standard alkali using brom thymol blue as indicator. Measurements were carried out at 0°, 15°, 25°, 40° and, with reduced accuracy, at 100°. At least six determinations were carried out at each temperature. The best value for the solubility at each temperature is summarized in Table I.

The logarithm of the mole fraction N plotted against the reciprocal of the absolute temperature T gives a close approximation to a straight line. The equation

$$\log N = 1.344 - \frac{665}{T}$$

corresponding to a heat of solution of 3.04 kcal. per mole, may be relied upon to give the solubility of aniline hydrochloride in water to within 0.7% over the temperature range 0° to 50° and to within 2.5% over the range 50° to 100°. It will be noted that the previously accepted solubility at 15° is almost exactly one-fifth of the emended value.

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The Spectrophotometric Determination of the Rate Constant of First Order Reactions[1]

BY EDWARD L. KING

The optical density of a solution in which the change A → B is occurring is given by the equation

$$D_t = \log I_0/I = l\,\{\epsilon_A(\mathrm{A})_t + \epsilon_B(\mathrm{B})_t\}$$

where l is the cell length in cm., ϵ_A and ϵ_B are the molar extinction coefficients of A and B and $(\mathrm{A})_t$ and $(\mathrm{B})_t$ are the molar concentrations at time t. If the rate law for this change is $d(\mathrm{A})/dt = -k(\mathrm{A})$, the dependence of D upon t is given by equation 1

$$\{D_t/l(\mathrm{A})_0 - \epsilon_B\} = (\epsilon_A - \epsilon_B)\, e^{-kt} \qquad (1)$$

and thus a plot of the logarithm of the quantity on the left side of the equation *versus* time will give a straight line of slope $-k$. To make such a plot, however, requires knowledge of the quantities $(\mathrm{A})_0$ and ϵ_B. In a modification of the method suggested by Guggenheim,[2] the rate constant may be obtained without knowledge of either of these two quantities.

Equation 2 relates the optical densities of the solution at times t and $t + \tau$

$$(D_t - D_{t+\tau}) = l(\mathrm{A})_0\,(1 - e^{-k\tau})(\epsilon_A - \epsilon_B)\, e^{-kt} \qquad (2)$$

and it is seen that a plot of logarithm $(D_t - D_{t+\tau})$ *versus* time would give a straight line of slope $-k$ if τ is a constant time interval. In the usual procedure readings of the optical density of the reaction mixture *versus* a solvent "blank" would be made at times: $t_1, t_2, \cdots, t_n, t_1 + \tau, t_2 + \tau, \cdots$ and $t_n + \tau$. In view of the relationship

$$D' = (D_t - D_{t+\tau}) = \left\{\log\frac{I_0}{I_t} - \log\frac{I_0}{I_{t+\tau}}\right\} = \log\left(\frac{I_{t+\tau}}{I_t}\right)$$

a convenient means of determining the first order rate constant is available. If in the two cells in the usual arrangement for spectrophotometric measurements, there are placed two identical reaction mixtures in one of which the reaction has been proceeding for a time τ longer than in the other, the value of the "optical density," D', of the less transparent sample compared with the more transparent sample is the value of the desired $(D_t - D_{t+\tau})$. A plot of logarithm D' *vs.* t will be a straight line of slope $-k$. As was true in the conventional Guggenheim method, the time interval τ should be several times as great as the half-time of the reaction in order to obtain optimum precision.

The above considerations indicate a method for determination of the rate constant of a first order reaction in which the extinction of a reacting system is measured against that of an identical mixture at a different stage of the same reaction. This method has advantages compared to the conventional Guggenheim method applied to a spectral study in which a solvent "blank" is used in that fewer readings must be taken for the same number of points, the readings extend over a shorter time interval, and the readings need not be taken at planned time intervals. The somewhat larger slit widths which are required because of the absorption of the "blank" are a disadvantage in the study of reactions in which the rate of change of ϵ values for reactant and/or product with changing wave length is large.

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[1] This work was supported by a grant from the U. S. Atomic Energy Commission.

[2] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

Sodium Perborate as a Reagent in Organic Chemistry. I. Preparation of Azo-Compounds

BY S. M. MEHTA AND M. V. VAKILWALA

Sodium perborate has received little or no attention as a reagent for organic oxidations. Serantes[1] found it to be satisfactory for the oxidation of benzoic acid. Allen and Clark[2] used it as a satisfactory substitute for sodium peroxide in many oxidation reactions and described its action on α-diketones. A study of sodium perborate as a reagent for the oxidation of organic compounds is underway in this Laboratory. The present paper describes the oxidation of aniline and a number of its para-substitution products with sodium perborate in acetic acid as a solvent.

In glacial acetic acid the corresponding azo-compound may be obtained in relatively pure form and, with the exception of aniline and *p*-anisidine, relatively free of tarry by-products. The yield of azo-compound varies with the temperature of reaction and with the concentration of the acetic acid. Maximum yields are obtained in glacial acetic acid and at temperatures of reaction between 40 to 50° (Table I). Addition of water to the acetic acid solvent markedly lowers the yield of oxidation product.

The product of the action of sodium perborate on aniline cannot be recovered by direct crystallization but must be removed from the reaction mix-

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[1] M. T. Serantes, *Rev. farm.*, **65**, No. 4 (1923); *Anales asoc. quim. argentina*, **12**, 58 (1923); *C. A.*, **19**, 1134 (1925).

[2] C. F. H. Allen and J. H. Clark, *J. Chem. Education*, **19**, 72 (1942).

TABLE I

OXIDATION OF AROMATIC AMINES[a] WITH SODIUM PERBORATE[b]

Amine	Reaction temp., °C.[c]	Normality of acetic acid	Product	M.p., °C. found	M.p., °C. reported	Yield, %
p-Bromoaniline	35	20.68[d]	4,4′-Dibromoazobenzene	204–205	205[e]	44.08
	40	20.68	4,4′-Dibromoazobenzene			49.40
	40	18.93	4,4′-Dibromoazobenzene			20.83
	40	10.67	4,4′-Dibromoazobenzene			7.30
	45	20.68	4,4′-Dibromoazobenzene			50.42
p-Chloroaniline	35	20.68	4,4′-Dichloroazobenzene	187	188[f]	37.67
	40	20.68				43.61
	40	18.93				19.11
	40	10.67				6.52
	45	20.68				44.77
	50	20.68				48.37
p-Toluidine	35	20.68	4,4′-Azotoluene	144	144[g]	15.17
	40	20.68				20.08
	45	20.68				26.43
	50	20.68				29.95
p-Nitraniline	40	20.68	4,4′-Dinitroazobenzene	216	216[h]	20.31
p-Aminobenzoic acid	40	20.68	Azobenzene-4,4′-dicarboxylic acid	Dec. at 330	Dec. at 330[i]	38.8

[a] One-hundredth mole dissolved in 20 cc. of acetic acid. [b] Sufficient to yield 0.01 atom proportion of oxygen (1.66 g.). [c] The reaction was carried out for 3 hours. [d] Glacial acetic acid. [e] Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. 1, Eyre and Spottiswoode Ltd., 1943, p. 680. [f] *Ibid*., p. 739. [g] *Ibid*., p. 892. [h] Zincke und Kuchinbecker, *Ann.*, **330**, 28 (1904). [i] Heilbron and Bunbury, ref. *e*, p. 202.

ture by steam distillation. Anisidine undergoes too rapid oxidation in glacial acetic acid yielding an intractable black amorphous powder. However, the sodium perborate oxidation of anisidine can be successfully accomplished in aqueous media.

In general the sodium perborate–acetic acid reagent produces higher yields of azo-compounds by oxidation of aniline and its para-substitution products than equivalent mixtures of hydrogen peroxide–acetic acid. Addition of an amount of boric acid, equivalent to that in sodium perborate, to this latter mixture improves the yields of oxidation products.

Experimental[3]

General Procedure.—The aromatic amine and sodium perborate are individually dissolved in a convenient volume of glacial acetic acid and after adding the solution of the aromatic amine to that of perborate, allowed to react at about 40 to 50°. After cooling to room temperature, the crystals so obtained are collected and washed with water to remove the adhering acetic acid. No other process for the isolation or purification of the crystals is required except in the case of aniline and anisidine. Table I summarizes the data obtained for a series of para-substituted aromatic amines in which variations in reaction temperature and normality of acetic acid were studied.

Oxidation of Aniline.—Freshly distilled aniline (3.72 g., 0.04 mole) was dissolved in 80 cc. of glacial acetic acid and added to the same volume of glacial acetic acid containing 6.628 g. (0.04 atom of oxygen). After 3 hours reaction at 40°, the mixture was steam distilled. The solid distillate obtained (yield 17.9%) was recrystallized from absolute ethanol. The orange colored crystals weighed 0.547 g. (15.05%) and melted at 68°. The reported m.p. of azobenzene is 68°.[4]

Oxidation of Anisidine.—Sodium perborate (3.314 g., 0.02 atom of oxygen) dissolved in 75 cc. of distilled water was added to 2.46 g. (0.02 mole) of anisidine suspended in 75 cc. of water containing sodium acetate (8 g.) and the mixture allowed to stand at room temperature (29°) for 48 hours. The brown precipitate thus obtained was recovered by filtration, eluted with 40 cc. of absolute ethanol at room temperature (29°) yielding a yellow residue which after recrystallization from hot absolute ethanol yielded 0.3466 g. (13.43%) of bright yellow needles, m.p. 118° (turbid melt becoming clear at 133°). The reported m.p. of 4,4′-azoxy-anisole[5] is 118–119° clearing at 135°.

Hydrogen Peroxide, Boric Acid, Acetic Acid as Oxidation Media.—Experiments were carried out in order to compare the effect of (a) sodium perborate and acetic acid, (b) hydrogen peroxide, boric acid and acetic acid and (c) hydrogen peroxide and acetic acid. The sodium perborate used was 1.657 g. (0.01 atom of oxygen) dissolved in 40 cc. of glacial acetic acid. The hydrogen peroxide comprised 11.4 cc. of 1.75 *N* (0.01 atom of oxygen) dissolved in 40 cc. of glacial acetic acid. The quantity of boric acid (0.686 g.) was the same as present in 1.657 g. of sodium perborate. The reactions were carried out at 50° for three hours and the products recovered by the method described in the General Procedure.

YIELDS OF RECRYSTALLIZED PRODUCTS

	a	*b*	*c*
4,4′-Dibromoazobenzene	25.22	21.85	18.68
4,4′-Dichloroazobenzene	23.80	19.23	17.26
4,4′-Azotoluene	11.63	9.01	5.77

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[3] All melting points are uncorrected.

[4] Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. I, Eyre and Spottiswoode Ltd., 1943, p. 201.

[5] Heilbron and Bunbury, *ibid*., p. 819.

New Esters of Pentaerythritol[1]

BY G. E. MCCASLAND AND DONALD ARTHUR SMITH[2]

For use in stereochemical studies, which we hope to describe in a later publication, the following compounds were prepared and characterized.

Experimental

Pentaerythritol Tetrachloroacetate (A).—Under anhydrous conditions 2.0 g. of pentaerythritol was refluxed with 8.3 g. of chloroacetyl chloride for 45 minutes. Excess acid chloride was then removed by vacuum distillation. The residue solidified on cooling, giving 7.0 g. of product, m.p.[3]

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[1] We are indebted to the National Research Council (Canada) for a grant in support of this work.

[2] Fellow of the Canadian Industries, Limited, 1949–1951.

[3] Melting and boiling points corrected. M.p.'s were determined on the Köfler micro-block. Analyses by Mr. R. Pyke.