

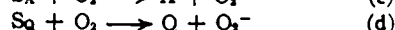
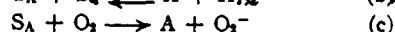
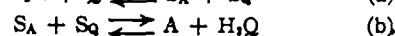
James and Weissberger<sup>4b</sup> for the sulfite inhibition of the autoxidation of hydroquinone. In the absence of foreign substances the latter reacts according to Class I-E.<sup>5</sup> Figure 2 shows that the rate approaches independence of the sulfite concentration with increasing concentration of the inhibitor. Figure 3 shows that the dependence of the rate upon the concentration of hydroquinone is approximately first-order in air, and about three-halves order in oxygen. Equations (26) and (37) to (40) indicate that the rate for mixed inhibition becomes independent of the inhibitor concentration when the latter becomes sufficiently high. Equations (37) to (40) also indicate a rate dependency between first- and second-order with respect to hydroquinone and oxygen, respectively. Both dependencies conform with the experimental observations.<sup>4b</sup> The inverse proportionality of rate to inhibitor concentration reported by James and Weissberger<sup>4b</sup> follows from specific conditions, particularly from those leading to equation (40).

The autoxidation of an inhibitor is occasionally catalyzed by the substrate. The mechanism is similar to that outlined in the catalysis section of this paper where C is replaced by S or T, and R by I.

When *l*-ascorbic acid is added to solutions of *N*-methyl-*p*-aminophenol prior to the start of autoxidation, the reaction is inhibited, but if it is added after the start of the autoxidation, the reaction is accelerated.<sup>4a</sup> When *l*-ascorbic acid is added to solutions of pseudocumohydroquinone or 2,4-diaminophenol, the autoxidation is catalyzed when the ascorbic acid is added prior to or after the start of the reaction.<sup>4a</sup> When pseudocumohydroquinone is added to a solution of ascorbic acid after autoxidation has commenced, a very efficient catalysis of the autoxidation takes place.<sup>4a</sup>

These phenomena were explained<sup>4a</sup> with the rapid reduction of the respective quinonoid compound to the semiquinone by the ascorbic acid. If the reduction of the quinone by ascorbic acid is too slow, for instance, when duroquinone is added

to an oxidizing solution of ascorbic acid, no catalysis is observed. On the other hand, if the reduction of the quinone to the hydroquinoid state is so fast that the reduction of the semiquinone prevails over its autoxidation, the rate behaves not as though the quinone had been added but as though ascorbic acid had been replaced by an equivalent amount of the hydroquinone. This is observed when benzoquinone is added to an autoxidizing solution of ascorbic acid. Let  $H_2A$ ,  $S_A$ , and  $A$  represent *l*-ascorbic acid, its semiquinone, and dehydroascorbic acid, respectively. Similarly, let  $H_2Q$ ,  $S_Q$ , and  $Q$  represent the given hydroquinone, its semiquinone, and the quinone, respectively



$k_a \gg k_b > k_c \gg k_d$ : The quinone will be reduced to the hydroquinone, no catalysis will take place (benzoquinone and *l*-ascorbic acid).

$k_a \gg k_b$ ,  $k_d \gg k_c > k_b$ : The reduction will stop at the semiquinone and the quinone will act as a catalyst (pseudocumohydroquinone and *l*-ascorbic acid).

$k_a \gg k_b$ ,  $k_c$ ,  $k_d > k_b$ : Inappreciable catalysis, slow reduction of the quinone (duroquinone and *l*-ascorbic acid).

"Induced oxidation" ("oxygen activation")<sup>20,21</sup> will be observed if the hydrogen peroxide, the perhydroxyl ion or semiquinone oxidizes a compound which has been added to the reaction mixture.

### Summary

The rate laws of the oxidation of enediols, hydroquinones, enolamines and their vinyl analogs in the presence of foreign catalysts and inhibitors are derived and discussed.

(20) Jorissen, *Rec. trav. chim.*, **64**, 147 (1945).

(21) Jorissen and VanCalcar, *ibid.*, **64**, 284 (1945).

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## NOTES

### On the Addition of Formic Acid to Dicyclopentadiene

BY FELIX BERGMANN AND HELENE JAPHE

Several examples, reported in the literature,<sup>1,2</sup> demonstrate the outstanding ability of one double bond in dicyclopentadiene (I) to add various reagents. Those additions, which proceed under the influence of strong electrophilic catalysts (*e. g.*,

(1) Alder and Stein, *Ann.*, **488**, 211 (1931).

(2) Bruson and Riener, *THIS JOURNAL*, **67**, 1178 (1945); **68**, 8 (1946).

sulfuric acid, boron trifluoride, etc.), involve a molecular rearrangement,<sup>3</sup> which, according to Bartlett and Schneider,<sup>4</sup> follows the ionic mechanism of the Wagner-Meerwein reaction and leads to the "exo"-derivatives of dicyclopentadiene. Bruson, in a recent patent,<sup>5</sup> states that organic acids with "dissociation constants of about  $1.5 \times 10^{-3}$  or more" promote the addition reaction by their own acidity. We have now observed

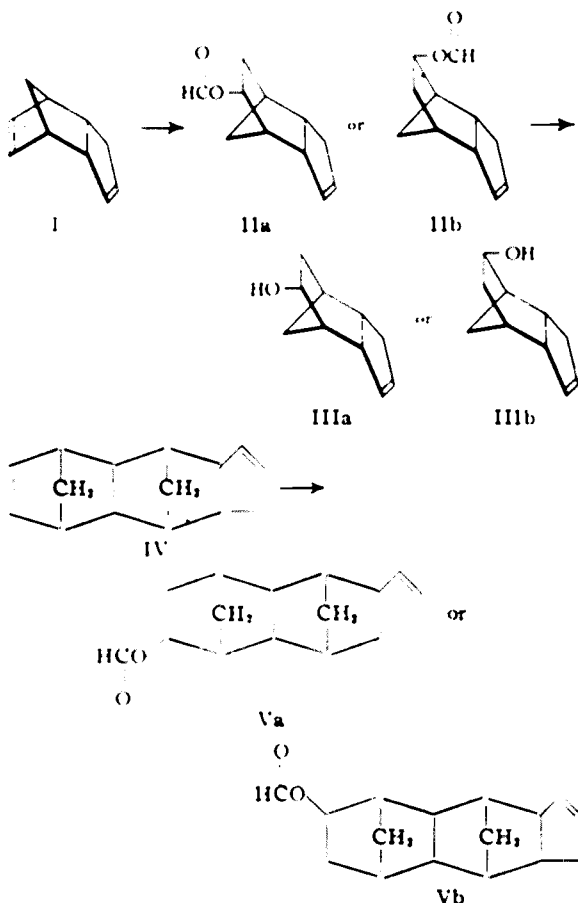
(3) Bruson and Riener, *ibid.*, **67**, 723 (1945).

(4) Bartlett and Schneider, *ibid.*, **68**, 6 (1946).

(5) U. S. Patent 2,395,452; C. A., **40**, 8138 (1946).

that even boiling formic acid ( $K_a^{25} = 1.77 \times 10^{-4}$ ;  $K_a^{100} = 1.55 \times 10^{-4}$ )<sup>6</sup> adds directly to I to produce dicyclopentenyl formate (IIa or b) in nearly quantitative yield, whereas Bruson states in his example that the addition of formic acid is achieved in about 71% yield by catalysis with 40% sulfuric acid. That our reaction likewise involves an "endo-exo-rearrangement," was shown by saponification of II to dicyclopentenol (IIIa or b), identical with the product obtained by direct hydration of I in the presence of sulfuric acid.<sup>3</sup>

The reaction described here provides a most convenient route for the preparation of dicyclopentenol and its higher homologs. We have found, *e. g.*, that tricyclopentadiene (IV) by the same method gives a quantitative yield of tricyclopentenyl formate (Va or b). In addition, we have been able to develop the uncatalyzed addition of formic acid into a method for the quantitative determination of dicyclopentadiene.<sup>7</sup>



#### Experimental

**Dicyclopentenyl Formate (II).**<sup>4</sup>—Crystalline dicyclopentadiene, m. p.  $32^\circ$  (132 g.; 1 mole), and formic acid, 99–100% (138 g.; 3 mole), were refluxed for four hours, and the mixture then fractionated. After removal of the excess formic acid, the formate II distilled at  $136^\circ$  (25

mm.). Yield was 171 g., 96%. Bruson<sup>3</sup> reports a boiling point of  $111$ – $112^\circ$  (10 mm.):  $n_D^{20}$  1.4980;  $n_D^{25}$  1.5040;  $d_4^{16}$  1.113;  $M_R$  46.28.

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 72.4; H, 7.9. Found: C, 74.3; H, 7.7.

The formate was saponified by refluxing with 1.5 equivalents of ethanolic potassium hydroxide for eight hours. The solvent was then distilled off, the residue taken up with benzene and washed with water. Dicyclopentenol (III) distilled at  $92$ – $95^\circ$  (2 mm.), as a clear, colorless liquid of high viscosity. It exerts a strong anesthetic effect on the human tongue:  $n_D^{20}$  1.5206. Bruson<sup>3</sup> reports  $n_D^{20}$  1.5246. The phenylurethan of III melts at  $163^\circ$  (Bruson, 164–165 $^\circ$ ) and shows no depression upon admixture of the phenylurethan, prepared from dicyclopentenol according to literature.<sup>3</sup>

**Dihydro-dicyclopentenyl Formate.**—The formate (II) was mixed with an equal volume of 96% alcohol and hydrogenated over Raney nickel at room temperature and atmospheric pressure. The required amount of hydrogen was absorbed during two hours. Distillation gave a 92% yield of a colorless oil, b. p.  $137^\circ$  (35 mm.),  $n_D^{20}$  1.4870.

*Anal.* Calcd. for  $C_{11}H_{16}O_2$ : C, 73.3; H, 8.9. Found: C, 73.1; H, 9.0.

Tricyclopentenyl formate (V) was prepared in the same way, as described before, by eight hours of reflux. It boils at  $136^\circ$  (0.2 mm.) and forms a colorless, viscous liquid:  $n_D^{20}$  1.5352;  $d_4^{16}$  1.162  $M_R$  65.40; yield was quantitative.

*Anal.* Calcd. for  $C_{15}H_{20}O_2$ : C, 78.7; H, 8.2. Found: C, 78.6; H, 8.3.

Saponification of V, as described above, gave a 95% yield of tricyclopentenol in an excellent state of purity, b. p.  $156^\circ$  (0.4 mm.). The substance formed a hard, brittle glass, which after standing for three months crystallized spontaneously and then showed an m. p. of  $115^\circ$ , as described by Bruson and Rieter.<sup>3</sup> No indication of the presence of an isomer was found.

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#### A Parabolic Relation between Bond-Order and Interatomic Distance

BY J. L. KAVANAU

The author<sup>1</sup> has advanced an empirical relation between bond-order,  $N$ , and interatomic distance,  $D$  (in Å.)

$$D = a + b \left( \frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N \quad (1)$$

where  $n_1$  and  $n_2$  are the principal quantum numbers of the valence electrons in the bonded atoms and  $a$  and  $b$  are constants for the specific atom pair.

Lagemann<sup>2</sup> has recently proposed a generalized modification of (1) to

$$D' = K_1/Z + K_2Z \left( \frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N \quad (2)$$

where  $Z$  is the sum of the atomic numbers of the bonded atoms and  $K_1$  and  $K_2$  are constant for all atom pairs having the same values for  $n_1$  and  $n_2$ . Lagemann has shown an average per cent. deviation of only 1.3% between experimental interatomic distance values and those given by equation (1) for a number of first row linkages.

(6) Harrod and Embree, *This Journal*, **96**, 1042 (1934)

(7) F. Bergmann and Japbe, *Ind. Eng. Chem., Anal. Ed.*, in press

(1) J. L. Kavanau, *J. Chem. Phys.*, **12**, 467 (1944)

(2) R. T. Lagemann, *ibid.*, **14**, 743 (1946)