melt which became clear liquid at about 320°. It was believed to be impure hexaphenyldisilane. The benzene extract was concentrated to about 10 ml., and to this was added 20 ml. of petroleum ether (b.p. 60–70°). On cooling to room temperature 2.2 g. (53% based on diphenyldichlorosilane) of white solids melting at 238–244° was obtained by filtration. The crude product was recrystallized three times from a mixture of benzene and ethanol to give 1.2 g. (29%) of colorless needles melting at 260–262° to form a somewhat gelatinous mass which became water-clear liquid at 266° (uncor.).

*Anal.* Calcd. for $C_{48}H_{40}Si_3$: Si, 12.00. Found: Si, 11.98, 11.84.

Three check runs were made. In two of these runs a product melting at 302–303° was isolated. Analysis showed that it, too, had the composition of octaphenyltrisilane. From molecular model studies we suspected that this inconsistency in the melting points of these two products might possibly be due to the existence of isomeric forms. Further studies are now in progress.

**Pentaphenylchlorodisilane.**—A triphenylsilylpotassium suspension prepared according to the procedure described above was added fairly rapidly to 4 g. (0.016 mole) of diphenyldichlorosilane dissolved in 20 ml. of ether. It was noticed that the first few drops of triphenylsilylpotassium was decolorized immediately when it was added to the diphenyldichlorosilane solution. When addition was completed, a gray suspension was formed. Color Test I[11] immediately after the addition was negative. The mixture was stirred 1 hour at room temperature and was filtered by suction. The solvent was distilled from the filtrate to give 7.1 g. of colorless solids melting at 120–140°. The crude product was recrystallized twice from petroleum ether (b.p. 60–70°) to give colorless granular crystals melting at 154–155° (uncor.). The yield of pure product was 3.7 g. (50%).

*Anal.* Calcd. for $C_{30}H_{25}Si_2Cl$: Si, 11.79; Cl, 7.43. Found: Si, 11.76, 11.81; Cl, 7.42, 7.36.

Pentaphenylchlorodisilane is an interesting compound because even though it can be hydrolyzed in aqueous basic solution to give the corresponding hydroxy compound, still, unlike the triphenylchlorosilane, it is quite stable in air. A sample of this compound was put in a vial loosely plugged with cotton. After 3 months there was no depression in its melting point. Its preparation has been checked several times.

From some preliminary work it was found that pentaphenylchlorodisilane can be treated with sodium in boiling xylene to give a white solid, presumably decaphenyltetrasilane. Further work is now in progress.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED AUGUST 24, 1951

---

## Phenylphosphine[1]

BY ROBERT J. HORVAT AND ARTHUR FURST

Phenylphosphine has been previously prepared by reducing dichlorophenylphosphine directly with anhydrous hydrogen iodide,[2,3] or by first converting the dichlorophenylphosphine to diiodophenylphosphine hydrogen iodide and treating this with absolute alcohol.[4] Yields were increased only after many hours of reaction.

It is possible to obtain phenylphosphine in much shorter time and in comparable over-all yields by simply reducing the dichlorophenylphosphine with lithium aluminum hydride.

### Experimental

To an ice-cold solution of 4.18 g. (0.11 mole) of lithium aluminum hydride in 200 ml. of absolute ether was added drop by drop 35.5 g. (0.2 mole) of dichlorophenylphosphine (Victor Chemical Works) dissolved in 200 ml. of absolute ether. The reaction mixture turned yellow and soon began to reflux. After the addition was complete the mixture was refluxed for one hour, cooled and filtered through glass wool. In an atmosphere of nitrogen the ether was first removed; then the phenylphosphine was distilled and collected as a colorless liquid at 160–161°. The yield was 5.6 g. (25.4%); hydrogen iodide salt, m.p. 136° (uncor.).

DEPARTMENTS OF CHEMISTRY
ST. MARY'S COLLEGE AND
UNIVERSITY OF SAN FRANCISCO
SAN FRANCISCO 17, CALIFORNIA

RECEIVED SEPTEMBER 24, 1951

---

[1] A grant-in-aid from Research Corporation is gratefully acknowledged; also the technical assistance of O. Clark Chisim.

[2] A. Michaelis, *Ber.*, **7**, 6 (1874).

[3] H. Lecoq, *Bull. soc. chim. Belg.*, **42**, 199 (1933).

[4] H. Kohler and A. Michaelis, *Ber.*, **10**, 807 (1877).

---

## The Solubility of Aniline Hydrochloride in Water

BY EDWARD H. HOUSE AND JOHN H. WOLFENDEN

Three values for the solubility of aniline hydrochloride are recorded in the literature and regularly quoted in works of reference. Two of these relate to 25° and are in fair agreement; at this temperature C. J. Peddle and W. E. S. Turner[1] report that 100 g. of water dissolves 107.1 g. of the salt while N. V. Sidgwick, P. Pickford and B. H. Wilsdon[2] report that 100 g. of the saturated solution contains 52.1 g. of the salt. The third solubility determination relates to 15°, at which temperature S. v. Niementowski and J. v. Roszkowski[3] report that 100 cc. of water dissolves 17.762 g. of aniline hydrochloride. This last figure is at variance with common observation in the purification of the salt by recrystallization, and suggests a remarkably high temperature coefficient of solubility. The molal heat of solution computed from the recorded solubilities at 15° and 25° implies an absorption of about 29 kcal. of heat, a value much larger than the value of 2.7 kcal. measured by Louguinine,[4] than the heats of solution of other amine hydrochlorides, which commonly range between 1 and 4 kcal. per mole, and than the heat of fusion of the salt as deduced from the cryoscopic data of Leopold[5] (*ca.* 2 kcal. per mole).

The paucity of information about the solubility of this common organic compound and the implausibility of the only determination at any temperature other than 25° prompted us to measure the solubility over the temperature range from 0° to 100°. Saturated solutions of the pure recrystallized salt in water containing 0.2% of aniline to repress hydrolysis were analyzed by titration with

TABLE I

SOLUBILITY OF ANILINE HYDROCHLORIDE

| Temp., °C. | g./100 g. $H_2O$ | Mole fraction |
|---|---|---|
| 0 | 63.50 | 0.08112 |
| 15 | 88.36 | .1094 |
| 25 | 107.35 | .1299 |
| 40 | 143.7 | .1665 |
| 100 | 396 | .355 |

---

[1] C. J. Peddle and W. E. S. Turner, *J. Chem. Soc.*, **103**, 1202 (1913).

[2] N. V. Sidgwick, P. Pickford and B. H. Wilsdon, *ibid.*, **99**, 1122 (1911).

[3] S. v. Niementowski and J. v. Roszkowski, *Z. physik. Chem.*, **22**, 145 (1897).

[4] Cited by M. Berthelot, *Ann. chim. Phys.*, 6e. ser., **21**, 355 (1890).

[5] G. H. Leopold, *Z. physik. Chem.*, **71**, 59 (1910).

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.

DEPARTMENT OF CHEMISTRY
DARTMOUTH COLLEGE
HANOVER, NEW HAMPSHIRE
RECEIVED OCTOBER 4, 1951

## 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

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

where $l$ is the cell length in cm., $\epsilon_A$ and $\epsilon_B$ 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

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

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 $(A)_0$ and $\epsilon_B$. 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 $t + \tau$

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

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 $\tau$ 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 $\tau$ 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 $\tau$ 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 $\epsilon$ values for reactant and/or product with changing wave length is large.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
RECEIVED AUGUST 29, 1951

---

[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-

---

[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).