than the older photographs (X-ray film). (These differences are only typical, however, of the more or less gradual improvement which has occurred since 1933 in the electron diffraction technique employed in these Laboratories.) Moreover, it so happened that this investigation was undertaken concurrently with a very satisfactory series of check measurements on diatomic molecules[7] using the same technique and the same wave length calibrations.

There is some further information regarding the configuration of the sulfur dioxide molecule. Cross and Brockway[1] report the surprisingly consistent value 122 ± 5° as the bond angle obtained on fitting the three vibrational frequencies of the sulfur dioxide molecule to a two-constant, valence-force potential function. Much more important is the entropy determination of Giauque and Stephenson[8] which leads to the value $(10.58 \pm 0.99) \times 10^{-116}$ g. cm.^{2} for the product of the three principal moments of inertia of the molecule. This value and our S–O distance give 121° as a fairly precise value for the bond angle, substantiating our electron diffraction determination. A variation of 0.1 cal. mol.$^{-1}$ deg.$^{-1}$ in the entropy (corresponding to the uncertainty in the product of the moments of inertia given above), or of 0.02 Å. in the bond distance, would produce a change of 4° in the value calculated for the bond angle. In the calculations leading to the results reported in this paragraph the current values[9] of N, h, and k were used. A correction of +0.2% was applied to our bond distance in order to compare it with the results of the entropy calculations based on the "new" constants. When the "old" values of the fundamental constants are used, the correlation of the entropy of sulfur dioxide with our bond distance leads to a bond angle value of 123°.

Summary

The structure of sulfur dioxide has been reinvestigated by the electron diffraction method, with the following results: S–O = $1.43_3 \pm 0.01$ Å., and ∠ O–S–O = 120 ± 5°. This value for the bond angle is in excellent agreement with the value, 121 ± 5°, derived from the bond distance and the entropy.

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[7] Schomaker and Stevenson, to be published.

[8] W. F. Giauque and C. C. Stephenson, THIS JOURNAL, **60**, 1389 (1938).

[9] G. Herzberg, "Molecular Spectra. 1," Prentice-Hall, New York, N. Y., 1939, p. 3.

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Aldehyde Complexes of Copper Salts

BY TENNEY L. DAVIS AND WALTER P. GREEN, JR.

As part of an investigation of the ability of compounds containing the carbonyl group to enter into coördinative combination, we have found that acetaldehyde and butyraldehyde combine with certain copper salts, and have prepared the compounds listed below and have determined their dissociation pressures at 0°.

TABLE I

DISSOCIATION PRESSURES AT 0° (MM. AT 20°)

$CuNCS \cdot CH_3CHO$	65.6
$3CuNCS \cdot 2C_3H_7CHO$	30.0
$2CuI \cdot CH_3CHO$	6.3
$3CuI \cdot C_3H_7CHO$	5.6
$Cu(OCOCH_3)_2 \cdot CH_3CHO$	89.9

For comparison with these dissociation pressures, we have determined the vapor pressure at 0° of pure acetaldehyde, 333.0 mm., and of pure butyraldehyde, 32.3 mm.

The formulas of the complexes show several interesting relationships. Cuprous thiocyanate combines (to form a complex which is fairly stable at 0°) with twice as many molecules of either aldehyde as cuprous iodide does. Two molecules of butyraldehyde are equivalent to three molecules of acetaldehyde in respect to the capacity of the aldehydes to combine with the cuprous salts.

When samples of the cuprous salts were exposed at 0° in closed vessels to atmospheres saturated with the vapors of the aldehydes, they absorbed the aldehydes rapidly in quantities much greater than correspond to the complexes listed above. Cuprous thiocyanate actually deliquesced in either aldehyde, and the crystals became covered with a layer of liquid. Cuprous iodide showed the same behavior with acetaldehyde, but on exposure to butyraldehyde vapor it assumed a moist appearance but showed no distinct liquid phase after fifteen days. Different samples of the cuprous salts exposed to aldehyde vapors in the same vessel during the same interval of time absorbed different amounts of aldehyde, probably because of the formation of crusts. The results made it evident that pure complex compounds could not be produced conveniently by this procedure.

Cupric acetate absorbed acetaldehyde vapor more slowly than the cuprous salts; it remained dry in appearance but took on a deeper green color and absorbed about half a molecule of the aldehyde after five days.

Since the aldehydes attack mercury, the dissociation pressures could not be determined in an apparatus in which the vapors were allowed to come in contact with the mercury of a manometer. A torsion apparatus was used in which the pressure to be measured, within a spiral of very thin fused quartz tubing (without hysteresis), was balanced exactly by an external pressure measured with an ordinary manometer. The technique which had been used successfully in earlier researches[1] in this Laboratory, namely, that of adding to the dry salt an excess of the volatile component, pumping in the manometric apparatus, reading the equilibrium pressure, again pumping for a short time, again reading the equilibrium pressure, and so on until the equilibrium readings after successive pumpings were found to be the same, was satisfactory for determining the vapor pressures of the aldehydes but was found to be inapplicable to the complex compounds. The apparatus failed to come to equilibrium after standing for four or five days, evidently because dense, practically impervious crusts were formed which prevented the evaporation of the aldehyde from the interior of the mass.

The compositions of the complexes were determined by measurements of the weights of aldehyde retained by the dry salts. An excess of aldehyde was added to a weighed amount of the salt and the mixture was allowed to stand for several days at 0° in a closed container. The cuprous salts formed heavy, clay-like masses, while the complex of cupric acetate retained a granular texture. The materials were broken up and stirred over while the aldehyde evaporated freely at room temperature, until a complete change in the rate of evaporation of the aldehyde was noted, and dry, friable, meal-like masses were obtained. These were weighed, with the results indicated in Table II. The samples resulting from these experiments were used for the determinations of dissociation pressures. In the manometric apparatus they showed constant successive maximum equilibrium pressures after being successively pumped and allowed to stand. The pressures found in this way are reported in Table I.

TABLE II

COMPOSITION OF COMPLEX COMPOUNDS

Salt, g.	Aldehyde, g. Taken	Aldehyde, g. Retained	Molecular ratio aldehyde to salt	Complex compound
		Cuprous thiocyanate and acetaldehyde		
4.3709	3.0755	1.5749	0.996	
3.4896	2.4832	1.2391	.981	$CuNCS\cdot CH_3CHO$
4.1038	3.3671	1.4235	.961 *i e.* 1:1	
		Cuprous thiocyanate and butyraldehyde		
1.6179	1.3785	0.6586	0.690	
1.5700	1.3095	.6400	.689	
3.8064	3.5672	1.5476	.682	
3.9111	2.3847	1.5301	.662	
5.1654	7.9887	1.9969	.654	
3.9967	3.2817	1.5353	.649	$3CuNCS\cdot 2C_3H_7CHO$
3.5500	2.9417	1.3476	.641 *i. e.* 2:3	
		Cuprous iodide and acetaldehyde		
5.4018	2.0247	0.6454	0.520	
4.9528	2.1453	.5810	.508	$2CuI\cdot CH_3CHO$
5.5608	1.9940	.6474	.504 *i. e.* 1:2	
		Cuprous iodide and butyraldehyde		
8.8736	2.5579	1.1691	0.348	
4.5774	3.0933	0.6010	.347	$3CuI\cdot C_3H_7CHO$
8.2229	1.9422	1.0243	.330 *i. e.* 1:3	
		Cupric acetate and acetaldehyde		
7.7980	3.8399	1.9353	1.022	
2.9960	1.3022	0.7170	0.986	$Cu(OCOCH_3)_2\cdot CH_3CHO$
6.1460	3.5703	1.4465	.972 *i. e.* 1:1	

The aldehydes used in this work were purified from Eastman Kodak Co. "pure" materials. The acetaldehyde was treated with a small amount of 33% aq. sodium bisulfite solution for the removal of peroxides, allowed to stand six hours, and distilled through a Davis column; the upper fraction was dried with a mixture of sodium bicarbonate and anhydrous calcium sulfate, allowed to stand five hours, again distilled, and the middle fraction was taken. The butyraldehyde was distilled through a 3-foot (90-cm.) Podbielniak column to remove most of the acid and other high-boiling impurities; the middle fraction, b. p. 74.7–75.0°, was treated with sodium bisulfite for the removal of peroxides, washed with water, dried with anhydrous sodium and calcium sulfates, allowed to stand for two days at the temperature of dry-ice, and filtered clear from the impurities which had frozen out.

The vapor pressure of butyraldehyde at 0° has not been measured heretofore. The vapor pressure of acetaldehyde has been measured by de Leeuw[2] and by Emeleus,[3] whose data do not give straight lines on a semi-logarithmic chart,

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(1) Davis and Batchelder, THIS JOURNAL, **52**, 4069 (1930); Davis and Ou, *ibid.*, **56**, 1061, 1064 (1934); Davis and Logan, *ibid.*, **58**, 2153 (1936).

(2) De Leeuw, *Z. physik Chem.*, **77**, 296 (1911).

(3) Emeleus, *J. Chem. Soc.*, 1735 (1929).

and by Gilmour,[4] who reported twenty-one values between +16.91° and −24.15°, and these values give a straight line on a semi-logarithmic chart which cuts the zero axis at a point corresponding to a value of 331.0 mm. for the vapor pressure of acetaldehyde at 0°. From Gilmour's data a writer in the "International Critical Tables"[5] has deduced a mathematical equation according to which we calculate the vapor pressure of acetaldehyde at 0° as 333.1 mm., in close agreement with our experimental value of 333.0 mm. Burton, Ricci and Davis[6] have recently reported the values 335.6 and 334.6 mm.

Summary

Complex compounds of cuprous thiocyanate and iodide with acetaldehyde and butyraldehyde, and of cupric acetate with acetaldehyde, have been prepared.

The dissociation pressures of the complexes at 0° and the vapor pressures of the pure aldehydes at 0° have been determined.

Cuprous thiocyanate at 0° forms a stable complex with twice as many molecules of aldehyde as does cuprous iodide.

Two molecules of butyraldehyde are equivalent to three molecules of acetaldehyde in respect to the capacity of the aldehyde to combine with cuprous salts.

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[4] Gilmour, *J. Soc. Chem. Ind.*, **41**, 293 (1922).

[5] *Int. Crit. Tables*, Vol. III, 1928, p. 215.

[6] Burton, Ricci and Davis, THIS JOURNAL, **62**, 265 (1940).

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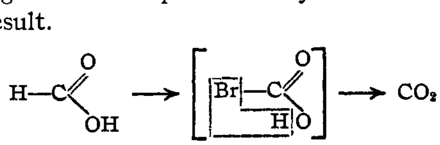
A New Reaction of Formic Acid

BY TENNEY L. DAVIS AND WALTER P. GREEN, JR.

If formic acid exists in the tautomeric form of dihydroxy divalent carbon, as has been suggested,[1] then it is possible that the reaction of formic acid with bromine might yield a certain amount of material produced from the tautomer, differing from any material which is likely to be produced from formic acid in its usual form. We find that the interaction of bromine and anhydrous formic acid produces a material (perhaps bromophosgene (carbonyl bromide) or, more probably, the hydrated form of bromophosgene, namely, dibromodihydroxy-methane) which reacts with aniline to form derivatives of urea, namely, carbanilide and brominated carbanilides, and conclude that the facts indicate with considerable probability that formic acid contains material of the formula $>C(OH)_2$.

The action of bromine on formic acid in dilute aqueous solution has been studied by Hammick, Hutchinson and Snell,[2] who concluded in 1925 that the reaction is of the second order and is essentially a reaction between bromine molecules and formate ions. They found that the influence of various reagents on the reaction is explained satisfactorily by a consideration of their effects upon the concentrations of the reacting molecules in accordance with the law of mass action. Jozefowicz[3] confirmed their results in 1929. Hell and Mühlhauser,[4] much earlier, in 1878, had studied the apparent catalytic effect of carbon disulfide on the rate of reaction of bromine with strong, but not anhydrous, formic acid. They postulated an intermediate compound but did not isolate it or assign any formula to it. In all these cases carbon dioxide was the product of the reaction, and the net result was as if the formic acid had been oxidized to carbonic acid.

Formic acid in its usual structure may perhaps brominate by a mechanism which involves the primary substitution of either of its hydrogen atoms. If the hydrogen attached to the carbon is replaced by bromine, then the resulting intermediate compound will contain bromine and hydroxyl attached to the same carbon atom; and this is an arrangement which commonly splits off hydrogen bromide spontaneously: carbon dioxide will result.



If, on the other hand, the hydrogen of the hydroxyl group is replaced by bromine, then an intermediate hypobromite will result which would

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[1] Baly, Heilbron and Hudson, *J. Chem. Soc.*, **121**, 1080 (1922); Edith H. Ingold (Usherwood), *ibid.*, **125**, 1530 (1924); Scheibler, *Z. angew. Chem.*, **40**, 1072 (1927).

[2] Hammick, Hutchinson and Snell, *J. Chem. Soc.*, **127**, 2715 (1925).

[3] Jozefowicz, *Roczniki Chem.*, **9**, 309 (1929).

[4] Hell and Mühlhauser, *Ber.*, **11**, 241 (1878).