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 pH 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 pH 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	pH	$E_{1/2}$ 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, pH 6.00, $n = 1.32$; phosphate buffer, pH 7.40, $n = 1.39$; glycine buffer, pH 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 pH values. The data obtained for the three buffer systems with the concentration of catechol and the diffusion current, respectively, are: acetate buffer pH 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 pH 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 pH 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 pH 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 pH range 10.77 to 12.40. In this pH 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 pH range by plotting dI/dE 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 pH, a Beckman model H meter was used, and National Technical Laboratory buffer (pH 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]

BY EDWARD SHAPIRO[3]

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.

vapor pressure data, and it was decided to make an experimental determination of the vapor pressure curve for thorium oxide. The method used was to determine the vacuum evaporation rate of thorium oxide from coated tungsten filaments by direct weight loss measurements and to correlate these rates to vapor pressures by use of the equation[4]

$$p_{\text{mm.}} = 17.14G(T/M)^{1/2}$$

where $p_{\text{mm.}}$ is the vapor pressure in mm., G the evaporation rate in g. cm.$^{-2}$ sec.$^{-1}$, T the absolute temperature and M the molecular weight of the evaporated material. Use of this equation assumes an accommodation coefficient of 1. The advantages of this method are in the ease of obtaining the temperatures required in the experiment, and in the ease of comparing evaporation rates with and without thermionic emission.

Apparatus and Experimental

A weighed 10-mil tungsten filament, hairpin shaped, was coated with thorium oxide (Foote Mineral Company, 99% pure) by cataphoresis from a butyl alcohol suspension using Hanley's method.[5] The coated filament was dried at 100° for 10 minutes and weighed. During these steps, the filament was held in a small aluminum sleeve by a set screw. A hook on one end of the sleeve was used to suspend the filament in the balance. Weighings, made on an Ainsworth Microbalance Model FDJ, were reproducible to within 20 micrograms. The glass system was assembled after attaching the filament to the filament lead-in wires by sleeves and set screws (Fig. 1, S_1 and S_2) and attaching the anode at S_3. The anode was a cylinder 1″ diam. × 2″ long rolled from a sheet of 10-mil tantalum. Holes were in it to permit sighting the filament for temperature measurements. After evacuation of the system to a pressure less than 10^{-5} mm., the filament was heated to the desired temperature and held at that temperature for a measured time interval. Electron emission from the thorium oxide was obtained by applying high voltage to the anode. After the heating period, the system was disassembled, and the filament removed and weighed. The thoria coating was wiped off and the clean filament weighed. The weight of thoria which had evaporated during the run was taken as the difference between the initial and final weights of the coating. Filament brightness temperatures were measured with a Leeds and Northrup optical pyrometer and were corrected to true temperatures by use of a calibration curve obtained on a thoria-coated filament to which a W–Mo thermocouple[6] was welded.

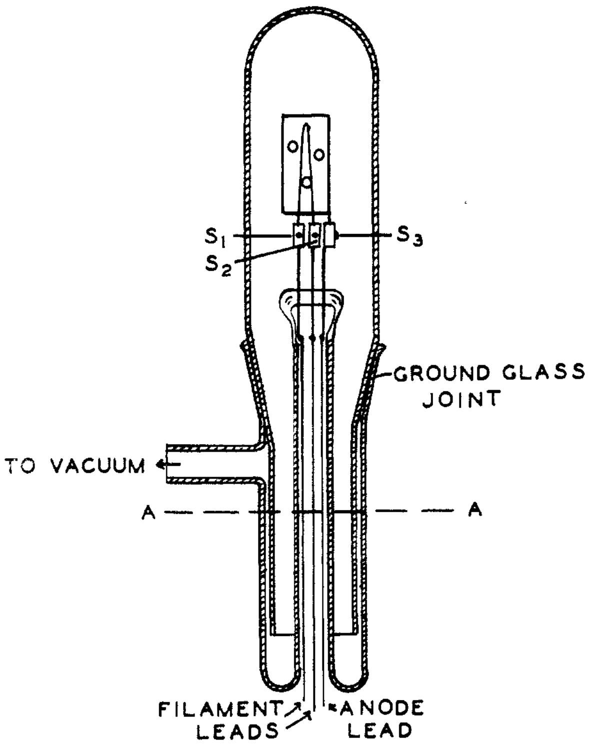

Fig. 1.—Evaporation apparatus: section below AA immersed in liquid N_2 during experiments.

Results and Discussion

The data are plotted in Fig. 2, as a log p vs. $1/T$ plot. The equation of the straight line, as obtained by the method of least squares, is

$$\log p_{\text{mm.}} = 3.71 \times 10^4/T + 11.53$$

The vapor pressure at 2000°K. is 10^{-7} mm. which is much lower than Born's value of 3×10^{-3} mm. The slope of the line corresponds to a heat of vaporization of 171 kcal./mole, in fair agreement with Fan's value of 184 kcal./mole obtained by an entirely different method.[7] Born's estimated value of about 100 kcal./mole is greatly in error.

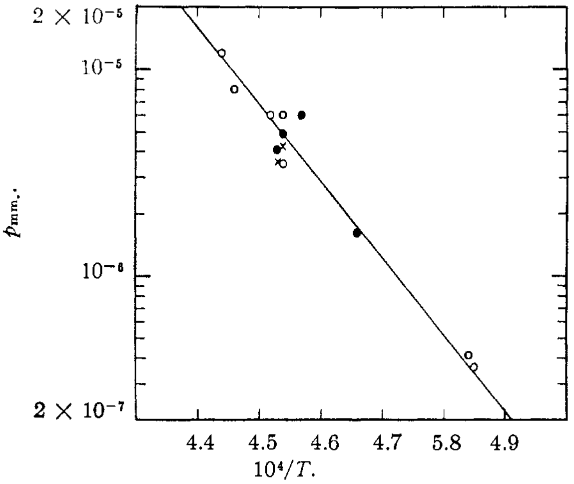

Fig. 2.—Vapor pressure of thoria: ○, ThO_2 on W with electron emission; ●, ThO_2 on W without electron emission; ×, ThO_2 on Mo without electron emission.

The results showed no difference between evaporation rates from tungsten or molybdenum or between evaporation rates with or without electron emission currents to 1 amp. cm.$^{-2}$ from the thoria. The latter comparison was made to determine qualitatively whether electrolytic decomposition arising from the passing of current through the coating was appreciable. The results indicated that this fraction was less than 10^{-4}.

The largest source of error was in the temperature measurements. It was extremely difficult to get pyrometer readings reproducible to within ±20°, particularly at the higher temperatures. Errors in temperature readings of 10–15° could readily account for the observed scatter of the experimental points. The temperature used for a given run was determined as the average of a series of 10–30 temperature readings taken during the

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(4) S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 20.

(5) T. E. Hanley, *J. Applied Phys.*, **19**, 583–584 (1948).

(6) F. H. Morgan and W. E. Danforth, *ibid.*, **21**, 112 (1950).

(7) H. Y. Fan, *ibid.*, **20**, 689 (1949).

run. Improvement might have been effected by the use of coated ribbons to increase the area pyrometered.

At temperatures above 2400°K., relatively large losses of tungsten were noted. These losses were more than could be accounted for by evaporation, and were assumed to be the result of a reaction between thorium oxide and tungsten in which volatile tungsten oxides were formed.

Acknowledgment.—Mr. F. H. Morgan's help in obtaining the calibration curve with the W–Mo thermocouple and Mr. H. Bleecher's technical assistance are gratefully acknowledged.

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Ethyl β-Morpholinocrotonate

BY J. F. TINKER AND T. E. WHATMOUGH

RECEIVED JUNE 9, 1952

Monoalkylation of acetoacetic ester is seldom clean and sometimes difficult. Alkylation of β-aminocrotonic ester[1] stops cleanly after a single alkyl group. A most satisfactory member of this series is the one derived from morpholine, using directions for the preparation of β-anilinocrotonate.[2]

Ethyl β-Morpholinocrotonate.—A mixture of 511 g. (3.93 moles) of ethyl acetoacetate, 400 cc. (4.60 moles) of morpholine, 10 cc. of 85% formic acid, and 2.5 l. of benzene was refluxed, and the water separated.[2] In 8 hours 75 cc. had been collected. The solution was then distilled, and yielded 592 g., 76%, of the product, b.p. 120–124° (0.5 mm.), d^{25}_{25} 1.099, $n^{23.5}\text{D}$ 1.5162. A sample was redistilled (b.p. 116° (0.35 mm.)) and analyzed.

Anal. Calcd. for $C_{10}H_{17}NO_3$ (199.24): C, 60.28; H, 8.60. Found: C, 60.20; H, 8.65.

Treatment of the aminoester with either propargyl bromide or propargyl *p*-toluenesulfonate, followed by treatment with hot water,[1] yielded **3-carbethoxy-5-hexynone-2**, b.p. 69–73° (1 mm.), in excellent yield. A single redistillation gave a sample of analytical purity (b.p. 71° (1 mm.)).

Anal. Calcd. for $C_9H_{12}O_3$ (168.19): C, 64.27; H, 7.19. Found: C, 63.60; H, 7.20.

3-Carbethoxy-5-hexynone-2, 2,4-dinitrophenylhydrazone, m.p. 97–98°.[3]

Anal. Calcd. for $C_{15}H_{16}N_4O_3$ (348.31): C, 51.72; H, 4.63; N, 16.09. Found: C, 51.74; H, 4.69; N, 15.94.

Acid hydrolysis yields **5-hexynone-2**,[4] b.p. 62–64° (12 mm.). The **2,4-dinitrophenylhydrazone** of **5-hexynone-2** melts at 138–139°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4$ (276.25): N, 20.28. Found: N, 20.34.

Treatment of ethyl β-morpholinocrotonate with 2,3-dichloropropene, followed by refluxing with water, yielded directly **5-chloro-5-hexenone-2**, b.p. 74–77° (16 mm.) in 86% yield. **The 2,4-dinitrophenylhydrazone** has m.p. 84–85°.

Anal. Calcd. for $C_{12}H_{13}ClN_4O_4$ (312.71): C, 46.09; H, 4.19; N, 17.92. Found: C, 46.12; H, 4.31; N, 18.34.

Treatment of the chloroketone with sodium amide in liquid ammonia, in an attempt to effect the condensation of two molecules to a derivative of 1,6-cyclodecadiyne, yielded no detectable tertiary alcohol.

Acknowledgment.—We wish to thank Dr. M. C. Whiting for informative discussions during the course of this work.

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(1) (a) R. Robinson, *J. Chem. Soc.*, **109**, 1043 (1916); (b) W. M. Lauer and G. W. Jones, THIS JOURNAL, **59**, 232 (1937).

(2) C. S. Hamilton, ed., *Org. Syntheses*, **29**, 42 (1949).

(3) All melting points taken with Anschütz thermometers in a Hershberg apparatus.

(4) T. E. Gardner and W. H. Perkin, *J. Chem. Soc.*, **91**, 851 (1907).

CONVERSE LABORATORY
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COMMUNICATIONS TO THE EDITOR

THREE NEW NEUTRON DEFICIENT ISOTOPES OF YTTRIUM

Sir:

Three new yttrium isotopes have been discovered by proton bombardment of spectroscopically pure yttrium oxide[1] in the Rochester 130-inch cyclotron. Targets of yttrium oxide were placed in an aluminum foil envelope which was mounted on the end of a probe and placed inside the tank of the cyclotron. The target was bombarded with both 240 and 130 Mev. protons for exposure times of one and two hours.

The yttrium oxide was dissolved in hot nitric acid and inert carriers of zirconium, strontium, rubidium and bromine were added to the solution. The yttrium fraction was purified from all the spallation products and the sample was followed under a Geiger-Müller tube for gross decay. The activities found had half lives of: 2–4 hours, 14 hours, 38 hours, 80 hours, 25.5 days and finally 65 days. In one experiment 105-day Y^{88} was also observed. The half-lives of the known[2] yttrium isotopes in this region are: Y^{88} 2 hours, 105 days; Y^{87} 14 hours, 80 hours; Y^{86} 14.6 hours; and Y^{84} 3.7 hours. The 38-hour, 25.5-day, and 65-day activities found in the yttrium gross decay curve can be identified with Sr^{83}, Sr^{82}, and Sr^{85}, respectively. This means that these strontium isotopes found in the purified yttrium sample are the daughters of their respective yttrium parents which are previously unreported yttrium isotopes. Thus, Y^{82} decayed to 25.5-day Sr^{82}, Y^{83} decayed to 38-hour Sr^{83}, and Y^{85} decayed to 65-day Sr^{85}.

Since the yttrium gross decay curve was so complex, it was impossible to resolve the half lives of these new isotopes directly. Therefore, a series of isolation experiments were performed in which the strontium daughter isotopes were removed from the yttrium at periodic intervals. These strontium

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(1) The yttrium oxide was supplied through the courtesy of Ames Laboratory, Iowa State College.

(2) Nuclear Data by K. Way, *et al.*, Circular of the National Bureau of Standards 499; General Electric Research Laboratory Chart of the Nuclides.