absolute value of A, which according to equation 7 has a negative sign, increased as the amount of covalent bonding increased.

The observation by Pake and Sands[19] of an eight-line spectrum for oxovanadium(IV) in aqueous solution confirms the presence of an isotropic contribution to the hyperfine structure. Further, because of both Cu(II) and V(IV) having $3d^9$ ground states it is reasonable to suppose that A and B for oxovanadium(IV) are given by equations of the same general form as equations 7 and 8 and therefore A and B would both become more negative as the configuration interaction constant κ increases.

We have observed that the absolute values of both A and B increase as the covalent bonding increases. Hence, we may conclude that both A and B are negative.

The thirteen line spectrum observed by Kozyrev[13] for oxovanadium(IV) salts in non-aqueous solutions at 90°K. is undoubtedly a random pattern of the sort observed in this investigation. The reduction of molecular motion at the low temperature would produce a random orientation of the symmetry axes such as occurred in the powder spectra reported here. Interpretation of Kozyrev's results in this manner leads to $g_{\|} = 1.92$; $g_{\perp} = 1.960$; $A = 0.0178$ cm.$^{-1}$; $B = 0.0070$ cm.$^{-1}$; which are in good agreement with the results of this investigation.

Acknowledgments.—This work was supported, in its initial stages, by the Office of Naval Research through contract Nonr 02300, NR358,232. We are indebted to Professor Clyde Hutchison, Jr., University of Chicago, for advice on the construction of the spectrometer.

[19] G. E. Pake and R. H. Sands, *Bull. Amer. Phys. Soc.*, **29**, No. 8, 18 (1954).

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE CATHOLIC UNIVERSITY OF AMERICA]

Absorption Spectra of Some Active Species[1]

BY FRANCIS OWEN RICE AND RONALD B. INGALLS

RECEIVED JUNE 19, 1958

We have measured the absorption spectrum of the blue solid obtained in the thermal decomposition of HN_3 as well as those of S_2, RS (where R represents various organic radicals and $(NH_2NH)_n$. Films were deposited in a plane aluminized quartz surface kept at liquid nitrogen temperatures and the percentage of absorbed monochromatic light over the range 20,000 to 3000 Å. was measured. The measurements are only semi-quantitative because we were not successful in preventing considerable scattering of the light by the film.

Recent work in this Laboratory has shown that it is possible to decompose various compounds in a flowing system at low pressures and freeze out active species on a liquid nitrogen cooled surface. In this way colored deposits were obtained which are stable indefinitely at liquid nitrogen temperatures, are usually paramagnetic, and always undergo on warming (at temperatures below −100°) a transition to stable colorless compounds. It seemed desirable to obtain the absorption spectra of the colored materials in the visible, near ultraviolet and near infrared. In this paper we shall describe the results of a spectroscopic study of the blue deposit (possibly a polymer of NH) formed by the decomposition of hydrazoic acid,[2] the purple deposit (S_2) formed from sulfur vapor,[3] the yellow and red deposits[4] formed by the decomposition of symmetrical organic disulfides (probably RS) and the yellow deposit formed by the thermal decomposition of hydrazine[5] (possibly the hydrazyl radical, NH_2NH or tetrazane, $NH_2NHNHNH_2$).

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[1] This work was supported in part by Contract AT-(40-1)-1305.

[2] F. O. Rice and M. J. Freamo, THIS JOURNAL, **73**, 5529 (1951); **75**, 548 (1953).

[3] F. O. Rice and C. Sparrow, *ibid.*, **75**, 848 (1953).

[4] J. Michaelson, Ph.D. Dissertation, Catholic University of America, 1955.

[5] F. O. Rice and F. Scherber, THIS JOURNAL, **77**, 291 (1955).

Experimental

The essential part of our experimental set up consisted of an aluminum-backed plane quartz window fitted in an apparatus, which was sealed into an inner vertical quartz tube filled with a low boiling liquid such as liquid nitrogen so as to cool the mirror to the boiling point of the cooling liquid. This tube could be rotated about the 34/45 standard taper so that the quartz mirror faced the exit end of the furnace tube. Thus the radicals leaving the furnace condensed on this cold surface.

After a suitable deposit was obtained, the inner tube was rotated again about the 34/45 standard taper through an angle of 90° without breaking the vacuum, so as to bring the quartz mirror with its deposit, parallel to the plane quartz window which formed part of the outer wall of the apparatus. The absorption spectrum of the deposit could then be taken by passing light through the outer quartz window and the deposit on the cold mirror and measuring the intensity of the reflected light.

For taking the spectrum of a deposit a monochromatic beam of light from a Beckman model D Spectrophotometer first strikes the deposit and after passing through is reflected by a second mirror and then onto a photo cell. By comparison of the intensity of the reflected light with and without a deposit the absorption curve can be obtained over the range 20,000 to 3,000 Å. We did not go to wave lengths shorter than 3,000 Å., partly because of the necessity of changing the lamp and partly because of the relatively strong absorption in the ultraviolet of stable species which condense out with the free radicals.

We had considerable trouble with crystallization and consequent general scattering of the light by the films. We found that the light scattering could usually be reduced enough by putting the deposit on very slowly. By freezing out a gaseous mixture of the free radicals and a hydrocarbon such as 2,2,4-trimethylpentane (m.p. −107°), we always obtained a film suitable for spectroscopic measurements.

Results

Figure 1 shows the spectrum of hydrazoic acid frozen on the cold mirror before and after irradiation by the unfiltered light from a high pressure quartz Hg lamp at a distance of one foot. Pure hydrazoic acid shows a broad absorption band with a maximum absorption at 15,000 Å. and no other absorption until wave lengths shorter than 3,300 Å. When it is illuminated at −200° a new band appears having a center at about 6,500 Å. This band is rather broad and is presumably responsible for the blue color. A second and smaller band also appears having a center at about 3,600 Å. Figure 2, curve 1, shows the absorption spectrum of the blue material frozen out from the pyrolysis products of hydrazoic acid on a liquid nitrogen cooled surface. The absorption band at 6,500 Å. is clearly present and there is some indication of a band at 3,600 Å. Curve 2 shows the absorption spectrum of the blue solid frozen out from the electric discharge decomposition of hydrazoic acid. It also appears where bands at 6,500 and 3,600 Å. which have broadened sufficiently to overlap.

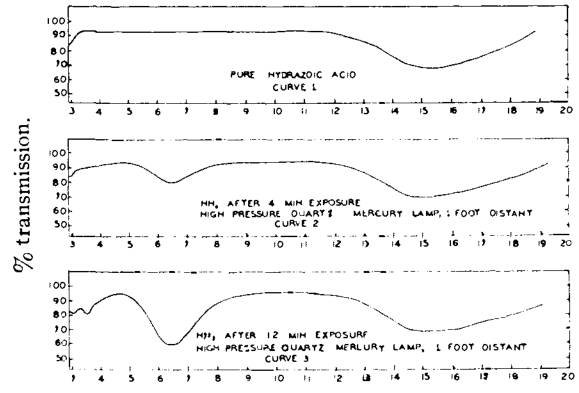

Fig. 1.—Absorption spectra of hydrazoic acid before and after illumination by ultraviolet light.

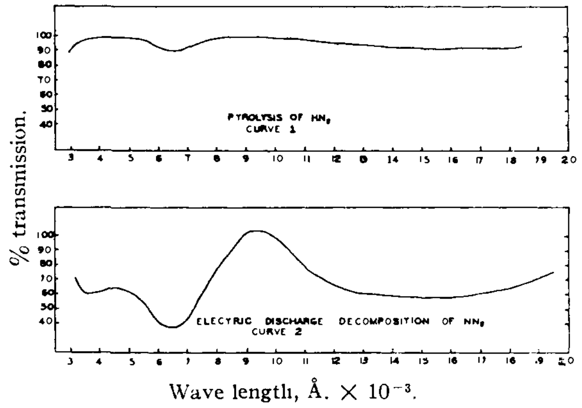

Fig. 2.—Absorption spectra of the blue material formed by the pyrolysis and electric discharge decomposition of hydrazoic acid.

In Fig. 3, we show the effect of temperature on the absorption spectrum of the blue material diluted by 2,2,4-trimethylpentane. At liquid nitrogen temperatures the blue material is stable indefinitely, but upon warming to −125° the undiluted material changes suddenly to an opaque white solid. If a mixture of hydrazoic acid and a hydrocarbon is frozen out at −200° and photolyzed, however, it can be warmed to boiling methane temperatures where the disappearance of the blue material proceeds at a measurable rate and may be followed spectroscopically because this solution remains transparent upon warming. At −161° (the boiling point of liquid methane) both absorptions bands gradually disappear, first the one at 3,600 Å. followed by the one at 6,500 Å. The fact that the two bands disappear at different rates suggests that they are due to two different species.

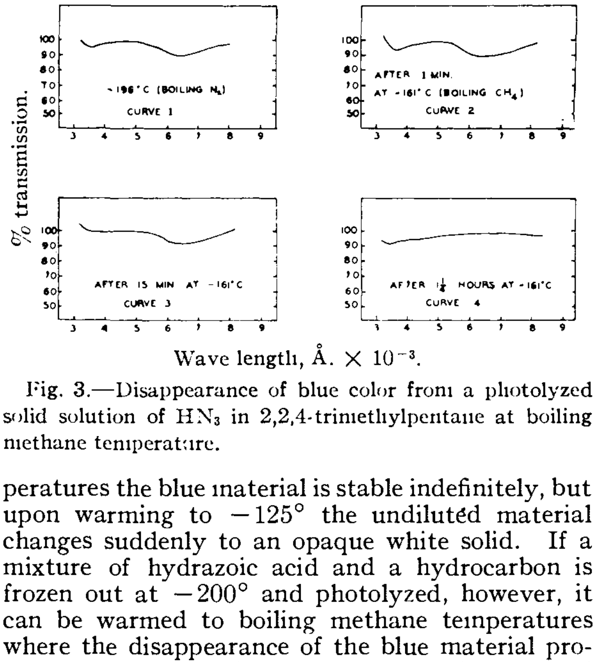

Fig. 3.—Disappearance of blue color from a photolyzed solid solution of HN_3 in 2,2,4-trimethylpentane at boiling methane temperature.

Figure 4 shows the absorption spectrum of purple sulfur and also the spectrum of the material formed (40% rhombic, 60% plastic sulfur) when purple sulfur is warmed to room temperature.

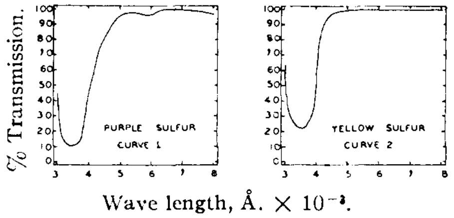

Fig. 4.—Absorption spectra of purple and yellow sulfur.

From the two curves it seems likely that "purple sulfur" contains only a very small fraction, perhaps a few per cent., of the purple form. The band at 3,400 Å. in the curve for purple sulfur is probably due to yellow sulfur present. However, the purple form absorbs at about 5,800 Å., and absorption commences again at about 7,500 Å.

We made an extensive study of the absorption spectra of the colored products obtained by freezing out the thermal decomposition products of symmetrical organic disulfides. We studied di-*n*-butyl and di-*t*-butyl disulfides, diphenyl disulfide and dibenzyl disulfide. Yellow deposits were obtained from dibenzyl disulfide whereas the others gave red deposits. As might be expected the colored products frozen out from the pyrolysis products of the aliphatic disulfides show spectra (see Fig. 5) different from the pyrolysis products frozen out from the pyrolysis of the aromatic disulfide shown in Fig. 6. The pyrolysis products of the aliphatic disulfides show absorption at 8,000 Å. or beyond, 5,400, 3,800 and 3,300 Å. The aromatic disulfides pyrolyze to give products with absorption bands at 8,000 Å. or beyond, 5,200, 4,600 and 3,300 Å.

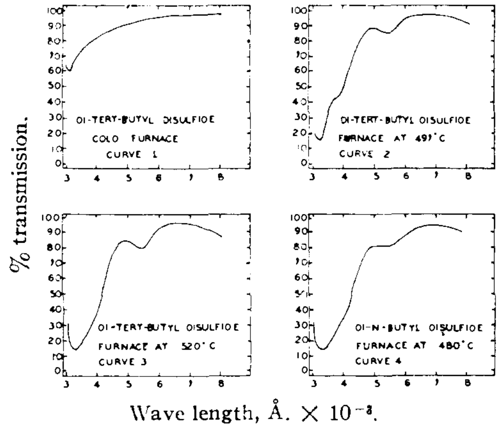

Fig. 5.—Absorption spectra of active species obtained by the thermal decomposition of di-*t*-butyl disulfide and di-*n*-butyl disulfide.

Figure 7 shows the absorption spectra of the products of pyrolysis of dibenzyl disulfide. There seems to be a well marked band with its center at about 3,100 Å. and less well marked bands with centers at 3,900 and 5,400 Å.

Figure 8 shows the absorption spectrum of the products frozen out from the pyrolysis products of hydrazine. There is a well defined band with the center at 3,200 Å. which cuts off the violet end of the visible spectrum and is presumably responsible for the yellow color of this material.

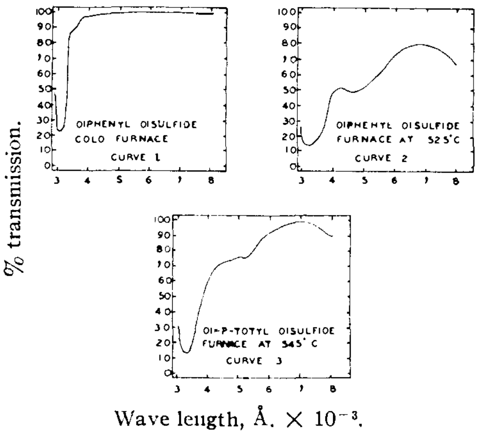

Fig. 6.—Absorption spectra of active species obtained by the thermal decomposition of diphenyl disulfide and di-*p*-tolyl disulfide.

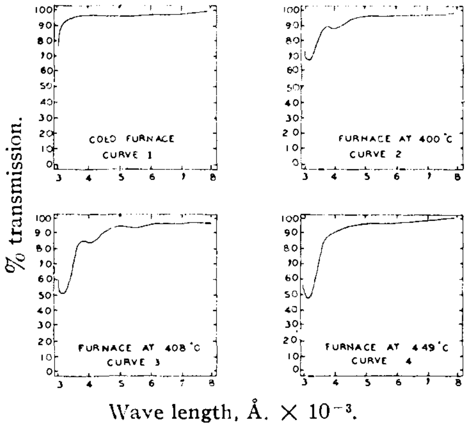

Fig. 7.—Absorption spectra of active species obtained by the thermal decomposition of dibenzyl disulfide.

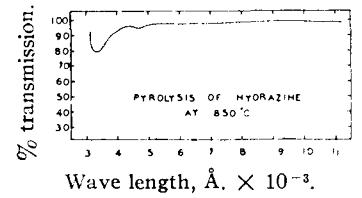

Fig. 8.—Absorption spectrum of the product of pyrolysis of hydrazine.

Discussion

It is hardly possible to say very much concerning our results since the absorption bands observed were all broad and without structure. We should, however, mention that the blue material[2] obtained in the thermal decomposition of hydrazoic acid has been investigated intensively both in this and in other laboratories.[6-8] Mador and Williams[9] observed that the blue material produced by the decomposition of hydrazoic acid in an electrical discharge has bands at 3500 and 6500 Å. They sug-

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(8) E. D. Becker, G. C. Pimentel and M. Van Thiel, *ibid.*, **26**, 145 (1957).

(9) I. L. Mador and M. C. Williams, *ibid.*, **22**, 1627 (1954).

gested that these bands result from the NH and NH_2 radicals, respectively. In connection with the suggestion that NH_2 radicals are present in the blue material, we have failed to find any trace of hydrazine in the warmed up product and have concluded that if NH_2 radicals are present, it can be present only in very minute concentration.

Originally[2] we thought that hydrazoic acid underwent a primary decomposition according to the equation $HN_3 \rightarrow N_2 + NH$ and much of the NH reached the color finger and was frozen either as a monomer, a polymer or a mixture of these. The ammonium azide was supposed to be formed at the transition temperature of the blue material since ammonium azide may be written $(NH)_4$. More recent work in this Laboratory on mass balances indicates that the NH radical builds up to ammonia in the furnace and the ammonia on reaching the cold finger combines with undecomposed hydrazoic acid to form ammonium azide. The stoichiometry of the decomposition is in agreement with this supposition so that the substance giving the blue color can be present in only small amount. Both Mador and Williams,[9] as well as Becker, Pimentel and Van Thiel,[8] observed that the amount of ammonium azide present did not increase on warming.

To sum up, we do not yet even after some ten years of intensive work have any proof of the constitution of the blue material. We have even examined the possibility that electrons might be trapped in the ammonium azide and that we might have a phenomenon analogous to f-centers,[10] but we could find no evidence for this.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Thermodynamics of Polymer Solutions. The Polystyrene–Cyclohexane System near the Flory Theta Temperature

BY W. R. KRIGBAUM AND D. O. GEYMER

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Solvent activities for the polystyrene–cyclohexane system were obtained over the entire concentration range by combining osmotic pressure, isothermal distillation and differential vapor pressure measurements. Three fractionated polymer samples were examined, and data were obtained at three temperatures. At the theta temperature the solutions behave more ideally than would be expected from the Flory lattice model equation, hence a minimum of two χ parameters is required to represent the activity, even at low polymer concentrations. Both the second and third virial coefficients vanish at theta, since $\chi_2 = {}^1/_2$ and $\chi_3 = {}^1/_3$ at this temperature. The ribbon model treated by Tompa furnishes a reasonable representation of the observed entropies of dilution for volume fractions up to 0.35. At higher concentrations both the heat and entropy of dilution increase rapidly, the latter exceeding the values computed according to the Flory lattice model for $v_2 > 0.6$, while the free energy of dilution follows a more normal course.

During the past fifteen years a growing interest has developed in the application of statistical mechanics to the problem of the thermodynamic behavior of polymer solutions. Paralleling this interest in obtaining a satisfactory theoretical description of polymer solution thermodynamics, there has been a continuing effort to obtain reliable activity measurements for polymeric systems. Although the majority of these studies have been concerned with dilute solutions, activity measurements covering a considerable portion of the concentration range have been obtained in several instances.[1–10] Most of the systems investigated have involved thermodynamically good solvents for the polymer. In the low concentration region one anticipates systematic deviations from the behavior predicted by the lattice model treatments due to the appearance of excluded volume effects. On the other hand, activity measurements performed under Flory theta conditions[11] would allow a test of the treatments based upon the lattice model over the entire concentration range. In addition, such measurements would provide information concerning the behavior of the higher virial coefficients which would be useful as a check on the validity of the theoretical treatments of dilute solutions.

With these objectives in mind, we have undertaken a study of the polystyrene–cyclohexane system in the vicinity of the theta temperature. The entire concentration range was covered by combining osmotic pressure, isothermal distillation and differential vapor pressure measurements. Since the inception of this work, papers have appeared by Bawn and Patel,[5,6] and Flory and Daoust[9] which, when combined, furnish fairly complete activity data for the polyisobutylene–benzene system at the theta temperature. The vapor pressure measurements of Jessup[10] give activities for the same system a few degrees above the theta temperature. In addition, Kabayami and Daoust[12] have reported calorimetric data for the

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(9) P. J. Flory and H. Daoust, *ibid.*, **25**, 429 (1957).

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(11) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, Chapter 12.

(12) M. A. Kabayami and H. Daoust, paper presented at the 132nd meeting of the American Chemical Society, New York, N. Y., Sept. 8–13, 1957.