be the same or different, alkyl, aryl, cyclic, and so forth. This process has a broad application, since, for a given disulfonate, a large number of secondary amines may be chosen. Moreover, the availability of the glycol disulfonates is being greatly increased by the ever-increasing number of glycols which are appearing on the market.

Table I lists the amines synthesized by this method and Table II contains the glycol disulfonates which were prepared as intermediates.

Experimental

General Procedure for the Preparation of Glycol Disulfonates.—The anhydrous glycol (1 mole) is dissolved in 3 to 5 volumes of anhydrous pyridine and the appropriate sulfonyl chloride (2 moles) is added to this well-stirred solution. The temperature is maintained between 5 and 15°. After the reaction is completed, the reaction mixture is stirred into three times its volume of finely crushed ice. The crystalline product which separates is washed with ice-water and then dried. It is purified by recrystallization from ethanol.

General Procedure for the Preparation of N,N,N',N'-Tetrasubstituted Diamines.—A glycol disulfonate is refluxed with 20 equivalents of anhydrous secondary amine under anhydrous conditions, with stirring, for approximately 20 hours. The secondary amine is fractionally distilled, after which an excess of 40% sodium hydroxide solution is added. The oil layer is separated and the water layer extracted with ether. The oil and ether extracts are combined and dried over anhydrous potassium carbonate. After distillation of the ether, the residual oil is fractionated under reduced pressure through a glass-packed column using a variable take-off stillhead.

RESEARCH LABORATORY
EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK
RECEIVED MARCH 22, 1951

On the Preparation of Xanthurenic Acid

BY ALEXANDER D. MEBANE AND WILLIAM OROSHNIK

Xanthurenic acid was first synthesized by Musajo and Minchilli,[1] who reported a melting point of 283–285° (dec.) "with fast heating." Subsequent preparations[2,3,4] have resulted in melting points varying from 250°[3] (in spite of correct elementary analyses) to as high as 289°.[4] When the synthesis was carried out in this Laboratory, a product of m.p. 255° was obtained, although all intermediates had been carefully purified. The explanation was found to lie in incomplete ether-fission under the conditions specified by Musajo and Minchilli; more exhaustive treatment with hydriodic acid raised the melting point to 294°. A subsequent examination of two of the above-mentioned preparations showed the 250° specimen[3] to contain 8.3% of methoxyl, corresponding to 58 mole per cent. of the 8-methyl ether; the 289° specimen,[4] on the other hand, proved to contain only 3.3 mole per cent. of the methyl ether.

Reprecipitation of methoxyl-free material was ineffective in freeing it of inorganic contaminants. None of the common organic solvents permitted recrystallization, but dilute hydrochloric acid proved to be quite satisfactory, giving a chloride-free crystalline product decomposing at 297°.

A simplified version of the Musajo–Minchilli synthesis which embodies these improvements is described below.[5]

Experimental

Commercial sodium salt of oxalacetic ester (49 g.) was shaken with 300 ml. of ether and 400 ml. of ice-cold 5% sulfuric acid until all had dissolved, and the aqueous layer was reextracted with ether. The combined extracts, after drying over anhydrous $MgSO_4$, were concentrated at 20 mm. The residue (38 g., 0.2 *M*) was heated in a boiling water-bath with 25 g. (0.2 *M*) of *o*-anisidine for 90 minutes, after which the water that had separated was evaporated at 20 mm.

The resulting orange sirup was stirred with 1 liter of mineral oil while heating to 240° in an electric mantle. After five minutes at 240–250°, the flask was cooled with an air blast. When the temperature had fallen to 60°, the solution was decanted from precipitated tar, diluted with 2 liters of petroleum ether, and stored for several days in the refrigerator. Tan-colored crystals of crude ethyl xanthurenate 8-methyl ether (23 g.) were obtained. Recrystallization of this material (from toluene, with ligroin) was undesirable for practical purposes, since the best crops were the later and smaller ones (colorless needles, m.p. 100–101°).

The crude ether-ester was dissolved in 350 ml. of 57% hydriodic acid (freshly distilled from hypophosphorous acid; b.p. 126–128°), and the liquid was distilled slowly at atmospheric pressure under an 8" Vigreux column until the still-head temperature had reached 110° (3 hours). The HI was then distilled off to near-dryness at 20 mm. and the residue taken up in water, made alkaline with bicarbonate, filtered, and acidified to *p*H 3 with dilute HCl in the presence of a little bisulfite. After chilling, the xanthurenic acid was filtered off with water washes and sucked as dry as possible: sulfur-yellow, non-crystalline.

The damp filter cake was dissolved, by boiling, in a mixture of 400 ml. of concd. HCl and 500 ml. of distilled water, and filtered hot with a little Norit and SuperCel, washing with 70 ml. of the hot solvent. To the filtrate was added 2400 ml. of boiling-hot distilled water, and the solution was allowed to stand overnight. Filtration, with water and then acetone washes, furnished 14.5 g. (35% based on *o*-anisidine) of crystalline xanthurenic acid; small, imperfectly-rhombic ochre-yellow flakes.

Anal. Calcd. for $C_{10}H_7NO_4$: C, 58.54; H, 3.44; N, 6.83. Found: C, 58.59, 58.34; H, 3.52, 3.67; N, 6.61, 6.66; methoxyl, none; ash, none; Cl^-, none; Fe, none.

The melting point is quite sensitive to the rate of heating. If the temperature was brought rapidly to 270° and thereafter raised 5° per minute, decomposition occurred at 297°.

At *p*H 6.95, the ultraviolet absorption spectrum of xanthurenic acid in water shows two smooth peaks: $\lambda_{max.}$ 243 mμ, ϵ 30,000; $\lambda_{max.}$ 342 mμ, ϵ 6,500.

Acknowledgments.—We are indebted to Mr. Robert A. Mallory for checking this procedure, and to Mr. Joseph Grodsky for the microanalyses.

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[3] C. C. Porter, I. Clark and R. H. Silber, *ibid.*, **167**, 575 (1947). A sample of this material was kindly made available to us by Dr. Silber.

[4] F. Rosen, J. W. Huff and W. A. Perlzweig, *J. Nutrition*, **33**, 561 (1947). The melting point was not reported in the original publication.

[5] A paper by A. Furst and C. J. Olsen (*J. Org. Chem.*, **16**, 412 (1951)), which appeared after this note had been submitted, describes more extensive improvements in this preparation. The melting point of 284° for crystalline material reported by Furst and Olsen is presumably due to a difference in heating rate.

ORTHO RESEARCH FOUNDATION
RARITAN, NEW JERSEY
RECEIVED MARCH 19, 1951

The Activity Coefficients of the Alkaline Earth and Magnesium Perchlorates from Freezing Point Data

BY DAN E. NICHOLSON[1] AND W. A. FELSING

In a previous article,[2] experimental data were presented in which the freezing points for aqueous solutions of barium, strontium, calcium and magnesium perchlorates had been used to calculate the

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[1] Materials Chemistry Division, Oak Ridge National Laboratory.

[2] D. E. Nicholson with W. A. Felsing, THIS JOURNAL, **72**, 4469 (1950).

activity coefficients of these salts over a wide range of solute concentrations hear 0°. Dr. R. A. Robinson[3] has pointed out that in our calculations an error in *sign* was made for the term

$$\int_0^M \Delta j \text{ d} \log M$$

in the Scatchard[4] modification of the Lewis–Randall[5] equation relating the freezing point depression to the activity coefficient, at a given concentration of electrolyte. The recalculated values are given in Table I.

TABLE I

VALUES OF THE ACTIVITY COEFFICIENT, γ', FOR THE ALKALINE EARTH AND MAGNESIUM PERCHLORATES

Molality	Lim. Law	$Ba(ClO_4)_2$	$Sr(ClO_4)_2$	$Ca(ClO_4)_2$	Mg-$(ClO_4)_2$
0.001	0.910	0.897	0.900	0.900	0.901
.002	.841	.864	.871	.869	.869
.005	.760	.805	.815	.814	.814
.01	.678	.751	.763	.763	.764
.02	.577	.689	.706	.706	.707
.05	.420	.602	.630	.633	.633
.1	.293	.541	.580	.587	.587
.2	.176	.489	.543	.554	.567
.3	.119	.463	.526	.551	.575
.4	.086	.449	.534	.561	.598
.5	.064	.441	.542	.579	.630
.6		.438	.555	.603	.668
.7		.437	.572	.633	.713
.8		.438	.594	.668	.767
.9		.442	.619	.710	.828
1.0		.449	.648	.763	.898

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(3) Private communication from University of Malaya, Singapore.

(4) Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2676 (1932).

(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 286.

DEPARTMENT OF CHEMISTRY
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RECEIVED MARCH 19, 1951

Ferric-Catalyzed Hydrogen Peroxide Decomposition: Effect of Nitrate Ion

BY SIGFRED PETERSON[1]

The ferric-catalyzed hydrogen peroxide decomposition in nitrate solution shows deviations from first order kinetics which have been explained by Andersen[2] in terms of a non-chain mechanism involving atomic oxygen. It appears necessary, however, to use a chain mechanism as first proposed by Haber and Weiss[3] to explain the rapid evolution of oxygen when the iron is first added as ferrous,[3] the effect of ferric ion on the ferrous reaction,[4,5] the promotion of both ferrous and ferric reactions by cupric ion,[5] the oxidation of organic compounds,[6] the hydroxylation of aromatic compounds[7] and the initiation of polymerization[8] by ferrous–peroxide solutions and the inhibition by acetanilide[9] of the decomposition.

The mechanism evolved by several investigators[3,4,5] consists of the chain initiating step

$$Fe^{+++} + HO_2^- \longrightarrow Fe^{++} + HO_2 \tag{1}$$

and three chain carrying steps

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH \tag{2}$$
$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \tag{3}$$
$$Fe^{+++} + O_2 \longrightarrow Fe^{++} + O_2 \tag{4}$$

with the chain ended by the reverse of (1)

$$Fe^{++} + HO_2 \longrightarrow Fe^{+++} + HO_2^- \tag{5}$$

The species O_2^- and HO_2^- are presumed to be in rapid equilibrium with their conjugate acids. Application of steady state considerations to these equations gives the first order rate equation of Bertalan[10]

$$-\text{d}(H_2O_2)/\text{d}t = k(Fe^{+++})(H_2O_2)/(H^+)$$

Barb, Baxendale, George and Hargrave[5] suggest that the additional chain termination becomes important with diminishing peroxide/iron ratio and increases the order of reaction with respect to peroxide as found by Andersen.

$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^- \tag{6}$$

During the investigation of the inhibition of this reaction by acetanilide,[9] deviations from first order decomposition were observed in some of the experiments without inhibitor. These experiments have been analyzed in terms of Andersen's equation

$$\log \frac{a}{x} + A\left(\frac{1}{x} - \frac{1}{a}\right) = Bt$$

in which a and x represent the concentration of hydrogen peroxide at the start of the experiment and time t, respectively. Table I gives pertinent data and the values of A and B obtained from graphs of $\left(\log \frac{a}{x}\right)\Big/\left(\frac{1}{x} - \frac{1}{a}\right)$ *versus* $t\Big/\left(\frac{1}{x} - \frac{1}{a}\right)$. The materials used are described in the previous paper[9]; the experimental technique did not differ significantly from that of Andersen.

TABLE I

a[a]	(Fe^{+++})[a]	(H^+)[a]	(ClO_4^-)[a]	(NO_3^-)[a]	A[a]	B (min.$^{-1}$)
0.077	0.019	0.040	1.78[b]	0.000	0.0004	0.0182
.085	.061	.133	0.317	.000	.0008	.0214
.442	.066[c]	.28	.47	.000	−.001	,0079
.425	.102	.22	.53	.000	.0005	.0208
.212	.31	.66	1.58	.000	.0002	.0266
.059	.12	.18	0.18	.37	.022	.034
.059	.12	.18	.18	.37	.025	.038
.059	.11	.36	.36	.34	.025	.018
.059	.11	.36	.36	.34	.037	.022

[a] Moles/l. [b] $NaClO_4$ added. [c] 24°. Other experiments at 25°.

The uncertainties in A in Table I are of the order of magnitude of the value for the first five experi-

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(1) The experiments reported in this paper were performed at the University of California under the direction of the late Prof. William C. Bray.

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(6) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S15 (1949); I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777, 3784 (1949).

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(9) W. C. Bray and S. Peterson, THIS JOURNAL, **72**, 1401 (1950).

(10) J. van Bertalan, *Z. physik. Chem.*, **95**, 328 (1920).