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]

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

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

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

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

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 $(A)_0$ 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 $t + \tau$

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

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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[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).