NOTES

Induced Oxidation of *p*-Benzophenone

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During preliminary experiments on the effect of *o*-benzoquinone on the tyrosinase-catalyzed oxidation of *p*-cresol the effect of the *p*-benzoquinone was also tried. In view of the well-known stability of aqueous solutions of *p*-benzoquinone the results were unexpected.

It was found that in the presence of a substrate which was being oxidized *p*-benzoquinone was also oxidized with the consumption of one atom of oxygen per mole of quinone. When only enzyme but no substrate was present *p*-benzoquinone was not oxidized. If the quinone was added to the system after the substrate had been completely oxidized with the normal consumption of oxygen (*e.g.*, 3 atoms per mole for *p*-cresol) no oxidation of the *p*-benzoquinone took place. Thus it appears that some intermediate form of the oxidized substrate is able to induce the oxidation of *p*-benzoquinone.

This reaction displayed another peculiar feature in that the *p*-benzoquinone had to be added in the *solid* form in order for this phenomenon to be observed. All attempts to find this reaction with aqueous solutions of *p*-benzoquinone, no matter how freshly prepared, failed.

The nature of the substrate appeared to have no influence on the induced oxidation of solid *p*-benzoquinone as the use of *p*-cresol, catechol, 4-chlorocatechol and 4,5-dichlorocatechol all showed a normal oxygen consumption plus one atom per mole of *p*-benzoquinone.

Table I shows a typical result of the oxidation of a mixture of *p*-cresol and solid *p*-benzoquinone.

Table I

Oxidation of *p*-Cresol + Solid *p*-Benzoquinone in the Presence of Tyrosinase

*p*H 6.48 (citrate–phosphate buffer); enzyme strength 2.5 cresolase units[1] per ml., 25°

p-Cresol, mg.	Quinone, mg.	Oxygen consumption, cu. mm. Calculated *p*-Cresol	Quinone	Obsd. total
0.01	10	3.1	1030	1003
0.1	10	31	1030	1060
1.0	10	310	1030	1370
2.0	10	620	1030	1690
4.0	10	1240	1030	2315

Fresh enzyme was added whenever the oxygen consumption had nearly ceased until the addition of fresh enzyme caused no further oxygen consumption. The measurements were made by use of the Warburg respirometer, according to the technique of Graubard and Nelson.[2] The enzyme was obtained from the common mushroom, *Psalliota campestris*. It was purified by precipitation with trichloroacetic acid from the press juice, taken up in water, precipitated with chilled acetone, redispersed in water, absorbed on alumina, eluted with secondary sodium phosphate, and dialyzed against distilled water.

The author does not intend to continue this work and has submitted these data with the hope of provoking further investigation.

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(1) Mark H. Adams and J. M. Nelson, This Journal, **60**, 2472 (1938).

(2) Mark Graubard and J. M. Nelson, *J. Biol. Chem.*, **111**, 757 (1935).

Brown Condensation Products from Acetaldehyde and Aliphatic Amines

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Previous papers from this Laboratory have shown that the reaction of acetaldehyde with proteins[1] has many features in common with the reaction of glucose with proteins.[2] In an effort to elucidate the mechanisms of these "browning" reactions, studies are being extended to simple model systems.[3] This report describes some reactions of acetaldehyde with several aliphatic amines and ammonia and, in particular, the properties of the brown water-soluble polymers resulting. Reactions were conducted at 3–25° in aqueous solutions held at *p*H 6–7 with phosphate buffers.

The rates of browning, measured colorimetrically, for methylamine, ethylamine and *n*-butylamine with acetaldehyde were very similar and significantly greater than the rates of browning of primary aliphatic amines containing only one hydrogen atom on the α-carbon atom, such as cyclohexylamine, isopropylamine and *sec*-butylamine, and were much faster than the rate for ammonia–acetaldehyde combinations. For example, in aqueous solution, 0.5 *M* in amine and in acetaldehyde, buffered at *p*H 6.75–6.80 with phosphate at 25°, the times in hours to reach the same brown color[4] for methylamine, cyclohexylamine, isopropylamine, *sec*-butylamine and ammonia were 1, 2.5, 7, 8 and 18 hours, respectively. Under the same conditions, mixtures of aliphatic secondary amines with acetaldehyde did not yield water-soluble brown products but deposited yellow ether-soluble resins. With primary amines the browning reaction was very sensitive to *p*H, the rate increasing rapidly with increasing *p*H between *p*H 5 and 10. Below *p*H 5, very little color development was observed; at *p*H 10 or above, yellow, water-insoluble, ether-soluble resins precipitated. The rate of browning

(1) A. Mohammad, H. S. Olcott and H. Fraenkel-Conrat, *Arch. Biochem.*, **24**, 270 (1949).

(2) A. Mohammad, H. Fraenkel-Conrat and H. S. Olcott, *ibid.*, **24**, 157 (1949).

(3) J. F. Carson, This Journal, **75**, 4300, 4337 (1953).

(4) For this comparison, a reading of 100 on the Klett–Summerson colorimeter with a green filter was used. The same qualitative order was observed throughout later stages of browning.