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.

CAMBRIDGE, MASS. RECEIVED MARCH 5, 1940

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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).

[CONTRIBUTION NO. 218 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

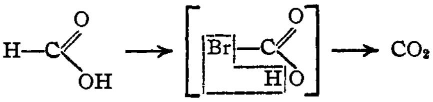
A New Reaction of Formic Acid

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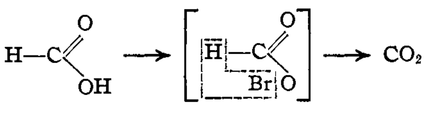
(1) Baly, Heilbron and Hudson, *J. Chem. Soc.*, **121**, 1080 (1922); Edith H. Ingold (Usherwood), *ibid.*, **125**, 1530 (1924); Scheibler, *Z. angew. Chem.*, **40**, 1072 (1927).

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

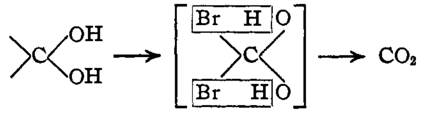
(3) Jozefowicz, *Roczniki Chem.*, **9**, 309 (1929).

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

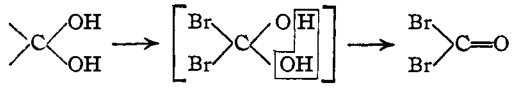
be expected to break up in the same manner that ethyl hypobromite breaks up, by the loss of hydrogen bromide from the bromine of the hypobromite group and the hydrogen attached to the same carbon atom: and again carbon dioxide will result.



The mechanism of the action of bromine on the tautomer of formic acid may perhaps involve first the addition of bromine to the two free valences, in the same way that bromine adds to carbon monoxide. The resulting intermediate dibromo-dihydroxy-methane may behave in three ways. (1) It contains bromine and hydroxyl on the same carbon atom, and would be expected to lose hydrogen bromide with the formation of carbon dioxide. This seems the most likely mode of its behavior, and the previously known comportment of formic acid with bromine may indeed occur through the intermediacy of this compound; and the formula of the tautomer explains the facts as conveniently as the more usual formula.



(2) There is however some chance, though a slight one, that this intermediate containing two hydroxyl groups on the same carbon atom, may lose the elements of water to form bromophosgene.



Since the other mode of decomposition seems more probable, and since bromophosgene is known to react readily with water, it is unlikely that more than traces of bromophosgene would be formed by the splitting out of water from a considerable amount of the intermediate. Bromophosgene reacts with aniline to form carbanilide; and a trace of bromophosgene indicates the probable presence in the original formic acid of at least some of the tautomer. (3) The intermediate itself would react with aniline to form carbanilide. There is also the possibility that the intermediate may not decompose at all to yield bromophosgene, but that while decomposing into hydrogen bromide and carbon dioxide, it may actually exist for a time in the presence of an excess of bromine with which it is probably in equilibrium.

When bromine and anhydrous formic acid were allowed to stand together at room temperature, and the mixture, still containing free bromine, was treated at room temperature or below[5] with an excess of aniline, a small quantity of carbanilide and of brominated carbanilide was formed. When a similar mixture was allowed to stand until the color of the bromine had disappeared, and was then worked up in the same way, no detectable carbanilide or brominated derivative of it was found. The substance from which the carbanilide was produced was therefore probably not bromophosgene but rather dibromo-dihydroxy-methane formed by the addition of bromine to the tautomeric form of formic acid.

Experiments

Anhydrous formic acid, m. p. 8.20°, was prepared by distillation with boric anhydride according to the method of Schlesinger and Martin,[6] who reported the melting point 8.26°.

6.9 Grams of bromine and 17.9 g. of anhydrous formic acid were allowed to stand together for thirteen days in a test-tube closed with a loosely fitting glass stopper. The mixture, which still consisted of two phases, was then frozen in dry-ice; 40.5 g. of purified and freshly distilled aniline was frozen in another tube; both tubes were allowed to warm somewhat, and the materials, partly frozen, were mixed with stirring and cooling. The temperature did not rise at any time above that of the room. The material was treated with aqueous sodium hydroxide in excess, and steam distilled for the removal of the aniline and of as much of the brominated aniline as possible. During the last part of the distillation a precipitate appeared in the flask. Precipitate and solution were extracted with ether, and the residue from the evaporation of the ether was recrystallized from alcohol, white crystals melting at 257–258° with some sintering at 230° (copper block). When this material was sublimed in the molecular still[7] it left about one-third of its mass behind in the form of tar. The sublimate, recrystallized from alcohol, yielded 0.0641 g. of material which melted at 260–265° dec., after another vacuum sublimation m. p. 278–281° dec., after another recrystallization from alcohol m. p. 279–281° dec., and further recrystallization did not raise the melting point. 2,4,2′,4′-tetrabromocarbanilide is reported[8] to melt at 281° dec. when heated rapidly. The purified product, now very small in amount, was heated with alcoholic ammonia in a sealed tube for twenty hours at 160°. The liquid on evaporation gave a tarry residue, the aqueous extract of

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(5) The production of formanilide by the interaction of formic acid and aniline *in the cold* seems extremely unlikely, and hence unlikely the hypothesis that the carbanilide is formed from phenylisocyanate resulting from the action of bromine on formanilide.

(6) Schlesinger and Martin, This Journal, **36**, 1589 (1914).

(7) Morton, Mahoney and Richardson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 460 (1939), Fig. 2.

(8) Chattaway and Orton, *Ber.*, **34**, 1080 (1901).

which, acidified with hydrochloric acid, gave with xanthydrol solution a white precipitate insoluble in alcohol, evidently dixanthylurea.

Another experiment with 5.7 g. of bromine and 7.9 g. of anhydrous formic acid, twenty-four days of standing, 25.7 g. of aniline, etc., yielded 0.4 g. of material. This was extracted with cold concd. hydrochloric acid in an effort to remove the last portions of brominated aniline, then with alcohol and the residue from the evaporation of the alcohol was sublimed in the molecular still. The several fractions of the sublimate, recrystallized from alcohol, appeared to consist of mixtures of 4,4′-dibromo- and 2,2′,4,4′-tetrabromocarbanilide. They were brought together and heated with alcoholic ammonia for five hours at 140–150°. The residue from the evaporation of the alcohol was extracted with water, and the aqueous solution, acidified with hydrochloric acid, gave with xanthydrol a white precipitate, insoluble in alcohol, m. p. 260° dec., showing the same behavior alone and in mixed melting point as a known sample of dixanthylurea prepared according to the directions of Werner and Fearon.[9]

Twelve grams of bromine and 30.7 g. of anhydrous formic acid were allowed to stand together for two days. The mixture, bromine being at the bottom, was allowed to run slowly from a dropping funnel into a solution of 108.3 g. of aniline in 300 cc. of benzene which was stirred vigorously with a mechanical stirrer. There was no considerable heating. A large amount of white precipitate appeared but this did not impede the stirring. The mixture, made alkaline, steam distilled, extracted with ether, etc., as described, yielded 0.2644 g. of crude product. Calculated as pure carbanilide this corresponds to 1.73% of the bromine. Fractional sublimation in vacuum and fractional crystallization yielded one fraction which consisted of impure carbanilide and another which consisted largely of brominated carbanilides. The first of these, recrystallized several times from alcohol, from dilute alcohol, and from water, and twice micro-recrystallized from alcohol, yielded carbanilide, m. p. 233.5–234.0°, identified by mixed m. p. 234.0–234.5° with a known sample, m. p. 234.5–235.0°. The other principal fraction was refluxed gently for forty-five minutes with 2 cc. of aniline in order that the brominated carbanilides by a "urea dearrangement" might be converted into carbanilide. The excess aniline was driven off by steam distillation, and the residue, dissolved out by ether, weighed 0.0341 g. In the molecular still it yielded 0.0199 g. of sublimate, light brown in color, and 0.0074 g. of residual tar. The sublimate, which evidently contained some brominated aniline, after several recrystallizations yielded carbanilide, m. p. 234.0–234.5°, mixed m. p. 234.5–235.0°, known m. p. 234.5–235.0°.

Summary

Bromine reacts with formic acid to produce a substance which, in the presence of an excess of bromine, reacts with aniline to form derivatives of urea, namely, carbanilide and brominated carbanilides.

The intermediate substance, evidently capable of existence only in the presence of free bromine, is probably dibromo-dihydroxy-methane formed by the addition of bromine to dihydroxy divalent carbon, the tautomeric form of formic acid.

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[9] Werner and Fearon, *J. Chem. Soc.*, **117**, 1360 (1920).

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Metal Pyridine Complex Salts. VI. Cobaltous and Nickelous Dipyridine Salts of Fatty Acids

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

In the preceding paper of this series[1] experiments were reported which showed that the pyridine in the pyridine complex cupric, cobaltous and nickelous cyanates is held by greater forces of affinity than the pyridine in the corresponding complex thiocyanates. The greater forces of chemical affinity are evident both from the lower dissociation pressures of the complex cyanates and from the greater shrinkages which occur when the complex cyanates, as compared with the complex thiocyanates, are formed from their component salts and pyridine. The thiocyanate radical to a greater extent than the cyanate radical exhausts the total affinity of the metal atom and leaves less of it available for coördinative combination with pyridine. The effect is due solely to the difference between a sulfur and an oxygen atom at the far end of the acid radical which is attached to the metal by an electrovalent linkage.

In the present paper we wish to report experiments on the dipyridine cobaltous and nickelous salts of acetic, propionic, butyric, isobutyric and valeric acids. We have determined their dissociation pressures over the temperature interval between 15–20° and 85–90° and the volume changes which occur at 25° when the complexes are formed by the combination of their compo-

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[1] Davis and Logan, THIS JOURNAL, **58**, 2153 (1936).