over Adams catalyst the acid absorbed 1.96 moles of hydrogen (theoretical value 2.00 moles).

From 4.0 g. of α-ionone was obtained 0.34 g. of a yellow oily acid which would not solidify. No investigation of its physical properties other than its absorption spectrum was made. Considerable unreacted α-ionone (2.57 g.) was recovered in this experiment.

Absorption Spectrum Measurements.—Determinations of the ultraviolet absorption spectra of the polyenes were made on the Beckman Spectrophotometer.

The authors are indebted to Dr. R. O. Clinton and to Mr. J. W. Ralls for the combustion analyses reported in this paper.

Summary

The α- and β-ionylideneacetones have been prepared from both the ethyl ionylideneacetates and the ionylideneacetonitriles, each of which may be prepared conveniently from the ionones. β-Ionylideneacetone shows an absorption maximum farther toward the ultraviolet than might be expected. A study of the spectra of all the intermediates in the preparation of the ionylideneacetones has been made. The structures of the ionylideneacetones have been established by the application of quantitative hydrogenation, ozonization and hypochlorite oxidation procedures

LOS ANGELES, CALIFORNIA RECEIVED SEPTEMBER 7, 1943

[CONTRIBUTION FROM THE HAYDEN LABORATORIES OF NORTHEASTERN UNIVERSITY]

Generalized Acid-Base Catalysis. I. Condensation of *o*-Benzoylbenzoic Acid in Sulfuric Acid

BY W. F. LUDER AND SAVERIO ZUFFANTI

Many of the catalytic effects observed in organic reactions can be explained readily as instances of simple acid-base catalysis if one adopts the conception of acids and bases proposed by G. N. Lewis.[1,2,3] One example is the condensation of *o*-benzoylbenzoic acid to anthraquinone, which has been studied by several authors[4,5,6] without arriving at a completely satisfactory explanation of the effects observed.

Deane and Huffman[6] have extended rate measurements of the *o*-benzoylbenzoic acid condensation into oleum of concentrations up to 29% SO_3 at 75 and 85°. They found that the velocity constant increased steadily up to their maximum sulfur trioxide percentage. In some work under way in this Laboratory on the acidity curve of oleum (to be reported in a later paper of this series), our preliminary measurements indicate the same steady increase at 40° up to 65% SO_3, the maximum concentration so far investigated.

This increase in reaction rate with increased concentration of sulfur trioxide in sulfuric acid is readily understood when considered from the Lewis viewpoint. It is merely due to increased over-all acidity. Sulfur trioxide is a stronger acid than sulfuric acid. Lewis and Bigeleisen[7] have shown that the acidity of sulfuric acid solutions increases with concentration of sulfur trioxide. Close correlation is evident in comparing the Lewis and Bigeleisen plot of Hammett's acidity function[8] with the plot of variation in reaction rate with concentration of sulfur trioxide given by Deane and Huffman.[6] This would indicate that the condensation of *o*-benzoylbenzoic acid is an acid-catalyzed reaction, and that the reaction rate does not depend upon a particular species, but rather upon the acid strength. Probably SO_3, H_2SO_4, and H_3O^{+1} are the three principal species involved, but the question of the exact proportion is unimportant since the over-all acidity can be measured experimentally. Of course it is obvious that in 65% oleum the ratio of SO_3 to H_3O^{+1} is very great.

According to this viewpoint the inhibiting effect of the product anthraquinone and of other substances can readily be explained. Anthraquinone is weakly basic. The oxygen atoms each can donate a share in a pair of electrons to a sufficiently strong acid. The presence of the anthraquinone in such a highly acidic medium simply decreases its acidity and therefore its effectiveness as a catalyst. A similar explanation applies to the other inhibitors tested by Deane and Huffman. This is especially interesting since several of these substances such as $AlCl_3$, HCl, and $CuCl_2$ are typical generalized acid catalysts. Even these acids, strong enough to catalyze Friedel–Crafts and similar reactions, are forced to behave as weak bases by the stronger mixture of sulfur trioxide and sulfuric acid.[3]

In view of this very great acidity of fuming sulfuric acid,[7] the statement of Deane and Huffman[6] that, "The effect of definite added amounts of concentrated hydrofluoric acid will more fully indicate the status of this reaction as a case of acid-base catalysis," is not likely to be upheld. They themselves had already tried a stronger acid than HF[3], namely, $AlCl_3$, and found that it did

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(1) Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(2) Luder, *Chem. Rev.*, **27**, 547 (1940).

(3) Luder and Zuffanti, "Catalysis from the Viewpoint of the Electronic Theory of Acids and Bases" presented as a part of the Symposium on Molecular Addition Compounds before the Division of Physical and Inorganic Chemistry of the American Chemical Society, 106th meeting, Pittsburgh, Penna., September 6, 1943, and to be published shortly in *Chemical Reviews*.

(4) Gleason and Dougherty, THIS JOURNAL, **51**, 310 (1929).

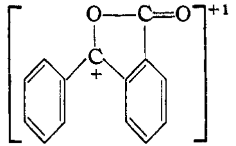
(5) Newman, *ibid.*, **64**, 2324 (1942).

(6) Deane and Huffman, *Ind. Eng. Chem.*, **35**, 684 (1943).

(7) Lewis and Bigeleisen, THIS JOURNAL, **65**, 1144 (1943).

(8) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940.

not increase the reaction rate in fuming sulfuric acid, but actually decreased it.

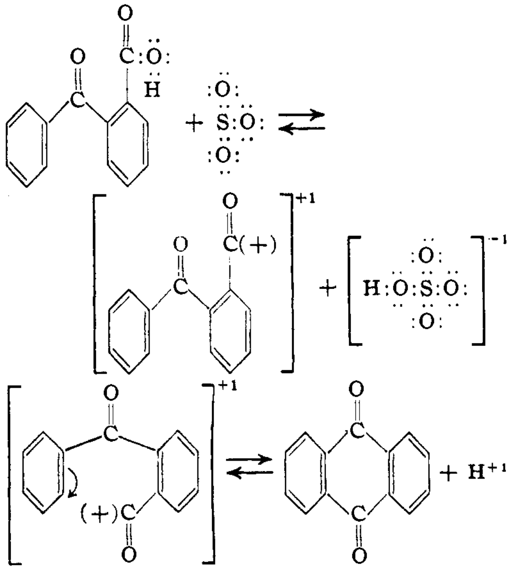
Newman[5] has postulated the formation of the cyclic carbonium ion  as the first step in the condensation. This suggestion is based on the formation of a quantity of pseudo-ester when methyl alcohol was present. The cyclic ion is considered as formed by the reaction of sulfuric acid on the *o*-benzoylbenzoic acid with H_3O^{+1} and $2HSO_4^{-1}$ as the other products. This explanation conforms to the Brönsted theory of acids and bases, but obviously the Brönsted theory cannot explain the large increase in velocity constant as the amount of sulfur trioxide is increased. On the other hand, the observed behavior is exactly what is expected on the basis of the electronic theory of acids and bases. Sulfur trioxide is a much stronger acid[7] (*i. e.*, has a greater tendency to appropriate lone electron-pairs) than H_2SO_4 or H_3O^{+1}.

However, this does not mean that the hypothesis of a cyclic ion is incorrect. The cyclic ion could be formed just as well by sulfur trioxide as by sulfuric acid

$$o\text{-Benzoylbenzoic acid} + SO_3 \rightleftarrows (\text{cyclic ion})^{+1} + HSO_4^{-1}$$

So whether the cyclic ion or some other explanation is adopted, the ability of the Lewis theory to explain the observed catalytic effects is not affected.

An alternative mechanism which we prefer for reasons discussed subsequently is as follows



(1)

(2)

The use of H_2SO_4, H_3O^{+1}, or any other acid species present, in place of the sulfur trioxide in the above equations would serve equally as well since according to the Lewis theory acids coördinate with lone electron-pairs. In equation (1) the sulfur trioxide behaves as a typical acid[2] by coördinating with the oxygen electron-pair to split off the OH^{-1} group thus leaving the carbon atom electron-deficient. This makes the carbon atom acidic since it now has a great tendency to appropriate a lone electron-pair to complete its octet again. The two possibilities are: the formation of the cyclic ion and the formation of anthraquinone according to equation (2) above. Both reactions undoubtedly take place since Newman seems to have demonstrated conclusively the existence of a large proportion of the cyclic ion at low temperatures. But since the reaction under discussion is the formation of anthraquinone, it seems unnecessary to involve the cyclic ion. We prefer to regard its formation as a side reaction to, rather than the first step in, the production of anthraquinone.

The reasons for this preference are: (1) it fits the experimental facts equally as well as Newman's explanation; (2) it is simpler and more direct; (3) it is in accord with the newer explanation of the mechanism of acylations[3,9]; (4) when the structural formulas of all three species are considered there seems to be no way of getting a cyclic ion from *o*-benzoylbenzoic acid except through the open-chain ion as an intermediate step.

However, whichever choice of mechanism is made, the interpretation of the experimental data by means of the electronic theory of acids and bases is still applicable. Both mechanisms involve a cyclic ion and both can be catalyzed by SO_3 as well as by H_2SO_4 or H_3O^{+1}. Both agree that the immediate percursor of anthraquinone is the open-chain ion.

Gleason and Dougherty[4] showed that the condensation is actually first order and not merely an apparent first order reaction because of an excess of sulfuric acid. No explanation of this has been offered nor of the rapid and large evolution of heat observed when oleum is added to the *o*-benzoylbenzoic acid. We have observed that this rapid evolution of heat on mixing is many times greater at high sulfur trioxide concentrations, corresponding roughly to the much greater velocity constant. A logical explanation of these two facts in keeping with the other aspects of the Lewis interpretation is that the carbonium ion is formed rapidly according to equation (1) upon mixing. The rate-determining step would then be equation (2), which is obviously first order. The difference in rate with increasing amounts of SO_3 is due to the shifting of the equilibrium in equation (1) so that the initial concentration of carbonium ion is greater as the acidity of the solution is increased.

Summary

An explanation of some effects in the catalyzed condensation of *o*-benzoylbenzoic acid to anthra-

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[9] Price, *Chem. Rev.*, **29**, 37 (1941).

quinone is given according to the electronic theory of acids and bases.

An alternative mechanism is proposed, but it is shown that the application of the Lewis theory is equally valid for both mechanisms considered.

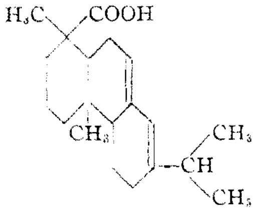
BOSTON, MASSACHUSETTS RECEIVED SEPTEMBER 29, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF FUEL TECHNOLOGY OF THE PENNSYLVANIA STATE COLLEGE]

The Hydrogenolysis of Abietic Acid[1]

BY H. B. CHARMBURY AND C. C. WRIGHT

Although many investigations on the hydrogenolysis of coal are reported in the literature, interpretation of the results has been hindered because of the lack of information concerning the mechanism of the reaction. One method of attack upon this problem has been through hydrogenolysis of pure organic compounds, several of which, such as benzene, indene, naphthalene, naphthols, phenol, cresols and carboxylic acids[2] have already been studied. The complexity of the compounds has been gradually increased with the ultimate goal of hydrogenating polynuclear structures as closely related to the so-called "coal molecule" as possible. The present work is concerned with the hydrogenolysis of abietic acid, I,



I

the structure of which is such that information may be secured concerning oxygen removal from the carboxyl group, alkyl severance of the two different alkyl groups, alicyclic decomposition due to the breakdown of the hydrophenanthrene structure and hydrogen consumption due to saturation of the double bonds and to hydrogenation cracking reactions.

Hydrogenolyses were conducted for two hours at temperatures ranging from 325 to 450°, with initial hydrogen pressures of 1900 to 1975 P. s. i. (133.6–138.9 kg./sq. cm.). Because the results of these experiments indicated that 400° is the critical temperature for oxygen removal, alkyl severance and hydrogen consumption, experiments were also conducted at this temperature, using the same initial hydrogen pressure, for 1, 2 and 3 one-hour periods. The reaction gases were removed and the retort charged with fresh hydrogen at the end of each one-hour period.

Oxygen Removal.—Using temperatures and pressures in the range of 300–500° and 1000–3000 P. s. i. several investigators[3,4,5,6] have shown that much of the oxygen present in coal is removed rapidly and in the early stages of hydrogenation and that the remaining oxygen is removed at a slow but rather constant rate. Boomer[7] has suggested a theory that coals contain at least two types of oxygen: oxygen as carboxyl which is removed rapidly, and oxygen as hydroxyl which is more resistant. Fisher[8] also supports this theory and shows that using a Pittsburgh coal 60% of the oxygen is eliminated much more rapidly than the remaining 40% and that most of the oxygen which is removed in the early stages appears in the products as water. Storch[9] has studied the oxygen removal of the anthraxylon fraction of various coals and found that the oxygen is removed as carbon dioxide and water in the early stages and that the oxygen removal increases with decreasing rank of the coal. An extended study by Storch[10] revealed that upon hydrogenation the low rank coals high in oxygen lose 10–20% of their oxygen as carbon dioxide whereas the higher rank coals lose only 3 to 6% in this form.

Cawley[11] has studied the removal of oxygen from the carboxyl linkage by hydrogenating benzoic acid (or ferrous benzoate) at 450° and 100 atmospheres pressure and reported 24% benzene and 41% toluene in the reaction products along with a relatively large amount of water. The presence of toluene and water indicates a removal of oxygen by a reduction of the carboxyl group.

The data of Fig. 1 show, however, that the removal of oxygen from abietic acid takes place for the most part as a straight decarboxylation with the formation of carbon dioxide, and that the total percentage of oxygen removed is directly proportional to the temperature of hydrogenolysis. At 450° the elimination of oxygen is virtually complete.

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(1) From the thesis of H. B. Charmbury presented to the faculty of The Pennsylvania State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The hydrogenolysis of these compounds has been studied by the British Fuel Research Board and their results will be found in the Board reports from 1931 to 1938 inclusive.

(3) Bakes, *Dept. Sci. Ind. Research Tech. Paper*, **37**, **214** (1933).

(4) Boomer and Saddington, *Can. J. Research*, **12**, 825 (1935).

(5) Graham and Skinner, *J. Soc. Chem. Ind.*, **48**, 129T (1929).

(6) Horton, King and Williams, *J. Inst. Fuel*, **7**, 85 (1933).

(7) Boomer, Saddington and Edwards, *Can. J. Research*, **13B**, 11 (1935).

(8) Fisher and Eisner, *Ind. Eng. Chem.*, **29**, 1371 (1937).

(9) Storch, *et al.*, *Fuel*, **19**, 13 (1940).

(10) Storch, *et al.*, *ibid.*, **20**, 5 (1941).

(11) Cawley, *ibid.*, **12**, 366 (1933).