TABLE I

TRANSFORMATIONS OF IODIDE AND BROMIDE SALTS TO CHLORIDES USING METHANOLIC HYDROGEN CHLORIDE

Reactant	Product[a]	M.p., °C.[b]	Chlorine, % Calcd.	Chlorine, % Found
1-Methyl-4-(4′-dimethylamino)-stilbazoline hydroiodide[c]	Dihydrochloride	212–213	22.2	22.2
N,N′-Dibenzylpiperazine methiodide[d]	Chloride hydrochloride	207–210	20.1	20.2
2-Stilbazole methiodide[e]	Chloride	255–256	15.3	15.3
2-Picoline methiodide[f]	Chloride[f]	*ca.* 70,[f] very hygroscopic		
Nicotinic acid methyl ester methiodide[g]	Chloride[g]	100–101		
Homoveratryltrimethylammonium bromide[h]	Chloride[i]	204–205		

[a] Under product is described just the nature of the anionic portions associated with the reactant molecule. [b] All melting points are uncorrected. [c] A. P. Phillips, THIS JOURNAL, **72**, 1850 (1950). [d] W. van Rijn, *Nederland. Tijdschr. Pharm.*, **10**, 5 (1898); through *Chem. Centr.*, **79**, I, 381 (1898). [e] A. P. Phillips, *J. Org. Chem.*, **12**, 333 (1947). [f] P. Murrill, THIS JOURNAL, **21**, 841, 842 (1899). [g] A. Hantzsch, *Ber.*, **19**, 31 (1886). [h] White crystals from alcohol-ether; m.p. 232–233°. *Anal.* Calcd. for $C_{13}H_{22}BrNO_2$: C, 51.3; H, 7.3; N, 4.6. Found: C, 51.3; H, 7.6; N, 4.6. [i] J. S. Buck, R. Baltzly and W. S. Ide, THIS JOURNAL, **60**, 1789 (1938).

of between one and two hours were commonly used. The desired chloride is obtained pure simply by crystallization from the methanol solution, either by cooling or by the addition of appropriate precipitating solvents.

The process is believed to go by the scheme

$$R_4N^+I^- + H^+Cl^- + MeOH \rightleftarrows MeO^+H_2 + I^- \longrightarrow MeI + H_2O + R_4N^+Cl^-$$

This depends upon the greater nucleophilic reactivity of iodide or bromide over that of chloride in combining with the alcohol solvent. Methanol is believed to represent a more favorable reactant than ethanol because of the greater susceptibility of methyl to nucleophilic attack than ethyl and because of the greater volatility of the lower alkyl halides allowing easier removal from the reaction mixture during the evaporation. In several experiments methyl iodide was collected from the evaporating mixture through a distilling condenser. It was identified by combination with dimethylaniline to form phenyltrimethylammonium iodide.

Experimental

Transformations of Iodide and Bromide Salts to Chlorides.—In general a solution of 0.02 mole of iodide or bromide salt in about 30–40 cc. of methanol containing 0.1 to 0.2 mole of hydrogen chloride was allowed to evaporate freely on a steam-bath. After one hour the product was crystallized from the methanol solution by cooling or by the addition of a second solvent such as ethyl acetate, acetone, or ether. The absence of any iodide in the product was determined by treating an aliquot in aqueous hydrochloric acid in the presence of carbon tetrachloride with a few drops of dilute sodium nitrite solution.

The transformation works well for quaternary ammonium iodides or bromides as well as for the hydrogen iodides or bromides of primary, secondary or tertiary amines.

The reaction is very rapid. In cases where the rate of disappearance of iodide was followed, using the test method given above, the test for iodide, strongly positive initially, was very faint after 15 minutes, and was negative after 20 minutes.

In several cases evaporation was accomplished through a distillation condenser collecting methanol and methyl iodide. After addition of an excess of dimethylaniline, evaporation of solvent, and recrystallization, a 50% yield of phenyltrimethylammonium iodide was obtained; melting point 215–216°. This gave a strong test for iodide.

Pertinent details for a number of specific compounds transformed by this procedure are shown in Table I.

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Anodic Polarography: Catechol[1]

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RECEIVED JUNE 17, 1952

In a recent paper, Doskocil[2] reported polarographic data for the system catechol-*o*-quinone in the *p*H range 6.20 to 7.89. Vlcek[3] and coworkers obtained polarographic data for catechol in the *p*H range 3.70 to 8.32. Each of the investigators uses phosphate buffers which give ill-defined diffusion currents for catechol in the low *p*H ranges. This is due to a sudden reversal of current at the dropping mercury electrode, occurring in phosphate buffer solutions at potentials corresponding to the oxidation potential of catechol in the *p*H range 5 to 6. The sharp discontinuity in the anodic wave prevents one from obtaining a complete polarographic wave for catechol in this *p*H range.

Vlcek considered the discontinuity observed to be the anodic oxidation wave of catechol. The present authors feel that the reversal of current is caused only by the anodic dissolution mercury and the formation of a film of mercurous phosphate at the electrode–solution interface. Work in progress in this Laboratory indicates that the potential at which the discontinuity is observed is dependent upon the concentration of the phosphate buffer.

Müller[4] has calculated the usable potential ranges for solutions containing the $HPO_4^=$ ion and we have found that actual values obtained from polarograms of solutions of phosphate buffers agree in general with his calculations. Polarograms of catechol in acetate buffer solutions obtained by Doskocil[2] and in this research indicate that the discontinuity observed by Vlcek in phosphate buffer solutions is due only to the buffer components, since no reversal of current occurs in acetate buffer solutions and a well-defined oxidation wave for catechol is obtained.

Because of the indefinite waves obtained for catechol due to the peculiar effect of phosphate

(1) Taken in part from the M. S. thesis of R. P. Vigneault.

(2) J. Doskocil, *Collection Czechoslov. Chem. Communs.*, **15**, 599 (1950).

(3) A. K. Vlcek, V. Mansfeld and D. Krkoskova, *Collegium*, No. 874, 245 (1943).

(4) O. H. Müller, "The Polarographic Method of Analysis," 2nd edition, Chemical Education Publishing Co., Easton, Pa., 1951, p. 152.

buffers, it was decided to investigate the anodic behavior of catechol in other buffer systems and in more basic solutions than have been reported.

Table I summarizes the values of $E_{1/2}$ obtained in the *p*H range 4.15 to 12.40. When these data are plotted a satisfactory straight line results, with a slope of -0.058 in close agreement with the theoretical value, -0.059. Extrapolation of the graph gives $E^0 = +0.570$ volt relative S.C.E. in perfect agreement with the value similarly obtained by Doskocil[2] over the shorter *p*H range 6.20 to 7.89. Ball and Chen[5] obtained the value 0.566 for this oxidation–reduction system from static measurements.

TABLE I

HALF-WAVE POTENTIALS OF CATECHOL, CONCENTRATION 1×10^{-3} *M*

Buffer	*p*H	$E_{1/2}$ *vs.* S.C.E.
Acetate	4.15	0.337
Acetate	4.82	.290
Acetate	5.20	.260
Acetate	6.00	.220
Phosphate	7.40	.135
Phosphate	8.05	.102
Glycine	9.10	.030
Glycine	10.77	− .058
Glycine	11.88	− .105
Glycine	12.40	− .160

Values for $E_{d.e.}$ *versus* $\log i/(i_d - i)$ plotted for well-defined catechol waves produced in the three buffers used, give straight lines and "*n*" values as follows: acetate buffer, *p*H 6.00, $n = 1.32$; phosphate buffer, *p*H 7.40, $n = 1.39$; glycine buffer, *p*H 10.77, $n = 1.15$. These values for "*n*" fall considerably below the value $n = 2$, which was assumed for the oxidation of catechol to *o*-quinone. This would indicate that the anodic reaction is not reversible.

In order to ascertain whether catechol obeys the Ilkovic equation, polarograms of varying concentrations of catechol were taken in each of the three buffers at certain selected *p*H values. The data obtained for the three buffer systems with the concentration of catechol and the diffusion current, respectively, are: acetate buffer *p*H 6.01, 5×10^{-4} *M* and 4.42 μa., 1×10^{-3} *M* and 7.9 μa., 2×10^{-3} *M* and 15.32 μa.; phosphate buffer *p*H 8.01, 5×10^{-4} *M* and 3.79 μa., 1×10^{-3} *M* and 7.74 μa., 2×10^{-3} *M* and 15.48 μa.; glycine buffer *p*H 11.9, 5×10^{-4} *M* and 4.52 μa., 1×10^{-3} *M* and 8.3 μa., 2×10^{-3} *M* and 15.48 μa. When these data are plotted a linear relationship between the concentration of catechol and the diffusion current is obtained.

Taking the mean value of i_d as 7.9 microamps., concentration of catechol 1×10^{-3} and *n* as 2, the diffusion coefficient, *D*, for catechol is found to be of the order of 5.0×10^{-6} cm.²/sec. at 25°. Kolthoff and Orleman[6] report the diffusion coefficient for hydroquinone at 25° to be about 7.4×10^{-6} cm.²/sec. Because of similar structure and identical molecular weight, catechol would not be expected to differ greatly from this. However, Doskocil[2] found a somewhat smaller diffusion current for catechol than for hydroquinone at the same concentration, although he does not report the diffusion coefficient for either compound.

In properly chosen buffer systems, well-defined catechol oxidation waves can be obtained over the *p*H range studied. These waves can be successfully employed for quantitative and qualitative determination of catechol.

Experimental

Polarograms were obtained at 25 ± 0.01° using a photographically recording Heyrovsky Polarograph Model XII, E. H. Sargent and Co. The electrolysis vessel was an H-shaped cell with a 4% agar plug, saturated with KNO_3, separating the solution being electrolyzed and the reference electrode, a saturated calomel electrode. Polarograms were obtained for buffer solutions to determine the residual current. The half-wave potentials were calculated directly from the polarograms by the method described in a technical bulletin distributed by E. H. Sargent and Co.[7] with the exception of half-wave potentials obtained in the *p*H range 10.77 to 12.40. In this *p*H range the limiting current of the catechol wave was not sufficiently flat to allow determination of $E_{1/2}$ by the method referred to above, half-wave potentials were calculated in this *p*H range by plotting $\mathrm{d}I/\mathrm{d}E$ against $E_{d.e.}$. All potential values reported in this paper are referred to the saturated calomel electrode.

Capillary characteristics for the dropping mercury electrode used are $m = 3.81$ mg./sec., $t = 2.25$ sec.; $m^{2/3}t^{1/6} = 2.79$. The height of the mercury reservoir, $h = 64$ cm.

Buffer solutions were prepared from 0.1 *M* stock solutions according to the directions of Britton[8] and Clark,[9] with the exception that all constituents of the buffers containing chloride ion were replaced by the corresponding nitrate compound to eliminate the presence of the chloride ion which produces an interfering wave in the potential range used.

For determination of the *p*H, a Beckman model H meter was used, and National Technical Laboratory buffer (*p*H 7.00 ± 0.02) was used for standardization of the glass electrode.

The catechol was Eastman Kodak Co. white label and melted sharply at 104.5°, literature[10] 105°. 0.1 *M* catechol solutions were prepared daily and all variations in concentrations were made by dilutions of the freshly-prepared stock solution.

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[5] E. G. Ball and T. T. Chen, *J. Biol. Chem.*, **102**, 691 (1932).

[6] I. M. Kolthoff and E. F. Orleman, THIS JOURNAL, **63**, 664 (1941).

[7] Technical Bulletin No. 2661, E. H. Sargent and Co., Chicago, 1949, p. 20.

[8] H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Co., Inc., New York, N. Y., 1932, Ch. XII.

[9] W. M. Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, Ch. IX.

[10] L. F. Fieser and M. Peters, THIS JOURNAL, **53**, 797 (1931).

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Vapor Pressure of Thorium Oxide from 2050 to 2250°K.[1,2]

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RECEIVED JUNE 7, 1952

F. Born's[2] reported values of the vapor pressure of thorium oxide, calculated from estimates of the heat of vaporization and of the chemical constant, are the only published references to thorium oxide vapor pressures. In the course of some studies of factors affecting the life of thorium oxide cathodes, it was necessary to have rather accurate

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[1] This work was supported by the U. S. Navy, Bureau of Ships, under Contract NObs-34141.

[2] F. Born, *Z. Elektrochem.*, **31**, 309 (1925).

[3] Tracerlab, Inc., Boston, Mass.