

expected is given by eq. 1. S_0 and S_∞ are styrene concentrations at zero time and at "infinite" time

$$\log_{10} (S_0/S_\infty) = 2(0.434)k_2(1/k_1k_3)^{1/2}(NA_0)^{1/2} \quad (1)$$

NA_0 is the initial nitrosoacetanilide concentration, and k_1 , k_2 and k_3 are rate constants for initiation, propagation and termination. Using the reported values of the rate constants ($k_1 = 7.7 \times 10^{-5}$, $k_2 = 44$, $k_3 = 2.4 \times 10^7$)^{7,8} the maximum amount of polymer expected is as follows: with nitrosoacetanilide initially at 0.05 *M* (the 0.5 mmole experiment of Table II) about 37%, at 0.1 *M* about 48%. The maximum amount of polymer is increased at lower temperatures since k_1 has a higher temperature coefficient than either k_2 or k_3 : 22 kcal., as compared with 7 kcal. or less.^{7,8}

Experimental Part

N-Nitrosoacetanilide.—This was prepared by the method of DeTar.⁹ The monomer samples were distilled before use to remove inhibitor.

Isobutylene Experiments.—A series of tubes of Pyrex glass was prepared, and weighed amounts of N-nitrosoacetanilide and of trinitrobenzene added. Phillips Pure Grade (99 mole % min.) isobutylene was distilled into these tubes which were immersed in a trichloroethylene bath at solid carbon dioxide temperature. The tubes were sealed, placed in shields and allowed to remain at room temperature for 24 hours. The tubes were cooled, the capillary tips broken, and the isobutylene allowed to evaporate at room temperature and atmospheric pressure. The top of the tube was cut off, the tube weighed, rinsed thoroughly with methylene chloride, and weighed again in order to determine the weight of residue. The results are given in Table I.

(7) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1800 (1934); R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

(8) M. S. Matheson, E. E. Aves, E. B. Bevilacqua and E. J. Hart, *THIS JOURNAL*, **73**, 1704 (1951).

(9) D. F. DeTar, *ibid.*, **73**, 1446 (1951).

BAKER LABORATORY OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

Reactions of N-Nitroso-2-acetamidobenzophenone

BY DELOS F. DETAR¹ AND CONSTANCE S. SAVAT

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We have been interested in reactions which may produce the *o*-benzoylphenyl radical (and other similar radicals) in our study of the mechanisms of certain free radical reactions.² The decomposition of diazotized 2-aminobenzophenone under alkaline conditions is under study at present as a source of these radicals. The thermal decomposition of N-nitroso-2-acetamidobenzophenone is a related reaction which might also be expected to yield the desired radical.³ A preliminary study of this nitroso compound has given interesting results, but the reactions of this compound are too complex to be useful for our purposes at the present time.

In benzene solution N-nitroso-2-acetamidobenzophenone gives 2-benzoylbiphenyl 15%, fluorenone 7%, and unidentified higher molecular weight products. In methanol acidified with sulfuric acid the products were fluorenone 20%, 2-methoxybenzophenone 40% and 2-aminobenzophenone 40%. In

acetic acid the products were fluorenone 23%, 2-acetoxybenzophenone 25% and 45% of 2-aminobenzophenone. The reactions in methanol and in acetic acid thus seem to be ionic reactions.

Experimental Part

N-Nitroso-2-acetamidobenzophenone.—2-Aminobenzophenone was prepared from N-tosylanthranoyl chloride, benzene and aluminum chloride.⁴ Acetylation with acetic anhydride gave 2-acetamidobenzophenone, m.p. 87–88.5°; Lothrop and Goodwin⁵ report a m.p. of 88°. This was converted to the nitroso compound. To 8 g. of the amide, 12 g. of potassium acetate, 56 ml. of glacial acetic acid, 24 ml. of acetic anhydride was added 4.6 g. of nitrosyl chloride in 13.4 g. of acetic anhydride during ten min. at 5°; after an hour at 0°, the mixture was stirred with 800 ml. of ice-water to precipitate the nitrosoamide. This was recrystallized from 125 ml. of acetic acid plus added water, giving 52% of yellow crystals, m.p. 72° dec. It is not stable at room temperature, but can be preserved for several days at Dry Ice temperature.

Anal. Calcd. for $C_{15}H_{13}O_3N_2$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.20; H, 4.63; N, 11.07.

Reactions.—The following thermal decomposition reactions of N-nitroso-2-acetamidobenzophenone were studied: 2 g. of the nitrosamide in 20 ml. of benzene for 15 hours at room temp.; 1 g. in 50 ml. of methanolic 0.04 *M* sulfuric acid for one hour at 60–65° and then for two days at room temp.; 1 g. in 15 ml. of glacial acetic acid for one hour at 100° and then two days at room temperature.

Isolation of and Estimation of Products.—The benzene reaction mixture was subjected to exhaustive steam distillation, yielding fractions of 0.26 g. and 0.23 g. after extraction with methylene chloride. A semi-quantitative analysis was made for fluorenone and for 2-benzoylbiphenyl by measurement of the optical absorbance of ethanol solutions of these fractions at 2300, 2570 and 2650 Å. On evaporation of the ethanol the first residue yielded crystals of 2-benzoylbiphenyl, m.p. 83.3–85.3°, m.p. with authentic material² 86–87°, and a small amount of yellow crystalline material, m.p. 83–84°. The yellow crystalline material was subjected to microscopic examination and was identical with fluorenone in the following respects: hexagonal plates, highly birefringent, four angles about 148°, two angles about 64°, parallel extinction. The second fraction yielded only 2-benzoylbiphenyl, m.p. 84.3–85.3°, in crystalline form.

The methanol reaction mixture was neutralized with sodium hydroxide, distilled to remove most of the methanol, water was added, and then the resulting mixture was extracted with methylene chloride. The methylene chloride layer was subjected to exhaustive steam distillation and the distillates, after extraction with methylene chloride and evaporation to dryness, yielded 0.95 g. of residue. The infrared spectra of this residue had peaks characteristic of fluorenone, benzophenone, 2-methoxybenzophenone, 2-aminobenzophenone and one or more unidentified other materials. A semi-quantitative analysis based on absorbance at 2150, 2350 and 2570 Å. was made for fluorenone, 2-aminobenzophenone and 2-methoxybenzophenone.

The acetic acid reaction mixture was distilled to remove most of the acetic acid and the residue was treated with methylene chloride and aqueous sodium hydroxide. The methylene chloride layer was subjected to steam distillation and gave 0.59 g. of neutral residue. Semi-quantitative analysis of an ethanol solution using absorbance at 2350, 2570 and 2650 Å. gave estimates of the amounts of fluorenone, 2-aminobenzophenone and 2-acetoxybenzophenone. On evaporation of the ethanol, yellow crystals of fluorenone separated, m.p. 78.5–81.5°, mixed m.p. with authentic fluorenone 79–82°. The infrared spectra of the residue obtained by evaporation of the mother liquor had peaks at 5.87, 6.24, 10.90 and 13.54 characteristic of fluorenone; at 5.70, 6.28, 6.95, 7.78, 7.95, 8.43 and 13.25 characteristic of 2-acetoxybenzophenone, and at 3.07 and 3.50 characteristic of 2-aminobenzophenone. In addition to the listed

(1) Department of Chemistry, University of South Carolina, Columbia, S. C.

(2) D. F. DeTar and S. Sagmanli, *THIS JOURNAL*, **72**, 965 (1950).

(3) D. F. DeTar, *ibid.*, **73**, 1446 (1951).

(4) D. F. DeTar and H. Scheifele, *Org. Syntheses*, **32**, 8 (1952).

(5) W. C. Lothrop and P. A. Goodwin, *THIS JOURNAL*, **68**, 368 (1943).

peaks, this residue showed absorption peaks for all of the individual peaks of the respective compounds.

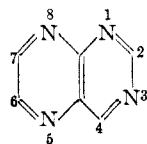
BAKER LABORATORY OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

Spectrophotometric Determination of the Ionization Constants of Pteridine, 2-Aminopteridine and 4-Aminopteridine

By DeLos F. DeTar,¹ C. K. Cain and B. Spencer Meeks, Jr.²

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Interest in the chemistry of pteridine (I) and its derivatives has been especially great since the discovery that the pteridine nucleus is an important part of the folic acid molecule. Until very re-



cently pteridine itself and its simple monofunctional derivatives were largely unknown, a situation perhaps stemming from the fact that all of the interesting naturally occurring derivatives were tri- and tetra-substituted pteridines.

A few years ago Jones³ made a preliminary report of the preparation of pteridine. More recently the chemistry of the simple pteridines has been admirably worked out by Albert, Brown and Cheeseman.⁴ The present investigation was undertaken before the report of this work was available. Albert, Brown and Cheeseman measured the pK of the acid forms (BH^+) of the pteridines by potentiometric titration. In this work the pK^* values have been measured spectrophotometrically by the general procedure described by Sager, Schooley, Carr and Acree.⁵ The results are presented in Table II.

TABLE I
SPECTROPHOTOMETRIC DATA FOR CALCULATION OF THE IONIZATION CONSTANT OF 2-AMINOPTERIDINE

| pH of buffer (0.02 M) | Extinction coefficients $\times 10^{-4}$ at various wave lengths, $m\mu$ | | | | |
|-----------------------|--|-------|-------|-------|-------|
| | 260 | 265 | 290 | 300 | 305 |
| 6.98 | 0.751 | 0.681 | 0.086 | 0.076 | 0.080 |
| 7.14 | .748 | .681 | .084 | .075 | .079 |
| 7.27 | .738 | .675 | .084 | .075 | .078 |
| Av. ϵ_B^a | .746 | .679 | .085 | .075 | .079 |
| 1.90 | 0.130 | 0.176 | 0.646 | 0.769 | 0.745 |
| 1.98 | .133 | .175 | .645 | .770 | .744 |
| 2.11 | .135 | .178 | .646 | .771 | .748 |
| Av. ϵ_A^a | .133 | .177 | .645 | .770 | .746 |
| 4.19 | 0.382 | 0.383 | 0.439 | 0.513 | 0.500 |
| 4.30 | .410 | .406 | .406 | .474 | .463 |
| 4.68 | .549 | .517 | .266 | .300 | .296 |

^a See text for definitions.

(1) Department of Chemistry, University of South Carolina, Columbia, S. C.

(2) From the Ph.D. thesis of B. Spencer Meeks, Jr.

(3) W. G. M. Jones, *Nature*, **162**, 524 (1948).

(4) A. Albert, D. J. Brown and G. Cheeseman, *J. Chem. Soc.*, 474 (1951); 1620, 4219 (1952); A. Albert, *Quart. Rev.*, **6**, 197 (1952).

(5) E. E. Sager, M. R. Schooley, A. S. Carr and S. F. Acree, *J. Research Natl. Bur. Standards*, **55**, 521 (1945).

TABLE II
CALCULATED VALUES OF pK^*

| pH | pK^* calcd. at | | | | |
|---|--------------------------------|------------|------------|------|------|
| | 275 $m\mu$ | 285 $m\mu$ | 285 $m\mu$ | | |
| Pteridine: av. pK^* 4.15 \pm 0.06 ^a (4 samples) | (4.12 \pm 0.05) ^b | | | | |
| 3.85 | 4.23 | 4.13 | | | |
| 4.21 | 4.28 | 4.09 | | | |
| 4.30 | | 4.12 | | | |
| 4.67 | | 4.07 | | | |
| | 305 | 320 | 325 | | |
| 4-Aminopteridine: av. pK^* 3.514 \pm 0.020 ^a (3 samples) | (3.56 \pm 0.08) ^b | | | | |
| 3.45 | 3.48 | 3.48 | 3.50 | | |
| 3.62 | 3.49 | 3.50 | 3.50 | | |
| 3.93 | 3.57 | 3.55 | 3.56 | | |
| | 260 | 265 | 290 | 300 | 305 |
| 2-Aminopteridine: av. pK^* 4.386 \pm 0.020 ^a (3 samples) | (4.29 \pm 0.03) ^b | | | | |
| 4.19 | 4.35 | 4.35 | 4.42 | 4.42 | 4.42 |
| 4.30 | 4.38 | 4.38 | 4.43 | 4.43 | 4.43 |
| 4.68 | 4.35 | 4.36 | 4.36 | 4.36 | 4.36 |

^a For error limits see text. ^b pK by titration as reported by Albert, Brown and Cheeseman.⁴ Error figures represent maximum deviations from the calculated titration curve and apparently are derived from a single determination.

The agreement between the two sets of pK values is very good.

Experimental Part

Pteridines.—The pteridine and 2-aminopteridine samples were prepared by a method similar to that described by Albert, Brown and Cheeseman⁴ but independently worked out in this Laboratory. The samples were sublimed and recrystallized several times until further purification gave no change in the ultraviolet spectra. The 4-aminopteridine was a sample prepared by Mr. N. T. Gehshan.⁶

Buffer Solutions.—The following buffers were used: pH 0.5–1.5, hydrochloric acid; 1.5–3.5, citrate; 3.5–5.5, acetate; 5.5–8.0, phosphate; 8.0–12.0, borate; 12.0, sodium hydroxide. Buffer concentrations were 0.02 M, and pH values were read using a Leeds and Northrup pH meter with calomel and glass electrodes standardized at pH 4 and pH 7 against Bureau of Standards potassium acid phthalate and Leeds and Northrup phosphate buffer.

Spectrophotometric Measurements.—A Beckman model DU spectrophotometer was used in this work. In obtaining the extinction coefficients such as those given in Table I two sets of absorbance readings were taken on each sample, one set of readings with solvent in cell 1 and solution in cell 2, and another set with solvent in cell 2 and solution in cell 1. The two absorbance values were averaged for each wave length. This averaging procedure increases the accuracy by cancelling out bias between the two cells, it provides increased precision, and it eliminates gross errors.

Equations for Calculation of pK^* .—For a compound BH^+ , the acid strength that is determined spectrophotometrically is defined by eq. 1

$$K = C_{BH_3O^+}/C_{BH^+} \quad (1)$$

The ionization constant is rather insensitive to ionic strength since $a_{BH_3O^+}$ and a_{BH^+} tend to be changed to about the same extent by the ionic environment. Since the buffer concentrations used were low (about 0.02 M), the pK^* values reported in Table II are probably equal to pK_s within the experimental error.

The values of pK^* were calculated using eqs. 2 and 3

$$pK^* = pH + \log [\alpha/(1 - \alpha)] \quad (2)$$

α = fraction of the compound which is in the form BH^+ . In terms of spectrophotometrically measured quantities α is given by eq. 3

$$\alpha = (\epsilon - \epsilon_B)/(\epsilon_1 - \epsilon_B) \quad (3)$$

where ϵ_B is the extinction coefficient of the basic form, ϵ_1 of

(6) N. T. Gehshan, M.S. Thesis, Cornell University, 1948.