

Structure—Optical Studies. II. Aqueous Dispersion of Polyvinyl Borate—Iodine and Its Heat of Formation

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TABLE I. List of observed bands.

Substance	Wave-length (μ)	Wave number (cm^{-1})
Chlorodibromomethane	26.2	381
	35.8	279
Dichlorobromomethane	22.9	437
	26.2	381
	30.3	330
Dichlorodibromomethane	22.6	442
	25.2	397
	26.7	375
	28.4	351
Trichlorobromomethane	23.8	420
	28.4	351
	34.0	294
Ethylene chloride	24.3	412
	36.7	272
Ethylene bromide	24.9	402
	28.1	355
s-Tetrachloroethane	28.4	352
	30.7	326
	34.5	290
Ethylcyclopentane	23.6	424
	25.4	393
cis-1,3-Dimethylcyclopentane	23.5	426
Methylcyclohexane	22.6	442
	24.7	405
1-Methyl-2-ethylbenzene	22.1	452
	22.9	437
	31.1	322
1-Methyl-3-ethylbenzene	22.9	437
1-Methyl-4-ethylbenzene	27.3	366
	32.5	308
2-Methyl-2-phenylpropane	25.3	395
	32.5	308
Chlorobenzene	23.9	418
	33.8	296
Bromobenzene	31.9	313
Iodobenzene	22.3	448
o-Dichlorobenzene	22.9	437
	29.8	335
1,2,4-Trichlorobenzene	22.8	438
	25.2	397
p-Chlorobenzotrifluoride	32.6	307
	24.4	409
	26.0	385
	31.9	313
	33.1	302
	36.5	274
o-Bromoanisole	22.9	437
	30.3	330
	35.7	280
p-Bromoanisole	30.7	326
	37.9	264
α -Bromonaphthalene	24.9	402
	33.5	298
Diethyl ether	22.7	440
	26.7	374

accordance with the known energy level scheme for CCl_4 , and include the difference bands at 20.73 and 22.43 μ , predicted by Herzberg as of sufficient intensity for observation. A detailed report is in preparation.

¹ Earle K. Plyler, J. Research Nat. Bur. of Stand. 41, 125 (1948).

² W. L. Hyde, J. Chem. Phys. 16, 744 (1948).

Structure—Optical Studies. II. Aqueous Dispersion of Polyvinyl Borate—Iodine and Its Heat of Formation

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December 27, 1948

AQUEOUS dispersions of polyvinyl borate (PVB), formed by mixing dilute polyvinyl alcohol (PVA) with boric acid solution, react to iodine in the same way as do amylose solutions by giving a blue color due to a

strong absorption band in the near red. If the boric acid is omitted from the reaction mixture, no blue color results because of complete dissociation of the blue PVA-iodine compound at the dilutions in question. The wave-length of maximum absorption for PVB-iodine solution is 670 m μ , while that of soluble starch-iodine is only 590 m μ under parallel conditions; that reported¹ for amylose-iodine is 628 m μ . The absorption bands of these compounds are symmetrical and are similar to each other in height and half-width. The triple color reaction of boric acid, PVA, and iodine, by reason of its marked specificity, has analytical possibilities for the detection or determination of any one of its three components, more especially the latter two. Colloidal polyvinyl phenylborate, made in the same way and having similar properties, does not give a color reaction with iodine under similar conditions. When bromine is added to rather concentrated soluble starch or PVB solutions, we observe a distinct color change from yellow to orange or red but have failed to measure an intense absorption band here; the spectrophotometric data suggest extensive dissociation of such compounds in solution.

(With E. Emerson.) We find unexpectedly large heats are evolved when one mole of halogen (iodine or bromine) is added to an excess of organic polymer in aqueous dispersion under conditions to give as complete formation of addition compound as possible. Our results, which we did not reproduce to better than 10 percent, are summarized as the starred figures in Table I, together with data from the literature.² All values here are in kcal. per mole of halogen and refer to the halogens in their standard (condensed) states. While the complexity of the colloidal systems (lines 2 and 3 of Table I) prevents a detailed interpretation of these figures taken by themselves, they suggest that the energy of formation of these compounds from halogen molecules is an appreciable fraction of the energy of formation of the molecules from neutral atoms, and is considerably greater than the heat of formation of simple crystalline trihalides from the crystalline halides (last line of Table I). It would be of considerable interest to know the heat of formation of the present dry addition compounds from the dry reactants, which is in principle determinable.

These findings are of interest in connection with the x-ray diffraction results reported in Paper I of this series.³ With the polymers there listed as showing the characteristic interferences of linear polyiodine we should have included the poorly crystalline polyvinyl silicate, made by esterifying PVA; we have since added the crystalline polymer known commercially as Terylene. Solid, oriented iodine-bearing polyvinyl silicates and borates have been described

TABLE I. Thermochemistry of halogens.

	Iodine	Bromine
Heat of formation from atoms	51	54
Heat of addition to PVB	20*	12.5*
Heat of addition to potato starch	10*	7*
Heat of solution in various solvents	-6 to 6*†	-1 to 3
Heat of addition to ionic halides to give trihalides	0.8(K, Cs)	5(NH ₄)

* New results.

† From measured heat of solution of 6.35 g (0.025 mole) I_2 in 180 cc EtOH containing 3.6 g (0.025 mole) NH_4I .

in patents⁴ as offering dichroic polarizer films of usefully enhanced stability over solid PVA-iodine films. Our present results show an analogous enhanced resistance of water-dispersed PVB-iodine to dissociation over PVA-iodine under the same conditions.

Concerning the recent papers of Rundle and Stein^{5a,b} we have no evidence to question the quite special pictures drawn by these writers for the structure of starch and of starch-iodine. Our position is that the PVB-iodine structure in the solid and dispersed states must include the starch-iodine structure as a special case. It is difficult for us, in view of the recent work of Bunn and Peiser⁶ on the PVA structure, to conceive in PVA or PVB an array of >C-O-X groups "held in such a way that each contributes a reinforcing component of dipole moment along the fiber axis;" it seems more probable to us that in these systems such components would effectively cancel out each other over both shorter and longer ranges.

It is of interest that our heat of addition of iodine to PVB (20 kcal.) is close to the comparable figure of Dube for the addition of iodine to starch (19.6 kcal. derived from electrochemical measurements, reference 5b).

¹ R. Baldwin, R. Bear, and R. Rundle, *J. Am. Chem. Soc.* **66**, 111 (1944).

² F. Bichowsky and F. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

³ C. West, *J. Chem. Phys.* **15**, 689 (1947).

⁴ A. Marks *et al.*, U. S. 2,432,113; F. Signaigo, U. S. 2,444,712; M. Hyman, Jr. *et al.*, U. S. 2,445,579; E. Land, U. S. 2,445,581.

⁵ (a) R. Rundle, *J. Chem. Phys.* **15**, 880 (1947); (b) R. Stein and R. Rundle, *J. Chem. Phys.* **16**, 195 (1948).

⁶ C. Bunn, *Nature* **159**, 161 (1947); **161**, 929 (1948).

Photographic Infra-Red Emission Bands of O₂ from the CO-O₂ Flame*

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December 27, 1948*

ONE of the authors recently reported some spectroscopic studies of the CO+O₂ reaction carried out by explosion in a spherical vessel.¹ It was noted that the Runge bands of the neutral O₂ molecule appeared in emission in the violet and near ultraviolet.²

Further investigations have been carried out in the spectral range 7200-8800Å in the first order of a 2-meter grating spectrograph (Eagle mounting, Baird Associates), the grating having 15,000 lines per inch. A mixture of CO and O₂ was ignited in a gold-plated spherical bomb of 7-liter capacity, provided with fused quartz windows 1 inch in diameter. The commercial CO employed was freed from iron carbonyl but contained about 1.5 percent of H₂

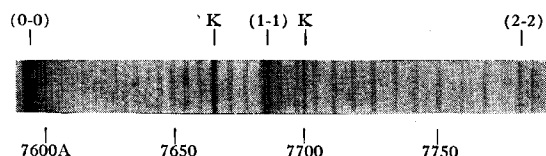


Fig. 1. A portion of the emission spectrum of O₂ obtained from the CO-O₂ reaction is shown in the spectral region 7590 to 7790Å. The heads of the (0-0), (1-1), and (2-2) transitions of $1\Sigma_g^+ \rightarrow 3\Sigma_g^-$, as well as the two potassium resonance lines at 7664.9 and 7699.0Å, respectively, are indicated.

impurity. The CO and O₂ were admitted to the bomb in the ratio of 1 to 2, to a total pressure of 1.5 atmospheres. This fuel/oxygen ratio produced spectra of optimum contrast. The mixture was ignited at the center of the bomb by means of an ordinary spark coil across tungsten electrodes with $\frac{1}{4}$ " separation.

A portion of the spectrum obtained is reproduced in Fig. 1. An Eastman X-thin I-N plate was employed, hypersensitized by the usual ammonia-ethyl alcohol method. A Corning filter No. 2424 was used to absorb higher orders of the spectrum. The exposure consisted of forty explosions, corresponding to a total exposure time of about 10 seconds. The plate reproduced shows some of the red bands of neutral O₂, heretofore obtained in absorption by the earth's atmosphere. The two most intense of these bands, the A band³ at $\lambda = 7593.7\text{\AA}$, identified as the (0-0) band,⁴ and the (1-1) band⁵ at $\lambda = 7683.8\text{\AA}$ have been analyzed previously as absorption bands and assigned⁶ to the $1\Sigma_g^+ \rightarrow 3\Sigma_g^-$ transition of neutral O₂. In addition to these two bands, Fig. 1 shows also the (2-2) band of the same system with head at $\lambda = 7779.0\text{\AA}$. The original plate further shows the (3-3) band at $\lambda = 7879.2\text{\AA}$ and faint traces of heads of still higher bands of the same sequence,

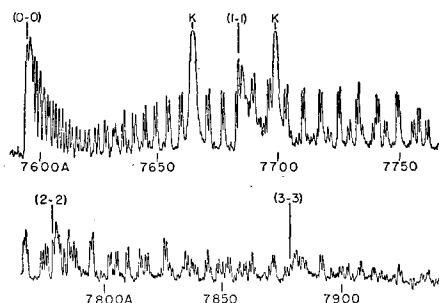


Fig. 2. Densitometer tracing of a portion of the emission spectrum of O₂ obtained from the CO-O₂ reaction, in the region 7590 to 7945Å. The heads of the (0-0), (1-1), (2-2), and (3-3) transitions of $1\Sigma_g^+ \rightarrow 3\Sigma_g^-$, as well as the potassium resonance lines, are indicated.

as well as heads of three bands of another sequence not previously observed: the (0-1), (1-2), and (2-3) bands. These band heads are at $\lambda = 8597.8$, 8697.8, and approximately 8803Å, respectively. The densitometer tracing of a portion of the same plate, reproduced in Fig. 2, shows the (0-0), (1-1), (2-2), and (3-3) bands.

Because of the inadequate dispersion and the extensive overlapping of bands, it is not feasible to analyze the bands completely from the plates which have been obtained. However, it has been possible to sort out many of the lines. The observed emission lines of the (0-0) band differ on the average from the corresponding absorption lines of Dieke and Babcock by about -0.1Å. However, there is no doubt about the identity of this band, since the intervals between successive lines in emission agree extremely well with those between corresponding successive lines in absorption.

The distribution of intensity as obtained in emission is markedly different from that previously obtained in absorption because of the higher temperatures involved. The peak intensity is shifted away from the origin of the band in