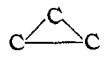
TABLE I

Temp., t° °C.	$n^{t}D$ Propane	Propene	Cyclopropane	Propyne	Propadiene	D^{t}_{4} (vac.) Propane[5]	Propene[6]	Cyclopropane	Propyne[6]	Propadiene
−20	....	....	....	1.3725	....	....	....	....	0.6670	....
−30	....	....	1.3706	1.3793	1.4137	....	....	0.6769	.6791	0.6575
−40	1.3378	1.3567	1.3769	1.3863	1.4214	0.5800	0.6002	.6886	.6911	.6699
−50	1.3447	1.3640	1.3833	....	1.4291	.5915	.6132	.7002	....	.6822
−60	1.3517	1.3712	1.3897	....	1.4368	.6029	.6258	.7119	....	.6944
−70	1.3587	1.3785	1.3960	....	1.4444	.6145	.6386	.7235	....	.7064
−80	1.3657	1.3857	1.4024	....	....	.6259	.6513	.7352	....	....
@N. b. p.	1.3392	1.3623	1.3726	1.3747	1.4168	.5829	.6100	.6807	.6698	.6624
Normal b. p.	−42.2[7]	−47.8	−32.7	−23.3[6]	−34.34[8]	−42.2[7]	−47.8	−32.7	−23.3[6]	−34.34[8]
	dn_D/dt° and, respectively, dD/dt°									
	−0.000698	−0.000725	−0.000638	−0.000690	−0.000768	−0.00115	−0.00128	−0.00117	−0.00120	−0.00122

TABLE II

Hydrocarbon	Carbon skeleton	Mol. volume at N. b. p., cc.	Experimental molecular refractions, MR^{LL}_{D} @N. b. p.	−80°	−60°	−40°	−20°	Extrapolated to +20°	Calculated MR^{LL}_{D} (at +20°)	Temp. coeff. MR^{LL}_{D}/°C. (from −80° to −20°)
Propane	C—C—C	75.65	15.83	15.76	15.79	15.83	...	15.9	16.05	+0.0017
Propene	C—C=C	68.98	15.30	15.15	15.24	15.34	...	15.6	15.62	+ .0047
Cyclopropane		61.82	14.06	13.94	13.99	14.04	14.10	14.2	(13.85)[a]	+ .0025
Propyne	C—C≡C	59.81	13.65	...	...	13.61	13.66	13.8	14.05	+ .0025
Propadiene	C=C=C	60.48	15.19	15.03	15.10	15.17	...	15.3	15.12	+ .0035

[a] 3 × CH_2.

corresponding to the boiling point of the pure substance. The n_D of each fraction was measured and a cut whose index did not vary over 0.0002 from adjacent cuts was used for our final measurements. These were made at temperature intervals of about 10°. For all hydrocarbons studied the n_D was a straight line function of temperature; the values of Table I were read off the line for even temperature intervals.

For measuring n_D below −50° reduced pressure was employed on liquid propene circulating through the refractometer. By this procedure we were able to measure easily n_D at as low as −75°, when using dry-ice as the cooling medium.

(5) O. Maass and C. H. Wright, THIS JOURNAL, **43**, 1098 (1921).
(6) F. R. Morehouse and O. Maass, *Can. J. Research*, **11**, 637 (1934).
(7) M. M. Hicks-Bruun and J. H. Bruun, THIS JOURNAL, **58**, 810 (1936).
(8) See J. H. Vaughn, L. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

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Two Notes on the Deamination of Glycine in the Presence of Tyrosinase and *p*-Cresol

BY STEPHEN S. HUBARD

When collecting data which indicate that *p*-cresol oxidized in the presence of tyrosinase functions reversibly in the oxidative deamination of glycine,[1] it was found that this reversibility, although considerable, is not complete. The smaller amounts of *p*-cresol do not take care of as much glycine as do the larger ones, although the amounts are greater than those theoretically equivalent, as discussed in the paper cited. Second, as found by others,[2] the amount of ammonia recovered is less than what corresponds to the amount of glycine deaminized. These two facts suggest that part of the oxidized *p*-cresol, and part of the glycine nitrogen, either as ammonia, or without being released as ammonia, are consumed in forming the intense dichroic coloration (red by reflected light, blue by transmitted light) characteristic of the digestion solutions. It seemed significant that the color of the one solution from which the theoretical amount of ammonia was recovered (1 mg. of *p*-cresol with 50 mg. of glycine) was green and showed no dichroism.

A few drops of dilute ammonia were added to a solution of 20 mg. of enzymically oxidized *p*-cresol; in a few hours the color of the solution had become greenish, similar to the one just mentioned. Formaldehyde is a possible *transient* end-product in the breakdown of glycine as studied here.[3] When two or three drops of formalin was added to another sample of oxidized *p*-cresol, a

(1) S. S. Hubard, *J. Biol. Chem.*, **126**, 489 (1938).
(2) C. E. M. Pugh and H. S. Raper, *Biochem. J.*, **21**, 1370 (1927).
(3) F. C. Happold and H. S. Raper, *ibid.*, **19**, 92 (1925).

cherry-red color was observed eventually. However, when both formaldehyde and ammonia were added, a dichroic effect similar to that of the glycine digestion solutions developed. Like the latter, the solution became red when made strongly alkaline, and blue when made strongly acid (caustic soda, hydrochloric acid).

Preliminary efforts to isolate the colored substance that seems from the experiment just described to be formed from ammonia, oxidized *p*-cresol, and the fragment of the glycine molecule were unsuccessful, but the important thing is that we have found at least a qualitative indication of the fate of the ammonia and *p*-cresol in question, whereas before there was only speculation.

There is a discrepancy in the literature regarding resorcinol as a possible inductor in the tyrosinase–glycine reaction, which should be mentioned. Robinson and McCance[4] state that it functions, although there is a long "induction period," and the deamination of glycine is far from complete. Pugh and Raper[2] and Happold and Raper[5] obtained completely negative results. The clue is that Robinson and McCance used a basidiomycete as the source of the enzyme; the other workers used meal-worms and potatoes, respectively. Since Gortner has shown[5] that tyrosinase not only does not oxidize *m*-dihydroxylic compounds, but also is hindered by them in its oxidation of other phenols, it follows that Robinson and McCance probably did not free their preparation from a laccase which functions with resorcinol,[5] and which is found in the fungus they used, whereas the other workers evidently had preparations free from this laccase. The delayed action and incomplete deamination observed by Robinson and McCance are just what one would expect from a preparation in which the laccase was only a contaminant.

(4) M. E. Robinson and R. A. McCance, *Biochem. J.*, **19**, 251 (1925).
(5) R. A. Gortner, *J. Biol. Chem.*, **10**, 113 (1911).

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Determination of the Ionization Constant of Aci-Nitroethane

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In a preceding paper[2] were reported kinetic measurements on the rate of isomerization of nitroethane from the nitro to the aci form. To explain the kinetics of the reverse process of isomerization from aci to nitro form, a knowledge of the ionization constant of aci-nitroethane, $CH_3CH{=}NOOH$, is essential. The only value available is that given by Junell,[3] 7×10^{-5}, and obtained from kinetic measurements at 0°. The importance of this constant for kinetic purposes lends interest to a direct determination by an electrometric method.

The determination involves the complication of the instability of the ions of the aci acid, which isomerize by mutual interaction to the nitro form. Any appreciable concentration of either hydrogen ion or aci ion leads to such a rapid rate of isomerization that the *p*H of the solution varies too much during the course of a *p*H measurement for the results to have significance. This difficulty can be obviated by measuring the *p*H of solutions where the concentration of both ions is very small, *i. e.*, solutions of the aci acid practically free of salt.

A solution of barium nitroethane, 0.06341 *N*, was prepared by dissolving a weighed quantity of nitroethane in water, adding an equivalent quantity of barium hydroxide, and allowing the solution to stand for several days. This stock solution was diluted then to the desired concentrations. In these salt solutions *nearly all* the acid was liberated by the addition of a definite quantity of either hydrochloric or sulfuric acid. The *p*H of the solution was determined with a sensitive glass electrode assembly, with which it was possible to make several measurements to 0.01 *p*H unit within one minute following the acid addition. The electrode[4] was calibrated with a potassium acid phthalate buffer.[5]

The results of three measurements at 23° are given in Table I. Line (1) gives the initial concentration of barium nitroethane, lines (2) and (3) the acid added and its final concentration, and (4) the observed *p*H, while (5), (6), and (7) give the concentrations of hydrogen ion, nitroethane ion, and the undissociated acid at equilibrium. The ionization constants, K_i,[6] calculated from

(1) Present address: Department of Chemical Engineering, Case School of Applied Science, Cleveland, Ohio.
(2) Maron and La Mer, THIS JOURNAL, **60**, 2588 (1938).
(3) Junell, *Svensk Kem. Tid.*, **46**, 125–136 (1934); Dissertation, University of Uppsala, 1935.
(4) Sendroy, Shedlovsky and Belcher, *J. Biol. Chem.*, **115**, 532 (1936); MacInnes and Longsworth, *Trans. Am. Electrochem. Soc.*, **71**, 73 (1937).
(5) MacInnes, Belcher and Shedlovsky, THIS JOURNAL, **60**, 1098 (1938).
(6) In the computation of K_i, which is on a concentration basis, it has been assumed that *p*H measures hydrogen-ion concentration. We are aware of the theoretical difficulties in such an assumption. It is, however, a sufficient approximation for our purpose.