skii and Frost[12] up to 920°. At 750°, accordingly, the free energy change for biphenyl formation from benzene is +4.3 kcal. Using the free energy change as criterion of the feasibility of a reaction, it is seen that thermodynamically the direct cyanogenation of benzene is much more favorable than the formation of biphenyl. On thermodynamic grounds, the direct cyanogenation reaction is predicted as capable of proceeding very far in the direction of benzonitrile, and the conditions for undertaking a catalyst search to promote the rate to a more favorable degree are thus good.

Acknowledgment.—The author wishes to express his appreciation to Dr. A. W. Patterson for the analyses of the dinitrile mixtures by ultraviolet absorption, and Canadian Industries Limited, Montreal, Canada, for kind permission to publish these results.

TROY, N. Y.

(12) A. A. Vvedenskii and A. V. Frost, *J. Gen. Chem. U. S. S. R.*, **2**, 542 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANADIAN SERVICES COLLEGE, ROYAL ROADS]

A Kinetic Study of the Alkaline Scission of 4-Hydroxy-3-methoxy-β-nitrostyrene

BY ROSS STEWART

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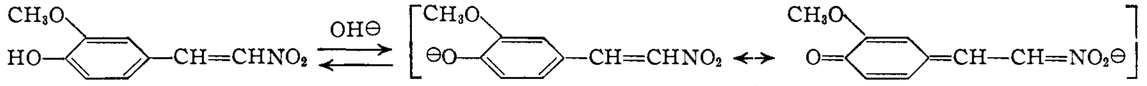
Kinetic and spectral evidence are presented to show that in basic solution the colored anion of 4-hydroxy-3-methoxy-β-nitrostyrene reacts with hydroxyl ion to produce an intermediate which, in turn, decomposes to give vanillin and nitromethane.

The compound 4-hydroxy-3-methoxy-β-nitrostyrene (BNS) has been recently examined as an acid-base indicator.[1] In acid solution it is yellow but in basic solution it possesses an intense red color which fades on standing to give a colorless solution. The structure of the red species is presumably the resonance hybrid BNS′. This research was undertaken to establish the mechanism of the fading in color of this ion.

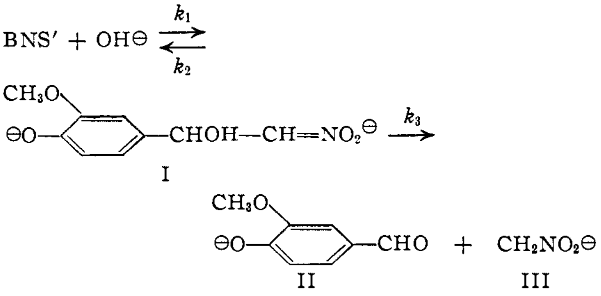
To test this postulate the rate of fading of BNS′ was studied under various conditions. If the first step is correct, the Brönsted–Debye–Hückel relation should hold since a reaction between two ions is postulated. The reaction should also be first order with respect to both BNS′ and hydroxyl ion. The intense red color of BNS′ permits this reaction to be followed colorimetrically. Both colorimetric and spectrophotometric methods were used in this study.



BNS

BNS′

In a study of *p*-hydroxy-β-nitrostyrene and related substances, Hahn and Stiehl[2] concluded that the colored species had the structure $O{=}C_6H_4{=}CH{-}CH{=}NO_2Na$, which faded to give $NaOC_6H_4CHOHCH{=}NO_2Na$ and, finally, *p*-hydroxybenzaldehyde. Proof for this mechanism was not advanced. A somewhat similar mechanism is postulated here involving a nucleophilic attack by hydroxyl ion at the α-carbon atom of the side chain of the hybrid anion, BNS′, to give I. This substance could then decompose to give vanillin and nitromethane, which would exist as the anions II and III if the solution were sufficiently basic.



Experimental

Materials.—BNS was prepared and purified as previously described.[1a] Vanillin (Eastman Kodak Co.) was recrystallized from water. Nitromethane (Matheson Co.) and all solvents required were distilled before use. Distilled water was boiled just before use. A standard solution of BNS containing 80 mg. of BNS per 50 ml. of absolute ethanol was made up before each series of kinetic runs and before all the spectral determinations.

Apparatus.—A Beckman model DU quartz spectrophotometer was used to obtain the absorption curves. This instrument equipped with thermospacers was also used for many of the rate measurements, the balance being obtained with the Fisher electrophotometer (model 7-089).

Rate Measurements.—The reaction vessels used were 100-ml. volumetric flasks immersed in a constant temperature bath at 25 ± 0.04°. At zero time one ml. of the standard solution of BNS in ethanol was pipetted into the reaction vessel which had been made up to 99 ml. with the required amount of carbonate-free sodium hydroxide, sodium chloride and distilled water. When the electrophotometer was used to follow the drop in concentration of BNS′ a certain volume of solution was withdrawn from the flask at regular intervals and the transmission of these samples measured. In some cases this procedure was also followed with the spectrophotometer. In others, the Beckman quartz cells were kept at constant temperature by means of thermospacers, and a series of transmission readings was obtained on the same sample. Good agreement between the three methods was obtained. A series of runs in which the one ml. of ethanol used as solvent for the BNS was replaced by methanol, dioxane, and pyridine showed the effect of the ethanol to be negligible. The only change in the rate was found when commercial dioxane was used. One ml. in 100 ml. had the effect of doubling the rate of fad-

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(1) (a) R. Stewart and R. H. Clark, *Can. J. Research*, **B26**, 7 (1948); (b) M. G. S. Rao, C. Srikantia and M. S. Iyengar, *J. Chem. Soc.*, 556 (1925).

(2) G. Hahn and K. Stiehl, *Ber.*, **71B**, 2154 (1938).

ing of BNS′ at pH 9.2, presumably because of the oxidizing action of peroxide impurities. With purified dioxane[3] the rate was the same as for the other solvents.

Calculations.—The density readings obtained with the spectrophotometer were used directly to calculate the pseudo first-order rate constants, k', by the method of least squares. Transmission readings from the electrophotometer were converted to concentrations by means of a calibration curve and then the rate constants were calculated in the same way. The second-order rate constants, k_1, were obtained by dividing these values by the hydroxyl ion concentrations. The latter values were obtained directly from the number of equivalents of sodium hydroxide added to the solution, corrected for the amount required to convert the BNS to BNS′.

Results and Discussions

The effect of varying the ionic strength of the solution on the rate of the fading reaction is shown in Fig. 1. The agreement with the theoretical slope of +1 predicted by the Brönsted–Debye–Hückel relation for a reaction between two ions of like, single, charge is reasonably good.

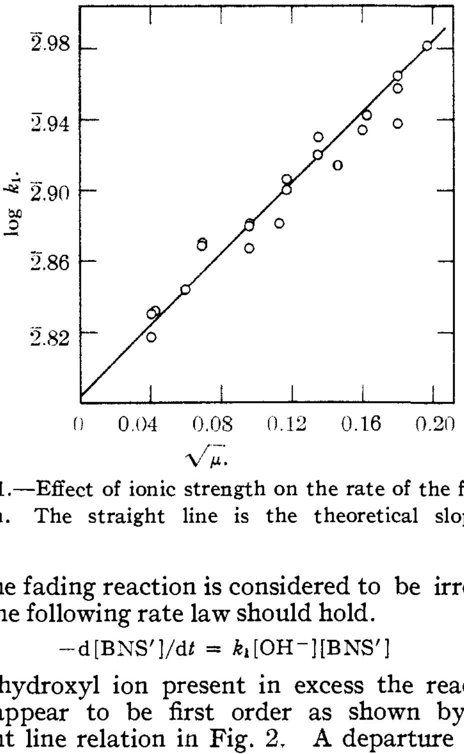

Fig. 1.—Effect of ionic strength on the rate of the fading reaction. The straight line is the theoretical slope of +1.

If the fading reaction is considered to be irreversible the following rate law should hold.

$$-\mathrm{d}[\mathrm{BNS}']/\mathrm{d}t = k_1[\mathrm{OH}^-][\mathrm{BNS}']$$

With hydroxyl ion present in excess the reaction does appear to be first order as shown by the straight line relation in Fig. 2. A departure from linearity, however, is observed at very high hydroxyl ion concentrations. An indication that under certain conditions the fading reaction is reversible is given by the fact that a rapidly fading solution of BNS′ in a strongly basic solution can have its intense color restored by addition of acid until the solution is almost neutral. However, if the solution becomes colorless and is allowed to stand overnight no trace of color can be obtained by reducing the hydroxyl ion concentration. The irreversibility of the second part of the reaction, *i.e.*, the decomposition of I to vanillin and nitromethane, which can be inferred from this evidence, is to be expected since it has been shown[2,4] that vanillin and nitromethane do not condense under the influence of sodium hydroxide.[5]

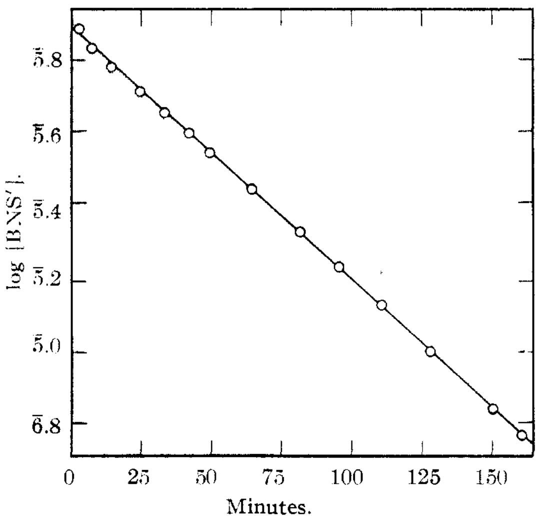

Fig. 2.—Rate of disappearance of BNS′: shown to 92% completion; $[\mathrm{OH}^-] = 3.63 \times 10^{-3}$ M.

The fading reaction is shown to be first order in hydroxyl ion by the results in Table I.

TABLE I

REACTION RATES AT VARIOUS HYDROXYL ION CONCENTRATIONS[a]

$[\mathrm{OH}^-] \times 10^4$, mole liter^{-1}	$k' \times 10^4$, sec.$^{-1}$	$k_1 = k'/[\mathrm{OH}^-]$, liter mole^{-1} sec.$^{-1}$
19.5	1.53	0.0785
21.8	1.68	.0771
24.1	1.76	.0730
26.3	2.01	.0765
28.4	2.20	.0775
30.7	2.33	.0759
33.0	2.56	.0776
35.4	2.84	.0802
36.3	2.74	.0755
	Mean	0.0769 ± 0.0020

[a] BNS = 8.2×10^{-5} M. The ionic strength of each solution was brought to a value of 0.00363 by the addition of sodium chloride.

The ultimate production of vanillin from BNS has been recently reported by Crowell and Ramirez[7] who studied the condensation of vanillin and nitromethane. They isolated vanillin as the 2,4-dinitrophenylhydrazone. The presence of vanillin as the final product of the fading reaction was demonstrated in this research by the use of ultraviolet spectra. Figure 3 shows the spectrum of a basic solution of BNS which has faded to colorless, and

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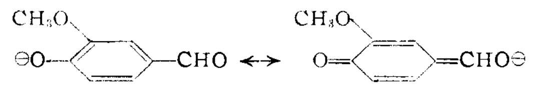
[3] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 369.

[4] K. W. Rosenmund, German Patent 247,817; *C. A.*, **6**, 2822 (1912).

[5] The reluctance of vanillin to undergo the normal Cannizzaro reaction has been explained[6] as being due the resonance stability of the hybrid anion



This reduction in carbonyl character when vanillin is treated with sodium hydroxide doubtless affects the condensation reaction as well.

[6] T. A. Geissman in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 105.

[7] T. J. Crowell and F. A. Ramirez, This Journal, **73**, 2268 (1951).

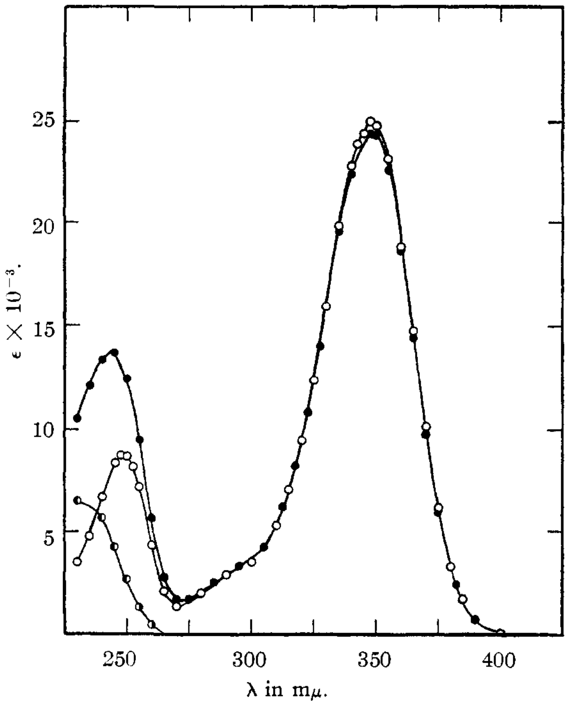


Fig. 3.—Ultraviolet spectra of vanillin ○, nitromethane ◐, and a solution of BNS which has faded to colorless ●; *p*H = 12.3.

also the spectra of vanillin and nitromethane in a solution of the same *p*H. To determine whether vanillin is produced immediately or whether the proposed intermediate I exists for a reasonable length of time, the rate of production of vanillin and the rate of disappearance of BNS' were measured simultaneously using the Beckman spectrophotometer. This was conveniently done since the peaks of BNS' and II are at 500 and 347 mμ, respectively. A correction was made for the small absorption of BNS' at 347 mμ when the concentration of vanillin was calculated from the transmission data. The concentration of the intermediate I (or intermediates if the route from BNS to vanillin is more complex than the simple route postulated here) was obtained from the difference in concentration of BNS' and vanillin at any time. No attempt was made to obtain the spectrum of the intermediate and measure its concentration directly because of its short half-life. This is apparent from the curves shown in Fig. 4. Figure 4a shows the plot of the concentrations of vanillin, BNS' and intermediate I (calculated by difference) against time at *p*H 11.5. Figure 4b is for *p*H 12.8 and shows that in this case, for a short interval, the intermediate reaches a relatively high concentration. The decomposition of the intermediate to give vanillin in this latter case is approximately first order, which is to be expected if the mechanism is correct. Indeed, Table II shows that the rate of production of vanillin at *p*H 12.8 is directly proportional to the concentration of I at any time.

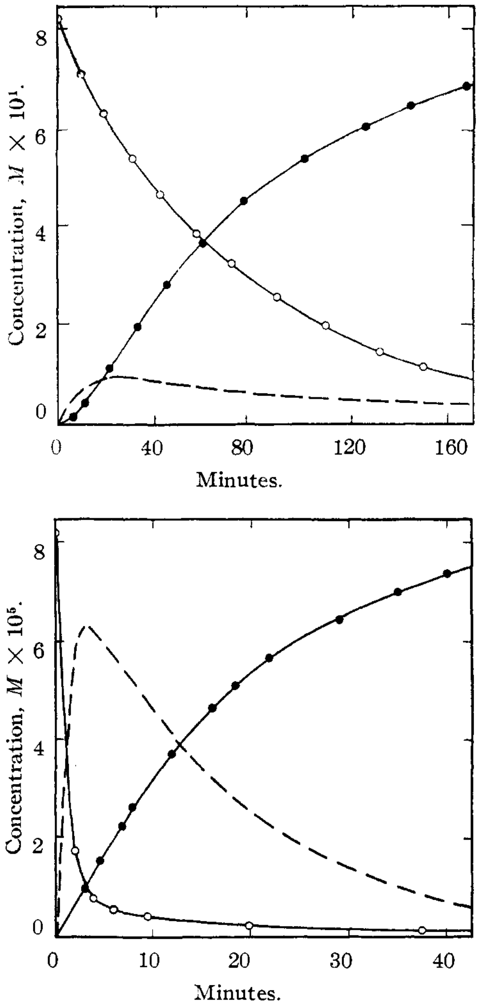


Fig. 4.—Concentration of BNS' and its reaction products as a function of time; BNS' —○—, I — — —, vanillin —●—. Fig. 4a upper, *p*H = 11.5; Fig. 4b (lower), *p*H = 12.8.

TABLE II

RATE OF PRODUCTION OF VANILLIN (II) AS A FUNCTION OF THE CONCENTRATION OF INTERMEDIATE (I) AT *p*H 12.8

Time, min.	$d[II]/dt \times 10^8$, mole liter^{-1} sec.$^{-1}$	$[I] \times 10^5$, mole liter^{-1}	$\frac{d[II]/dt}{[I]} \times 10^3$, sec.$^{-1}$
10	4.71	4.62	1.02
14	3.67	3.66	1.00
18	3.00	2.90	1.03
22	2.37	2.28	1.04
26	1.85	1.80	1.03
30	1.49	1.42	1.05

The spectral data for the compounds studied in this work are listed in Table III.

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA[a]

Compound	*p*H	λmax, mμ	ε
4-Hydroxy-3-methoxy-β-nitrostyrene (BNS)	4.0	376	15,900
		245–260	7,200
4-Hydroxy-3-methoxy-β-nitrostyrene'(BNS')[b]	10.4	500	24,600
		269	6,500
Vanillin (II)[b]	12.3	347	25,100
		248	6,800

[a] All data are for 8.2×10^{-5} *M* solutions containing 1 ml. of absolute ethanol in 100 ml. of distilled water. [b] As anion at this *p*H.

Acknowledgment.—Certain of the experimental results reported in this paper were obtained by the author in the chemical laboratories of the University of British Columbia and the University of Washington.

Victoria, B. C., Canada

[Contribution No. 98 from the Department of Chemistry, University of Tennessee]

The Catalytic Hydrogenation of the Benzene Nucleus. VII. The Hydrogenation of Benzilic Acid

By Hilton A. Smith, Comer D. Shacklett and Clark M. Welch

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The half-hydrogenated products of benzilic acid have been analyzed by means of the color developed by benzilic acid in sulfuric acid. It has been demonstrated that this color is influenced by the partially hydrogenated product, and an explanation given. It has been shown that benzilic acid is almost five times more readily adsorbed on platinum catalyst than phenylcyclohexylglycolic acid.

In an earlier publication[1] it was demonstrated that the rate of hydrogenation of a compound containing two benzene rings was essentially the same as that of the corresponding half-hydrogenated compound which contained one benzene and one cyclohexane ring. However, the original material was largely converted to the half-hydrogenated intermediate before complete saturation. Apparently the composition of a partially hydrogenated sample was determined by the adsorption characteristics of the unhydrogenated and half-hydrogenated materials rather than by their individual hydrogenation rate constants. For diphenylacetic acid, analyses by esterification rates indicated that the half-hydrogenated material was essentially pure phenylcyclohexylacetic acid; for diphenylglycolic (benzilic) acid, a similar situation was not found. The following gives the details of analysis of mixtures of these two acids together with the calculation of their relative adsorption on platinum catalyst.

Experimental

The preparations of benzilic and phenylcyclohexylglycolic acids have been previously described.[1]

Dicyclohexylglycolic acid was prepared by the complete hydrogenation of benzilic acid. All hydrogenations were carried out in a standard low-pressure Parr catalytic reduction apparatus using Adams platinum catalyst and acetic acid solvent.

A Beckman model DU ultraviolet spectrophotometer and a Coleman model 14 universal spectrophotometer were used for obtaining absorption spectra.

Analyses.—An investigation of the ultraviolet absorption of benzilic and phenylcyclohexylglycolic acids in ethanol solution showed that use of this property could not be made for following the course of the hydrogenations. The primary difference between the absorption curves is that of intensity only, see Fig. 1. However, benzilic acid develops a deep red color when dissolved in concentrated sulfuric acid.[2] The absorption spectrum of this solution is shown in Fig. 2. At 500 mμ similar solutions of phenylcyclohexylglycolic or dicyclohexylglycolic acids do not absorb. In addition, the benzilic acid "solution" was found to obey Beer's law over the concentration range of 1 to 8 micrograms per ml. Since it appeared that partially hydrogenated mixtures could be analyzed by this method, identical samples of benzilic acid were partially hydrogenated and the catalyst and solvent removed. Solutions of the resulting solids in sulfuric acid were compared with standard benzilic acid solutions, and the curve (dotted line) shown in Fig. 3 obtained.

A material balance calculation shows that this curve is impossible, for the minimum amount of benzilic acid present at any stage of the hydrogenation is represented by curve A in the figure. Further investigation showed that the spectral transmission of the solutions made from the partially hydrogenated benzilic acid were considerably different from those of pure benzilic acid. A new set of standards was made up from various amounts of phenylcyclohexylglycolic acid plus equimolecular mixtures of dicyclohexylglycolic and benzilic acids. The solids were completely dissolved in ether, the solvent evaporated, and sulfuric acid then added. By comparing half-hydrogenated benzilic acid with these standards it was found that 17.5% of benzilic acid was present. Since there must be an equal number of moles of completely hydrogenated product, 65% of the intermediate phenylcyclohexylglycolic acid was present.

Discussion

Colorimetric Standards.—It is known that certain carboxylic acids are ionized in sulfuric acid as[3]

$$\mathrm{RCOOH + 2H_2SO_4 \longrightarrow H_3O^+ + 2HSO_4^- + RCO^+}$$

It is also known that in sulfuric acid, diphenylcarbinol and triphenylcarbinol ionize thus[4]

$$\mathrm{(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^-}$$

$$\mathrm{(C_6H_5)_2CHOH + 2H_2SO_4 \longrightarrow (C_6H_5)_2CH^+ + H_3O^+ + 2HSO_4^-}$$

and that triphenylacetic acid liberates carbon monoxide.[5]

Since benzilic acid slowly liberates a gas (CO) when dissolved in sulfuric acid, one might expect a reaction such as

$$\mathrm{(C_6H_5)_2COHCOOH + 4H_2SO_4 \longrightarrow (C_6H_5)_2C^{++} + 2H_3O^+ + 4HSO_4^- + CO}$$

If such a reaction were correct, the use of colorimetric standards made from pure benzilic acid for analyzing partially hydrogenated benzilic acid should have been successful. If macroscopic crystals of benzilic and phenylcyclohexylglycolic acid are dissolved in sulfuric acid, the color charac-

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(1) H. A. Smith, D. M. Alderman, Jr., C. D. Shacklett and C. M. Welch, This Journal, **71**, 3772 (1949).

(2) *Cf.* "Beilstein's Handbuch der organischen Chemie," 4th ed., Vol. X, Verlag Julius Springer, Berlin, Germany, 1927, p. 342.

(3) H. P. Treffers and L. P. Hammett, This Journal, **59**, 1708 (1937).

(4) A. Hantzsch, *Ber.*, **54**, 2573 (1921); H. A. Smith and R. J. Smith, This Journal, **70**, 2400 (1948); C. M. Welch and H. A. Smith, *ibid.*, **72**, 4748 (1950).

(5) A. Bistrzycki and E. Reintki, *Ber.*, **38**, 839 (1905); A. Bistrzycki and L. Mauron, *ibid.*, **43**, 2883 (1910); H. R. Dittmar, *J. Phys. Chem.*, **33**, 533 (1929).