

Electron-donating substituents in the *p*- or *m*-position uniformly decrease the carbonyl frequency of the acetanilides but either have no effect on, or increase the frequency of, the phenyl acetate carbonyl. The only exception to this is the very powerful electron-donating *p*-amino (no. 22) which causes a barely perceptible decrease in phenyl acetate. We must conclude from this that the greater polarizability of the nitrogen lone-pair electrons is more sensitive to the partial negative charges induced on the ring by the substituent, and thus is more efficient at relaying the effect to the C=O. It is of interest that *p*-phenyl, which does not affect the absorption frequency of aceto-

phenone, causes a decrease of 6 cm.⁻¹ in acetanilide and an increase of identical value in phenyl acetate. It is well known that the phenyl group with a σ -constant of about zero may either donate or accept electrons and the complexity of the resulting situation makes further speculation unprofitable at this time.

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Kinetics of the Reduction of Nitrobenzenes by Sodium Disulfide

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The reduction of nitrobenzene by sodium disulfide to aniline has been studied kinetically at 60, 50, 40 and 30° in 70 and 40 vol. % aqueous methanolic solutions using an ultraviolet spectrophotometer. The rate was found to be proportional to the concentration of nitrobenzene and to the square of the concentration of sodium disulfide. The rate constant increased linearly with the concentration of sodium hydroxide added. The activation energy and the frequency factor of the reaction were evaluated to be 16.35 kcal. mole⁻¹ and 4.57×10^8 l.² mole⁻² sec.⁻¹, respectively. The effect of substituents fitted the Hammett equation well, its ρ -value being +3.55. The results are discussed on the standpoint of reaction mechanism involving an attack of the disulfide ion on the positive nitrogen of nitrobenzenes in conjunction with the hydrolytic equilibrium of the disulfide ion.

Although the reduction of substituted nitrobenzenes by sodium sulfides to yield the corresponding anilines is of much preparative significance, very little work has been carried out from the standpoint of reaction kinetics. The only available publication is that of Goldschmidt, *et al.*,¹ who measured the rate of sodium disulfide reduction of nitrobenzene by following the disappearance of the disulfide by acidimetry using phenolphthalein as an indicator. However, the authors' test proved this method of measurements to be unsatisfactory for deriving rate equations under various conditions.

The present study was undertaken to derive reliable rate equations, to get more information on this reaction and, if possible, to elucidate its reaction mechanism. At first, sodium monosulfide was chosen as a reducing agent, but the rates were too slow to follow the reaction kinetically. Therefore, in this study, rates of reduction of several substituted nitrobenzenes by sodium disulfide were determined spectrophotometrically using aqueous methanol as a solvent.

Experimental

Materials.—All reactants and solvents were obtained commercially or by standard methods of preparation and used after careful purification either by distillation or recrystallization. Sodium disulfide was prepared by the method of Gabel, *et al.*²

Isolation Experiments.—Reductions of all substituted and non-substituted nitrobenzenes were carried out under the same conditions as those of the kinetic experiments and after reaction of sufficient duration the resulting solutions were evaporated in vacuum, diluted with water, and ex-

tracted with ether. After washing with water, the ether was evaporated and the resulting anilines were, if necessary after acetylation, recrystallized and were identified by comparison with authentic specimens. Yields were in all cases above 70%.

In the case of nitrobenzene the product solution was worked up as in the kinetic experiments and its ultraviolet absorption spectrum was compared with that of an authentic solution of aniline. Coincidence was satisfactory, so that the absence of any appreciable amount of side reactions was assured.

Methods of Analysis.—The reaction was followed, at first, by electrometrical titration³ of sodium disulfide using a standard solution of ammoniacal silver nitrate. This method of determination proved to be very accurate with sodium monosulfide but less precise with sodium disulfide. Therefore this method was used as a supplemental check of runs with a large excess of nitrobenzene, while in most of the other runs the rates were measured by following the change of ultraviolet absorption spectra of nitrobenzene (absorption maximum 270 m μ).

Typical Procedure for Rate Measurements.—An appropriate amount of methanol, water, sodium disulfide and sodium hydroxide was placed in a 100-ml. three-necked flask equipped with a reflux condenser and an outlet tube, and the flask was immersed in a thermostat regulated at definite temperatures. The reaction was commenced by introducing a definite amount of a methanolic solution of nitrobenzene previously warmed to the reaction temperature, and by thorough shaking. At appropriate time intervals aliquots (0.5 ml.) were withdrawn, poured into a 10-ml. volumetric flask containing an appropriate amount of acidic aqueous methanol (2 *N* 50 vol. % aqueous methanolic solution of sulfuric acid), diluted accurately to 10 ml. and then warmed (50°) for 5 minutes. These solutions were further diluted by acidic methanol (0.5 *N* methanolic solution of sulfuric acid) to one-tenth of its concentration, and differences of optical densities, $E_{270m\mu} - E_{245m\mu}$, of the resulting solutions were measured using a Beckman spectrophotometer, model DU. Data for a typical run⁴ are given in Fig. 1.

(1) H. Goldschmidt and H. Larsen, *Z. physik. Chem.*, **71**, 437 (1910).

(2) Y. O. Gabel and L. F. Speier, *C. A.*, **42**, 4976 (1948).

(3) H. H. Willard and F. Fenwick, *This Journal*, **45**, 645 (1923).

(4) In those runs containing excess of nitrobenzene over sodium di-

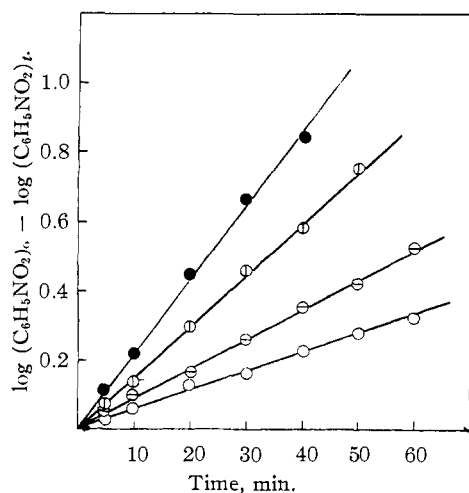


Fig. 1.—Typical runs in 40% aqueous methanol at 50°; initial concentrations: $(\text{Na}_2\text{S}_2) = 0.1125 M$, $(\text{C}_6\text{H}_5\text{NO}_2) = 0.025 M$; $(\text{NaOH}) = 0.500 M$ ●, $0.250 M$ ⊙, $0.100 M$ ⊗, none ○.

Results

The rates were measured at 50° in 70% (vol. %) methanol, the apparent third-order rate constants being given in Table I with varying molar ratio of both reactants. These constants were calculated

TABLE I
THIRD-ORDER RATE CONSTANTS FOR THE REDUCTION OF NITROBENZENE BY SODIUM DISULFIDE IN 70% AQUEOUS METHANOL AT 50°

Initial concentrations, M			Rate constants $k_3 \times 10^3$, $\text{sec.}^{-1} M^{-2}$
Na_2S_2	$\text{C}_6\text{H}_5\text{NO}_2$	Additives	
0.113	0.025	None	6.06 ± 0.08
.300	.050	None	$6.13 \pm .08$
.200	.050	None	$5.99 \pm .08$
.150	.050	None	$6.09 \pm .08$
.200	.100	None	$6.15 \pm .10$
.150	.100	None	$6.07 \pm .08$
.150	.200	None	$6.20 \pm .10$
.125	.200	None	$6.31 \pm .20$
.100	.200	None	$6.51 \pm .26$
.075	.200	None	$7.65 \pm .40$
.050	.200	None	13.6 ± 3.0
.025	.200	None	22.9 ± 7.0
.013	.200	None	46.1 ± 15.0
.150	.150	None	6.13 ± 0.08
.150	.100	None	$6.07 \pm .08$
.150	.050	None	$6.09 \pm .08$
.150	.025	None	$6.07 \pm .10$
.150	.013	None	$5.98 \pm .08$
.125	.200	$\text{Na}_2\text{S } 0.10$	$6.92 \pm .02$
.113	.025	$\text{LiCl } .30$	$6.70 \pm .20$
.113	.025	$\text{LiCl } .10$	$6.31 \pm .20$
.113	.025	$\text{NaCl } .30$	$6.68 \pm .20$
.113	.025	$\text{NEt}_3 .50$	$6.10 \pm .20$
.150	.050 ^a	None	$0.67 \pm .40$
.150 ^b	.050	None	Very slow

^a Azoxybenzene. ^b Sodium monosulfide.

as follows. In those runs containing a large excess of sodium disulfide over nitrobenzene, sulfide reactions are usually slow and hence they were followed only to a small extent (20–30%). Therefore the reaction order with respect to sodium disulfide was ascertained only by the dependence of the rates on the initial concentrations of sodium disulfide.

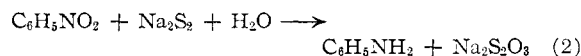
first-order rate constants with respect to nitrobenzene were calculated at first and then divided by the square of the respective initial concentrations of sodium disulfide. When nitrobenzene was present in large excess, second-order rate constants with respect to sodium disulfide were obtained at first, and then divided by the initial concentrations of nitrobenzene. If the two reactants exist in a comparable amount, third-order rate constants were calculated directly. As is shown in the table, the constancy is satisfactory over a wide range of initial concentrations, from which it is evident that the reaction is third order, first order in nitrobenzene and second order in sodium disulfide. However, if the concentration of sodium disulfide becomes fairly small, the third-order rate constants increase progressively. The rates are particularly slow in these runs and hence rate measurements are less precise. The extended reaction time also caused air oxidation of sodium disulfide; yet even when adequate corrections (blank experiments) were applied, the deviation of the k_3 values still exceeded the experimental error. But the progressive increase of the third-order constants with the decrease of sodium disulfide concentration cannot be denied. A tentative calculation showed these runs to fit a second-order equation, first order with respect to each reactant. But, as mentioned above, these values are less precise and no clear decision can be made whether it is a genuine second-order relation in this concentration range or merely an apparent one. At any rate, it is certain that the rates can be expressed by the equation

$$-d(\text{C}_6\text{H}_5\text{NO}_2)/dt = k_3(\text{C}_6\text{H}_5\text{NO}_2)(\text{Na}_2\text{S}_2)^2 \quad (1)$$

over a wide range of initial concentrations of each reactant.

Some complementary data are shown in Table I. The rates of reduction of nitrobenzene by sodium monosulfide and that of azoxybenzene by sodium disulfide are very slow. Foreign electrolytes show a small but obvious rate-promoting effect. Triethylamine has no effect on the rates.

As the water content in the solvent aqueous methanol increases, the rate becomes considerably faster (Fig. 2). This observation may be reasonable since this reaction involves water as a reactant



and enhanced solvent polarity may also be responsible.

The temperature effect obeys the Arrhenius equation (Fig. 3), from which the activation energy and frequency factor have been calculated to be $E = 16.35 \text{ kcal. mole}^{-1}$ and $A = 4.57 \times 10^8 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$, respectively.

Figure 4 represents the rates at various alkali concentrations in two media, 70 and 40 vol. % aqueous methanol, at 50°. In these runs sodium hydroxide was used, and in some cases it was replaced by potassium hydroxide. In both solvents the reaction shows first-order dependence on hydroxide ion concentration, and the rates of this reaction may be expressed as

$$-d(\text{C}_6\text{H}_5\text{NO}_2)/dt = (k' + k''(\text{OH}))(\text{C}_6\text{H}_5\text{NO}_2)(\text{Na}_2\text{S}_2)^2 \quad (3)$$

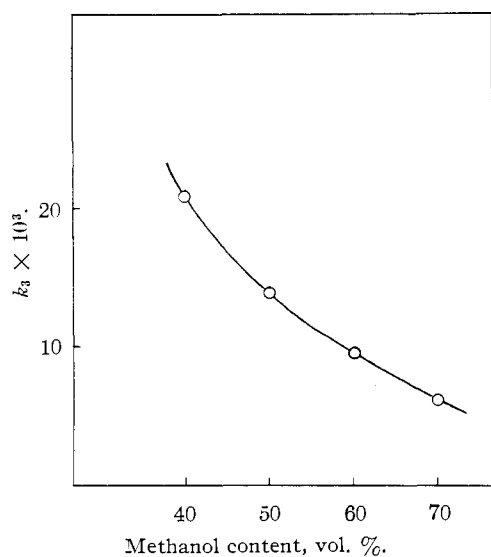


Fig. 2.— k_3 vs. methanol content of the solvent (aqueous methanol).

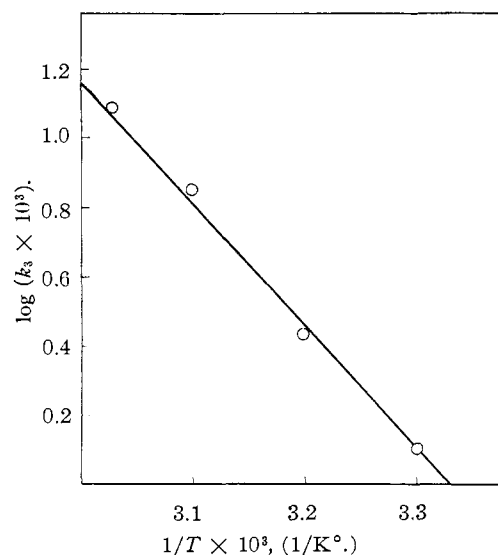


Fig. 3.—The temperature dependence of the third-order rate constant (in 70% methanol).

Using Fig. 4, constants k' and k'' can be calculated graphically as

$$\begin{aligned} \text{in 70\% methanol: } k' &= 6.06 \times 10^{-3} \text{ sec.}^{-1} M^{-2} \\ &k'' = 9.48 \times 10^{-2} \text{ sec.}^{-1} M^{-3} \quad (4) \\ \text{in 40\% methanol: } k' &= 17.5 \times 10^{-3} \text{ sec.}^{-1} M^{-2} \\ &k'' = 9.56 \times 10^{-2} \text{ sec.}^{-1} M^{-3} \end{aligned}$$

Table II lists the effect of substituents on the rate. The effect of substituents was unexpectedly large. Therefore these rates could not be measured under the same condition; rates of reduction of $p\text{-CH}_3\text{O}$, $p\text{-CH}_3$ and unsubstituted nitrobenzenes were measured in one condition, while those of $m\text{-COCH}_3$ and of unsubstituted nitrobenzenes were measured in another condition, and then these data were combined to obtain relative rates. As is seen in Fig. 5, these relative rates fit the Hammett equation well; electron-releasing substituents retard the reaction and electron-attracting substituents

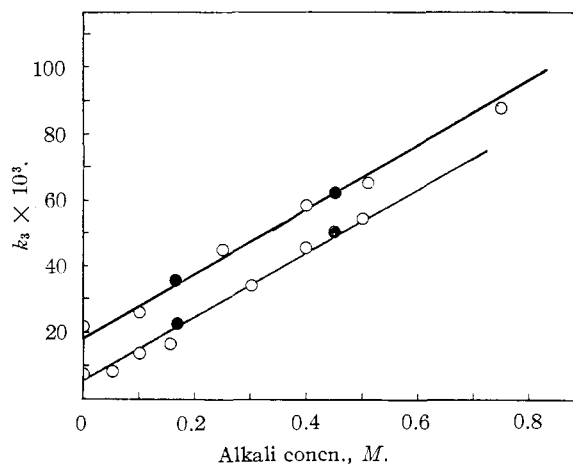


Fig. 4.— k_3 vs. alkali concentration: O, sodium hydroxide; ●, potassium hydroxide; upper curve in 40% MeOH; lower curve in 70% MeOH.

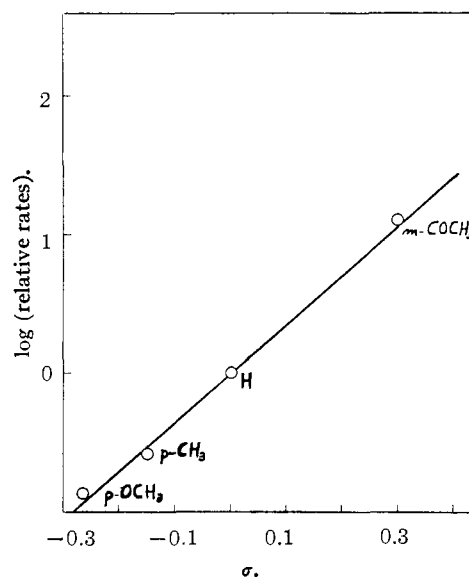


Fig. 5.—The effect of substituents in 70% methanol at 50°.

accelerate the reaction, the reaction constant ρ being a large positive value, +3.55.

TABLE II

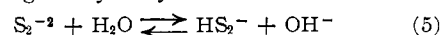
THE RATES OF THE REDUCTION OF SUBSTITUTED NITROBENZENE BY SODIUM DISULFIDE IN 70% AQUEOUS METHANOL AT 50°, $\rho = +3.55$

Substituents	Initial concentrations, M			$K_3 \times 10^3$, $\text{sec.}^{-1} M^{-2}$
	Na_2S_2	ArNO_2	NaOH	
$p\text{-OCH}_3$	0.1125	0.0163	0.500	7.17
$p\text{-CH}_3$.1125	.0182	.500	14.5
H	.1125	.0250	.500	53.3
$m\text{-COCH}_3$.075	.0152	.100	174
H	.075	.025	.100	13.6

Discussion

Our results may be explained.

Hydrolysis Constant of the Disulfide.—The disulfide undergoes hydrolysis as



How large might the hydrolysis constant K_h be?

The hydrolysis constant of sulfide ion, in aqueous solution, is approximately ten. Hydrogen peroxide is a somewhat stronger acid than water. Sulfide ion, by analogy, might be expected to act as a somewhat stronger base than disulfide ion so that for the latter a K_h value between 0.01 and ten might be estimated. Indeed, a comparison of known hydrolysis extent (in H_2O solution) of Na_2S (86%) and Na_2S_2 (65%) suggests a ratio of approximately four for the two K_h values; this would indicate, $K_h \approx 2$ for S_2^{-2} (in H_2O).

A rough estimate of K_h for the aqueous methanol media can be obtained by attributing the observed "OH⁻ ion catalysis" to an equilibrium shift in favor of disulfide ion (eq. 5). The rate constants in 40% methanol (eq. 4) predict the rate to be 2.41 times faster in the presence of 0.5 M added sodium hydroxide than in the presence of 0.1 M added sodium hydroxide. The assumption that the greater concentration of alkali (0.5 M vs. 0.1 M) increases the concentration of the kinetically effective species (disulfide ion) by a factor of 2.41 quickly leads to the result $K_h = 1.4$ for disulfide (in 40% methanol). This is, of course, well within the range predicted above.

The Effect of Alkali Added.—A rough quantitative analysis would suggest that the above assumption has some merit: for example, the initial concentrations of disulfide ion at hydrolytic equilibrium can be estimated with the K_h constant for solutions with different sodium hydroxide levels and these data can then be compared with the actual specific rates calculated from equation 3.

Added NaOH	In 40% MeOH, $(Na_2S_2)_0 = 0.1 M$	
	Ratio of initial S_2^{-2} concn. at hydrolyt. equil.	Ratio of obsd. rates (from eq. 3)
a, none		
b, 0.1 M		
c, 0.5 M	a/b/c/d = 0.59/1.0/2.4/4.3	
d, 1.0 M		a/b/c/d = 0.63/1.0/2.4/4.2

This coincidence seems promising, and this view has perhaps the further merit of correctly predicting a similar rate-promoting action for any other basic additive, such as sodium monosulfide (see Table I), which also leads to an increased equilibrium concentration of disulfide ion.

The Reaction Order with Respect to Disulfide.—Even though the reaction was presented above as being second order with respect to Na_2S_2 , the idea of substantial hydrolysis may alter the kinetic picture. The reduction might be first order with respect to disulfide ion provided its concentration is corrected for gradual shifts of the hydrolysis equilibrium as the reaction proceeds. A rough calculation gives support to this idea: this calculation applies to the concentration range of runs conducted in the presence of excess nitrobenzene (Table I). The first column of Table III indicates "determinate" concentrations of Na_2S_2 ; the second column lists the fractions of surviving Na_2S_2 as the run progresses; and the last column indicates the estimated equilibrium concentrations of the active species, S_2^{-2} ion, at each point using the value $K_h = 1.4$.

The last two columns show good coincidence. Since a linear relation is established already between the rate and the data in the third column

TABLE III
FIRST-ORDER DEPENDENCE ON DISULFIDE ION
Initial determinate concn., $(Na_2S_2)_0 = 0.10 M$; no NaOH added.

$(Na_2S_2)_i$ detd. concn., M	$(Na_2S_2)_e$ $(Na_2S_2)_0$	Column 2 squared	$(S_2^{-2})_e$ $(S_2^{-2})_0$
0.10	1.0	1.0	1.0
.050	0.50	0.25	0.26
.030	.30	.090	.091
.025	.25	.063	.066
.010	.10	.010	.011
.0075	.075	.0056	.0061
.0050	.050	.0025	.0028

(second-order dependence on (Na_2S_2)), a similarly linear relationship must exist between the rate and the data in the fourth column (first order with respect to disulfide ion). Now the equation 6 represents the experimental findings well, where $(S_2^{-2})_e$ denotes concentrations of disulfide ion at hydrolysis equilibrium.

$$\text{rate} = k_2(S_2^{-2})_e(C_6H_5NO_2) \quad (6)$$

If sufficient sodium hydroxide is added, the solution can be considered buffered with regard to hydroxide so that the fraction $(S_2^{-2})/(Na_2S_2)$ is constant and the determinate concentration of Na_2S_2 can hence be substituted directly into the equation 6. This is realized in the data of Table IV.

TABLE IV
SECOND-ORDER RATE CONSTANTS k_2 CALCULATED BY THE EQUATION RATE = $k_2(Na_2S_2)(C_6H_5NO_2)$ IN 40% AQUEOUS METHANOL AT 50°, $(NaOH) = 0.75 M$

Initial concentrations, M	Rate constants, $k_2 \times 10^4$ (sec. ⁻¹ M^{-1})	
Na_2S_2	$C_6H_5NO_2$	
0.075	0.025	6.91 ± 0.12
.113	.025	6.85 ± .09
.226	.025	6.72 ± .07
.339	.025	6.59 ± .13

The Effect of Additives.—The secondary salt effect, at greater ionic strength, must be expected to shift the hydrolysis equilibrium to the left, that is, in favor of the kinetically active species. This should result in rate increase and this is shown by the data (Table I). One would not expect a significant effect from the addition of triethylamine. This lacks the basic strength to push the pH above eleven or twelve so that catalytic action must then remain negligible.

The Effect of Substituents.—The above hypothesis would at once account for the large Hammett constant by visualizing an attack of S_2^{-2} ion on the positive nitrogen atom of nitrobenzene which must be particularly sensitive to substituent effects in view of the double negative charge of the reaction partner. The high Hammett's ρ value also accounts for the preparative use of this reagent for partial reduction of polynitrobenzenes.

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