merization; this is accomplished by keeping the pressure of acetylene very low during the irradiation. Under these conditions an unstable dimer might change into vinylacetylene before having the opportunity to react further with acetylene.

6. The assumption is made that this dimer is cyclobutadiene, and that the intermediate trimers characterized by their absorption spectra in irradiated acetylene, are acetylenecyclobutenes, very reactive in both isomeric forms. Cyclobutadiene ought to be present in an excited state of electrical asymmetry, since its ground state is completely unstable. In a similar way divinylacetylene and acetylenedivinyl found to be the volatile products in the irradiation of a vinylacetylene–acetylene mixture would be expected to be formed as side products from isomerization of the unstable intermediate vinyl-cyclobutadiene.

7. It is suggested that the further addition of acetylene proceeds in the same pattern, over cyclobutene structures. This suggestion is supported by the following experimental analogy: irradiated acetylene reacts with a sufficient amount of benzene in giving naphthalene, whereas no naphthalene is formed by irradiation of vinylacetylene mixed with benzene; thus acetylene and vinylacetylene differ in the formation of naphthalene in the same way as in the formation of benzene.

8. It is reasonable to assume that in each cycle an inactive aromatic isomer is formed, just as benzene is formed in the first cycle, so that some of the chains do not proceed any further. The average chain length depends on the relative probability of formation of these inactive compounds. This mechanism meets Melville's demand that acetylene ought to be responsible both for continuing and stopping the chain.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Color and Bond Character

BY KENNETH S. PITZER AND JOEL H. HILDEBRAND

A good deal of attention has recently been given to bond character, using as criteria mainly bond energy and bond distance, each of which has been shown to vary with the shift from covalent to ionic bonding.[1] The purpose of this paper is to discuss the use of color as an additional criterion.

Our attention was first drawn to this subject by the interesting behavior of stannic iodide, contrasting strongly with that of stannic chloride. The latter, for example, like most other tetrachlorides, is highly hydrolyzed, and cannot be prepared in the presence of water. The hydrolysis of the iodide, on the other hand, is so easily reversed that we can prepare pure stannic iodide by action of aqueous hydriodic acid upon solid SnO_2 and subsequent evaporation. This can hardly be explained otherwise than by a more covalent bond between iodine and tin. Indeed, if we use Pauling's negativity scale, we find that these elements are so close together as to indicate only about 11% of ionic bonding.

This conclusion is reinforced by the deep orange red color of the compound not only in the solid state and in solution in non-polar solvents, but in aqueous solution as well, if observed either immediately on solution before hydrolysis occurs, or later, if hydrolysis is prevented by using aqueous hydrochloric acid or hydriodic acid. The partition of stannic iodide between CCl_4 and HCl aq. is nearly equal. The color in all these solutions appears to be the same. Now if the iodine and tin did not form a covalent bond, we would expect the solution to be colorless since iodide ion is colorless, as in the alkali iodides, which are unquestionably ionic.

The first suggestion of this nature that we have been able to find was made by Bichowsky[2] in 1918 in a paper dealing with "atom color" and valence in which he remarked that when the color of a compound deviates from the sum of the ion colors "the electrons are no longer acted on by only one nucleus but are acted on by both," and later "compounds of one or more electronically stable atoms with one electronically less stable are likely to have a color which is the sum of the valence colors of its constituent atoms, while

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(1) For one discussion see L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(2) F. R. Bichowsky, THIS JOURNAL, **40**, 500 (1918).

compounds of two or more electronically unstable atoms will in general have a color which is not the sum of the valence colors of the constituent atoms but is, because the effect of one atom on the electron stability of the other atom (on account of the slope of the potential gradient) is to decrease the restraining forces acting on the electrons, a color which corresponds to absorption in the longer wave."

We wish to extend this concept as follows: if the color of a compound deviates from that of its constituent ions, then this may be taken as an index of the deviation from pure ionic bond character. Of course some ions absorb light only so far in the ultraviolet that largely or even completely covalent bonds might be formed with no visible color. The shift of the absorption in going from I_2 through Br_2 and Cl_2 to F_2 shows the presence of other factors, and the covalent H_2, N_2, and O_2 are colorless.[3] Thus one must note the color of completely covalent bonds between atoms of the size under consideration.

We do not now attempt to say how far this concept can be given quantitative significance, only to show that it appears qualitatively valid and useful. This need not be discouraging, for the other criteria are only semi-quantitative.

In addition to stannic iodide, silver iodide has come to our attention and its color has already been discussed briefly.[4]

In the discussion that follows the postulate will first be compared with other measures of bond character after which certain features will be examined in terms of the nature of the electronic states involved. Except for the section by Ley[5] in the "Handbuch der Physik," and the paper by Bichowsky cited above, the writers are aware of no general collection of data on the colors of simple inorganic compounds. Mellor,[6] in his treatise, mentions such data in many specific cases, mostly for solids. Since the experimental determination of colors by visual observation, either direct or with a simple spectrometer, is so easy, it was not considered efficient, nor essential, to search the literature completely. Full use has been made of the sources mentioned above, otherwise we report our own observations.

It was found quite generally that all colored substances here considered absorbed light from the ultraviolet down to a more or less sharp edge. Only with iodine is transmission found on the violet side. Yellow, orange, and red are thus the colors obtained and will be called increasing color in that order. This corresponds to absorption at increasing wave lengths.

The best criterion of the color of a given molecule would be the color of the vapor, with the color of a solution in a non-polar solvent, usually carbon bisulfide in these observations, a close second. In general the colors of the solids depend on their crystal structure. Thus stannous iodide and mercuric iodide both show red and yellow modifications. The colors of solids consequently are to be considered as uncertain indicators of bond character in the absence of detailed knowledge of crystal structure.

We compare in Table I the color with other criteria proposed for bond character. The substances are various iodides from silver through antimony. The limiting color for complete electron sharing may be taken as that of iodine. The column headed (Q_f/n) gives the heat of formation divided by the number of bonds. According to Pauling[1] this may be taken a measure of deviation from pure electron sharing; the following column lists the amount of ionic character calculated from his formulas and this heat of formation. In general there is very great similarity between the results from the heats of formation and from the colors. In fact a careful comparison of antimony and stannic iodides in carbon disulfide solution shows the former to be definitely more on the red side.

It is also interesting to note that both heats of formation and colors show silver iodide to be less ionic than cadmium iodide; a conclusion which is supported by the bond distances and structures of the two crystals. Except for this pair, the experimental data on bond distances are too fragmentary to be very useful.

The relative solubilities in polar and non-polar solvents are also consistent with our picture. Thus antimony iodide is more soluble in carbon disulfide than in methanol, while the situation is reversed for stannous iodide. If the melting point is about 200° or higher, the solubility is very low, except for the more ionic iodides in polar solvents.

Having thus shown this postulate to be consistent with other data, it is interesting to consider some specific cases. With several sub-

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(3) *Cf.* G. N. Lewis, "Valence," Chem. Catalog Co., 1923, p. 161.

(4) K. S. Pitzer, THIS JOURNAL, **63**, 516 (1941).

(5) H. Ley, "Handbuch der Physik," Vol. 21, p. 1, Verlag von Julius Springer, Berlin, 1929.

(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1922–1937.

TABLE I

	Melt. pt., °C.	Q_t/n^7	Per cent. Ionic	Color		Bond distances		
				Soln.	Solid	Covalent calc.[1]	Observ.[8]	Ionic calc.[1]
I_2	114	0	0	Violet (CS_2)	Violet	2.66	2.66	..
SbI_3	167	7.6	7	Orange-red (CS_2)	Red	2.74	..	..
SnI_4	143	12.5	12	Orange (CS_2 or CH_3OH)	Orange	2.73	2.63	2.87
AgI	557	14.9	15	(Insol.)	Yellow	2.86	2.80	3.42
InI_3	199	18.8	19	(Insol.)	Yellow	2.77	..	2.97
SnI_2	320	19.5	20	Yellow (CH_3OH)	(a) Yellow (b) Red	2.73	..	..
CdI_2	388	24.2	23	Colorless (CH_3OH)	White	2.81	2.98	3.13

stances, less color was observed in polar than in the non-polar solutions. The high dielectric constant of the solvent might be expected to encourage polar bonds, except possibly in symmetrical molecules such as stannic iodide. Actually stannic iodide appears about the same in water or carbon disulfide, but antimony triiodide shifts from orange in carbon disulfide to yellow in water.

Excess halide ions in polar solution usually form complex ions with these substances. With stannic iodide no color change was observed, but there may not be room for additional iodide ions around the tin. On the other hand, bismuth iodide shows definite darkening with excess iodide (shift of absorption edge from about 5000 to 5300 Å.). Stannous and antimony iodides also show more color with excess iodide ion.

Several concepts may be considered in connection with this effect. One would think that the increased number of bonds about the central atom in the complex ion, as compared to the neutral molecule, should give each bond less electron sharing character. On the other hand, the electronic excitation which leads to the color may involve all the atoms instead of just one bond. The spatial extent of the electronic system is known to be very important in the color of resonating organic molecules.[9] Another effect to be considered is that the polar solvent is pushed aside by the extra halide ions when the complex ion is formed. This might tend to reduce the polarity of the bonds thus shielded.

The molten salts of this type are all deep red. An experiment with a cadmium iodide melt containing excess lithium iodide showed less total light absorption per weight of cadmium iodide when the lithium iodide was also present. Furthermore, the color with the excess iodide ion seemed more orange. This might be interpreted either as complex ion formation, or as a polar solvent effect.

The picture commonly given[10] for the electronic excitation in essentially ionic systems is that an electron is removed from the outer shell of the negative ion and taken up by the positive ion, water, or whatever is nearby. It may later find a more stable position, such as in a lattice defect. Thus the greater the electron affinity of the particles bound to the negative ion, the longer will be the wave length of the light absorbed. But this greater electron affinity of the other atom tends also to make the bond less polar in the normal state. When the normal state is not completely ionic, then the excitation process can no longer be considered to be simple electron transfer. Nevertheless, a reasonably regular and continuous change can be expected to the states that are found for a completely non-polar bond as in iodine. This simple argument suffices to show that the results discussed above are in agreement with the general picture of the light absorption process. From another point of view, as the electronic system becomes larger spatially the wave length of the light absorbed may be expected to increase, other things being equal. In a purely ionic system, the negative ion is usually the largest electronic system. In a molecule such as stannic iodide, the electronic system is at least one tin-iodine bond, and may to some extent involve the whole set of four bonds. Thus in either case more color is expected than for stannic and iodide ions.

It remains to consider the application of the Franck–Condon principle to our structural considerations. Usually the minimum of the potential energy curve for an excited electronic state is at a greater bond distance than for the normal state. Thus longer interatomic distances lead to absorption at longer wave lengths or to more

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(7) (a) Bichowsky and Rossini, "Thermochemistry," Reinhold Publishing Co., New York, N. Y., 1936. (b) The heat of formation of stannic iodide, 50 kcal., is a preliminary value from unpublished experiments of M. A. Mosesman and K. S. Pitzer.

(8) *Z. Krist.*, "Strukturbericht.," Volumes I–III.

(9) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

(10) Rollefson and Burton, "Photochemistry," Prentice-Hall, New York, N. Y., 1939, p. 122.

color. Heating crystals of the type here considered necessarily leads to irregularity in the interatomic distances at any one instant. The unusually long distances cause light absorption farther in the red and therefore increasing color. This is observed very definitely in all cases. In the liquids the state is similar but even further developed. On vaporization, however, these relatively long bond distances become enormously less probable, because the molecules are closely bound internally and are usually very far apart. The intense absorption at long wave lengths should then disappear on vaporization. We have observed exactly this result for mercuric iodide.

While many of the arguments presented above lack rigor and the experimental data are incomplete, nevertheless, we believe that there is ample reason to regard this picture as substantially correct. Since these ideas are based upon such simple and direct observations, there seems little excuse for neglecting them in further work on these substances. On the other hand, the question as to the extent of quantitative development remains entirely open for future consideration.

Summary

An idea mentioned by Bichowsky in 1918 is extended into the following postulate. When the color of a compound deviates from that of its constituent ions, then this may be taken as an index of the deviation from pure ionic bond character.

The properties of the iodides of some heavy metals are discussed from this point of view. Vapors, polar and non-polar solutions, complex ions, solids, and molten salts are considered. Deductions from this principle are found to be in agreement with other criteria.

It is also shown that these ideas have reasonable interpretation in terms of the excited electronic state responsible for light absorption, and in terms of the Franck–Condon principle.

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Maximum Boiling Mixtures of Chloroparaffins with Donor Liquids

BY R. H. EWELL AND L. M. WELCH

This paper is concerned with azeotropic binary mixtures exhibiting maximum boiling points, each mixture consisting of a donor liquid and a liquid containing active hydrogen. The azeotropic behavior can be attributed to the formation of hydrogen bonds between the oxygen of the donor liquid, for example acetone, and the active hydrogen of the second liquid, for instance chloroform. The negative deviation from Raoult's law arises in such cases because neither chloroform nor acetone have any hydrogen bonds in the pure liquids, but hydrogen bonds are formed between the unlike molecules on mixing.

There are many pieces of evidence that some sort of bond is formed between chloroform and acetone, although there is no reason to expect hydrogen bonds in either of the pure liquids. There is a large evolution of heat and a decrease in volume on mixing, and there are minima in the fluidity–composition and vapor pressure–composition curves.[1,2] Many other mixtures of this general type, *i. e.*, a haloform as one component and a donor liquid, such as an ester, ketone, etc., as the other component, show similar pronounced negative deviations from the ideal solution laws.[1,2] Gaseous haloforms, such as dichlorofluoromethane have abnormally high solubilities in donor liquids.[3] The C–H absorption band in the spectra of chloroform and bromoform is shifted when these liquids are mixed with donor liquids.[4,5] Thus it seems that not only hydrogen atoms attached to nitrogen, oxygen or fluorine are capable of forming hydrogen bonds, as in ammonia, water, hydrogen fluoride and many related compounds, but also hydrogen atoms attached to carbon if there are some electronegative atoms or groups attached to the carbon.

Lécat[6] lists about forty maximum boiling azeo-

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[1] Timmermans, "Les Solutions Concentrées," Masson et Cie., Paris, 1936.

[2] Hildebrand, "Solubility," A. C. S. Monograph 17, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1936.

[3] Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).

[4] Gordy, *J. Chem. Phys.*, **7**, 163 (1939).

[5] Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2528 (1938).

[6] Lécat, "L'Azeotropisme," M. Lamartin, Brussels, 1918. This work was followed by a series of 25 supplementary lists of azeotropes published in various journals, 1926–1929. Most of the azeotropes in all of Lécat's publications are also listed in Timmermans, "Les Solutions Concentrées" (ref. 1), which is more widely available than Lécat's book.