of a few derivatives are as follows: acetate, 194–195°; benzoate, 191–192°; methyl ether, 183–184; carboxymethyl derivative, 239–240°. It is characteristic of the hydroxy compound and of the above derivatives that the red solution in concentrated sulfuric acid acquires, on the addition of a drop of concentrated nitric acid, a transient green color changing to deep blue.

The preparation of these and other derivatives desired for biological experimentation will be described later.

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RECEIVED JULY 22, 1935

THE PEROXIDE EFFECT IN THE CANNIZZARO REACTION

Sir:

The theory of Haber and Willstätter [*Ber.*, **64**, 2844 (1931)] that the Cannizzaro reaction has a chain mechanism, catalyzed by heavy metal ions, such as ferric ion, has been investigated in this Laboratory. Catalysis by ferric ion was indeed found to take place under ordinary conditions. However, when special precautions were taken to use peroxide-free aldehydes, and to run the reaction in the absence of oxygen, no Cannizzaro reaction took place, nor did the addition of ferric iron cause any appreciable degree of reaction. Thus it would appear that the Cannizzaro reaction is catalyzed primarily by peroxides, rather than by the heavy metals, and that the function of the latter is to facilitate the formation of peroxides in the mixture, being without any direct effect on the Cannizzaro reaction itself.

This has been shown to be the case with benzaldehyde, tolualdehyde and anisaldehyde. Typical results in the case of tolualdehyde and 55% potassium hydroxide solution are as follows.

CANNIZZARO REACTION WITH TOLUALDEHYDE

Technique of addition	Peroxide content of aldehyde	Time, hrs.	Added reagents	Extent Cannizzaro, %
Air	3+	8	......	33
Vac	Neg.	8	......	0
Air	3+	22	......	91
Vac	Neg.	22	......	2
Vac	Neg.	22	0.1 g. $FeCl_3$	12
Air	4+	20	......	100
Vac	Neg.	20	.2 g. $FeCl_3$	8
Vac	Neg.	20	.5 g. toluic acid	0
Oxygen	Neg.	20	.2 g. $FeCl_3$ and solution saturated with oxygen	38

Further experiments along these lines are in progress in this Laboratory, and a comprehensive report of the research will soon be published.

GEORGE HERBERT JONES CHEMICAL LABORATORY
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RECEIVED JULY 13, 1935

A MICRO QUINHYDRONE–SILVER CHLORIDE CELL FOR PRECISION E. M. F. STUDIES ON HEAVY WATER

Sir:

For the purpose of studying the exchange reaction

$$QH_2 \text{ (deuteroquinone)} + 2HCl = QH_2 \text{ (hydroquinone)} + 2DCl$$

we have investigated the reliability of the silver chloride electrode using a micro technique, applicable to heavy water, where the quantities of solution available for rinsing are severely limited.

The cells, which were of 2–4 cc. capacity, were similar in construction to the macro type employed by Harned and Wright [THIS JOURNAL, **55**, 4851 (1933)]. The Type A did not permit rinsing the silver chloride electrode compartment, nor did it have a long capillary tube to minimize diffusion of quinhydrone to the silver chloride electrode. In type B, these factors and in addition space for duplicate electrodes of each kind were provided. Oxygen was removed from the final solutions by repeated evacuation, followed by backing with nitrogen before admitting the solutions to the cells. Eastman quinhydrone was recrystallized at *p*H 5 to 6 in an atmosphere of nitrogen until it melted sharply between 170.5–171.0° (corr.).

The limiting factor appears to be the accuracy with which the concentration of the acid (0.01 *M*) can be prepared using small quantities. Constant boiling (H_2O) acid was added from a 1-cc. micro weight buret to 15 to 25 cc. of D_2O–H_2O mixtures of known density, using a balance accurate to 0.02 mg. We obtained more reproducible results in the quinhydrone half cell with spiral platinum wires than with large foils. The preparation of the silver chloride electrodes is described elsewhere [Armbruster and Crenshaw, THIS JOURNAL, **56**, 2525 (1934)]. They were washed well in distilled water, and then repeatedly with small amounts of the cell solution. In the micro cells, an equilibrium value is obtained within one-half hour, and is maintained to within 0.05 mv. for two to four hours, followed by a slow drift. The micro results are as reproducible as with the macro technique, the average value being only 0.01 mv. less than that computed from the Harned and Wright empirical eq. (2); namely, for $m = 0.01$; $E = 0.23549$ v.

Type	HCl, *M*	$E_{0.01}$, mv.
A	0.01002	0.23552 ± 0.07
	.01002	.23545 ± .04
	.01008	.23544 ± .03
B	.01006	.23550 ± .06
	.01006	.23548 ± .03

DEPARTMENT OF CHEMISTRY
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VICTOR K. LA MER
MARION H. ARMBRUSTER

RECEIVED MAY 23, 1935

THE E. M. F. OF THE QUINHYDRONE ELECTRODE IN HEAVY WATER. THE ACIDIC DISSOCIATION OF DEUTEROQUINONE

Sir:

By measuring the e. m. f. of the cell

Ag, AgCl, HCl (0.01 *M*), Quinhydrone ($Q \cdot QH_2$), Pt (I)

corresponding to the processes

$$2HCl(0.01\ M) + Q + 2Ag(s) = 2AgCl(s) + QH_2;\ E_H \quad (1)$$
$$2DCl(0.01\ M) + Q + 2Ag(s) = 2AgCl(s) + QD_2;\ E_D \quad (2)$$

when carried out in ordinary and heavy water, we obtain the free energy of the exchange process

$$2DCl(0.01\ M) + QH_2 = 2HCl(0.01\ M) + QD_2;\ E_D - E_H \quad (3)$$

If we assume that the activity of the chloride ion is the same in both waters, equation (3) may be considered as the difference of the dibasic acid dissociations

$$QH_2 = Q^{=} + 2H^+ \text{ (in } H_2O);\ K_H \quad (4)$$
$$QD_2 = Q^{=} + 2D^+ \text{ (in } D_2O);\ K_D \quad (5)$$

where K_H, the average dissociation constant, equals $K_1K_2 = (1.75 \times 10^{-10})(4 \times 10^{-12}) = 2.64 \times 10^{-11}$ for ordinary water [S. E. Sheppard, *Tr. Am. Electrochem. Soc.*, Preprint 39 (1921); La Mer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923)].

Extrapolation to pure D_2O indicates that $E_D - E_H = 0.0345$ v. Hence $\log K_H/K_D = 0.0345/0.05911 = 0.5837$, or $K_H/K_D = 3.84$, a result which accords with the decrease in acidic dissociation of other weak acids in D_2O; *e. g.*, deutacetic acid [Lewis and Schutz, THIS JOURNAL, **56**, 1002 (1934)], chloroacetic acid [*ibid.*, **56**, 1913 (1934)].

N_{D_2O}	Molality HCl	$E_{0.01m}$ mole/1000 g.	$E_{0.01m}$ mole/55.5 moles
0	0.011182	0.23548	0.23548
	.010855	.23541	.23541
0.103	.01192	.23736	.23677
.3454	.013576	.24604	.24409
	.00880	.24614	.24419
.5109	.01127	.25301	.25016
	.01018	.25306	.25021
.6925	.008844	.26173	.25770
	.009718	.26169	.25766
.9240	.010446	.27190	.26685
	.009991	.27195	.26690
(1.0000)		(.2752)	(.2700)

The measurements were made at 25° with Type B micro cells as described [La Mer and Armbruster, THIS JOURNAL, **57**, 1510 (1935)] where the reliability of the micro technique is established. In the last column of the table the e. m. f. is corrected to exactly 0.01 mole HCl/55.5 moles solvent for purposes of comparison. The normal potential is 0.4774 volt, but in heavy water the value extrapolated linearly would be 0.5119 v. if we make the highly plausible assumption that the activity coefficients in D_2O and H_2O are identical. N_{D_2O}, the mole fraction of heavy water was computed from density measurements using the formula of La Mer and Baker [*ibid.*, **56**, 2641 (1934)]. Both curves deviate from linearity at low D_2O concentrations. Experiments are in progress to check the reliability of extrapolation. The investigation is being continued, using the deuterium gas electrode to study the reaction, $QD_2 + H_2 = QH_2 + D_2$.

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VICTOR K. LA MER
SAMUEL KORMAN

RECEIVED JULY 22, 1935

THE OXIDATION AND REDUCTION OF DEHYDROANDROSTERONE

Sir:

It has been shown by Gallagher and Koch [*J. Biol. Chem.*, **104**, 611 (1934)] that highly active testicular extracts are sensitive to hydrogen-ion concentration, and show a decided decrease in their activity when boiled with alkalies, whereas active extracts obtained from male urine do not show this behavior. This fact strongly indicates that the active compound present in the testes is different in structure from that of androsterone. It is also known that this instability toward alkalies is a characteristic property of the corpus luteum hormone.