[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS
III. THE REDUCTION OF AZO DYES

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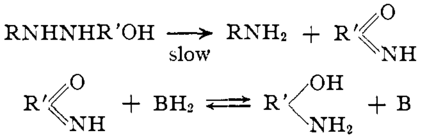
It has been shown[1] that in many instances the irreversible reduction of an organic compound may be formulated in electrochemical terms by determining the "apparent reduction potential" (A. R. P.). This has been defined as the normal potential of the reversible system that will just cause appreciable reduction (20–30% in 30 minutes) under the conditions specified. This method of investigating and formulating irreversible reduction processes can be employed only if the speed of the reduction is a function of the potential of the reagent employed. This point can be tested by examining the behavior of the compound in question with a series of graded reducing agents of known potential.

If the action of these reagents is a function of their potential the determination of an "apparent reduction potential" will be possible. The reduction of unsaturated 1,4 diketones and certain related substances, of many nitro compounds and azo dyes has been investigated in this way. In this paper we shall present some further experiments with certain hydroxy-azo dyes. These experiments confirm and amplify our general theory of irreversible reduction and in addition afford some quantitative information in regard to the relationship between structure and ease of reduction.

A relationship between the speed of reduction and the potential of the reagent is to be expected only if some reversible step controls the rate of the process.[2] The complete reduction of azo dyes according to the equation, $RN = NR'OH + 2BH_2$ (reducing agent) $\longrightarrow RNH_2 + R'(OH)NH_2 + 2B$ is irreversible, but as our preliminary work showed, the process can be formulated in terms of the potential of the reagent employed. The most probable mechanism to account for this is given below, in which Step *a* is reversible and rapid and Step *b* is irreversible and slow in comparison with Steps *a* and *c*. The reduction of the quinon-imine (Step *c*)

$$RN = NR'OH + BH_2 \rightleftharpoons RNHNHR'OH + B \qquad (a)$$



$$RNHNHR'OH \xrightarrow[\text{slow}]{} RNH_2 + R'\begin{smallmatrix} =O \\ =NH \end{smallmatrix} \qquad (b)$$

$$R'\begin{smallmatrix} =O \\ =NH \end{smallmatrix} + BH_2 \rightleftharpoons R'\begin{smallmatrix} -OH \\ -NH_2 \end{smallmatrix} + B \qquad (c)$$

would be expected to be very rapid and practically complete with the reducing agents necessary for the reduction of azo dyes; the question of

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[1] Conant and Lutz, THIS JOURNAL, **45**, 1047 (1923); **46**, 1254 (1924).

[2] Conant, *Chem. Rev.*, **3**, 1 (1926).

its reversibility is not involved in this discussion. It is evident that if this mechanism is correct the rate of the entire process will be controlled by that of the monomolecular reaction of Step *b*. The amount of hydrazo compound undergoing cleavage will be determined by the equilibrium in Step *a* and thus by the normal potential of the reducing agent. In support of this mechanism we shall present the following evidence: (1) Step (*a*) is probable because the change of certain azo to hydrazo compounds can be shown to be reversible and the oxidation-reduction potential may be measured; (2) even with the "mildest" reducing agents that can bring about reduction of azo dyes four hydrogen equivalents are involved—the reduction does not stop at the hydrazo stage; (3) the rate of the irreversible reduction of azo dyes is essentially independent of the total concentration of reactants; (4) the relative rates of reduction by two different reagents are in general agreement with the calculations based on the theory.

The Reversibility of the Azo-Hydrazo System

Since there was no information in regard to the reversibility of the azo-hydrazo system when this work was started, we investigated the potential of the azobenzenedisulfonate—hydrazobenzenedisulfonate[3] system and obtained satisfactory evidence of the reversibility. Biilmann's study of the potential of two different amino derivatives of azobenzene appeared when our work was nearly complete and afforded still more convincing evidence of the reversibility of the process of reducing azo compounds to hydrazo compounds. His results[4] were obained in dilute acid solution by the method of mixtures; because of the rearrangement of these particular hydrazo compounds, Biilmann extrapolated to zero time in order to determine the true potential.

Our results with the disulfonate were obtained by the method of mixtures, the solvent being 0.2 *N* aqueous hydrochloric acid and the total concentration of organic material 0.003 *M;* a saturated potassium chloride bridge connected the cell with a saturated calomel electrode of known potential. As the hydrazo compound in solution is very sensitive to oxidation by oxygen, it was added to the solution in an atmosphere of nitrogen and the usual precautions were observed for eliminating all traces of oxygen. Since hydrazobenzenedisulfonate does not rearrange in 0.2 *N* hydrochloric acid, the potentials were constant after equilibrium was once established. This process, however, required one-half to three hours and only platinized electrodes gave consistent results. The relative amounts of azo and hydrazo compounds were varied from 1:9 to 9:1. The observed potentials were converted to the hydrogen scale (the liquid-junction potential being

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[3] The potassium salts were employed; throughout this work sodium or potassium salts of the sulfonic acids mentioned were used.

[4] Biilmann and Blom, *J. Chem. Soc.*, **125,** 1719 (1924).

considered negligible) and the value of E'_0 (the normal potential in 0.2 *N* hydrochloric acid) calculated from Equation 1.[5] The values are summarized in Table I, and it is evident that the agreement is satisfactory and establishes the reversibility of the system: the average is +0.379. Since the *P*H value of 0.2 *N* hydrochloric acid is 0.76, the value of the normal potential at unit hydrogen-ion activity (*P*H = 0) is obviously +0.424. For comparison, Biilmann's values for the amino compounds are also given in Table II; since he measured the potential against the hydrogen electrode in the *same solvent*, his results are the equivalent of E'_0 at *P*H = 0.

$$E_h \text{ (obs.)} = E'_0 - 0.0295 \log ([\text{Hydrazo}]/[\text{azo}]) \qquad (1)$$

TABLE I

NORMAL POTENTIAL OF POTASSIUM AZOBENZENE-4,4'-DISULFONATE-POTASSIUM HYDRAZOBENZENE-4,4'-DISULFONATE IN 0.2 *N* HCl AT 25°

Ratio of azo to hydrazo compound	E.m.f. observed E_c (against calomel)	E_h (hydrogen scale)	E'_0 (Equation 1)
9.00	+0.170	+0.407	+0.379
4.00	+ .158	+ .395	+ .377
2.33	+ .152	+ .389	+ .378
1.50	+ .145	+ .382	+ .377
1.00	+ .142	+ .379	+ .379
0.666	+ .138	+ .375	+ .380
.429	+ .131	+ .368	+ .379
.250	+ .128	+ .365	+ .383
.111	+ .117	+ .364	+ .382
		Av.	+ .379

TABLE II

NORMAL POTENTIALS AT *P*H = 0° AND 25° OF CERTAIN REVERSIBLE AZO-HYDRAZO SYSTEMS

Name of azo component	Potential
Potassium azobenzene-4,4'-disulfonate	+0.424
3,3'-Diamino-4,4'-dimethyl-azobenzene	+ .3673
3,3'-Diamino-azobenzene	+ .4095

The Number of Equivalents Involved in the Reduction of Azo Dyes

The failure to stop the reduction of azo dyes at the hydrazo stage might be attributed to the fact that the usual reducing agents are too powerful. It was, therefore, of interest to determine the nature of the products formed when the mildest reducing agent was employed which would cause reduction. We have done this by titrating electrometrically a solution of the completely reduced reagent (for example, leuco indigo-disulfonate) with a solution of the dye. If the reaction under these conditions stopped at the hydrazo stage, the end-point would be reached when one mole of dye per mole of reagent had been added. As a matter of fact we found in every instance that only half of a molecular proportion was required to complete the re-

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[5] The European convention in regard to sign is used in this paper.

action. The equation is, therefore, $2BH_2 + RN = NROH \longrightarrow RNH_2 + R(NH_2)OH + 2B$. As a check on the method, azobenzene-monosulfonate- and -disulfonate also were used. With these substances the molar ratio of substance to reagent was 1:1, corresponding to the well-known reduction to stable hydrazo compounds, $C_6H_5N = NC_6H_4SO_3H + BH_2 \longrightarrow C_6H_5NHNHC_6H_4SO_3H + B$.

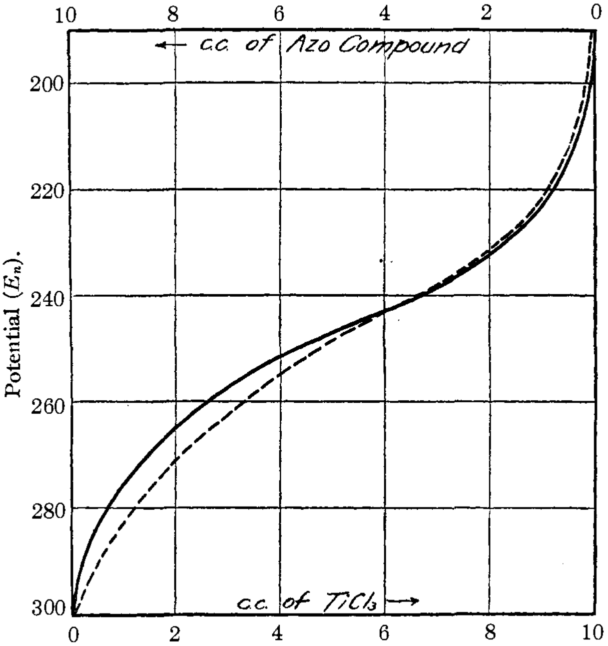


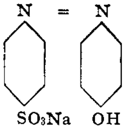
Fig. 1.—Titration of leuco indigo-sulfonate in 0.2 *N* HCl with an azo dye. The heavy line indicates the preparation of leuco compound by titration with $TiCl_3$; the dotted line represents course of titration with azo dye. The equivalent strengths of the azo solution and titanous chloride in this instance were equal.

The method is illustrated by the curves shown in Fig. 1. The heavy line shows the titration of the oxidized form of the reagent with titanous chloride; the dotted line indicates the back titration with the dye solution. The titrations were performed in the usual type of cell in the absence of air. The results are summarized in Table III. Since the end-point of the titration was not characterized by a sudden "jump" in potential, it was felt that the most accurate results would be obtained by reference to the mid-point of the titration curve rather than the end-point; this has been done as illustrated in the table. The ratio of azo compound to reagent given in Col. 7 was obtained by dividing one-half of the value given in Col. 3 by the amount of substance required for titration to the mid-point (Col. 6).

TABLE III

MOLES OF REDUCING AGENT INVOLVED IN THE REDUCTION OF HYDROXY-AZO DYES AND CERTAIN OTHER AZO COMPOUNDS

(All experiments were with 0. 2 N HCl as a solvent and at 23°)

(1) Azo Compound	(2) Reagent	(3) Reagent used, moles $\times 10^4$	(4) Azo cpd. in 100 cc. of soln., moles $\times 10^4$	(5) Azo solution to mid-point, cc.	(6) Azo cpd. to mid-point, moles $\times 10^4$	(7) Ratio of moles of azo cpd. to reducing agent
	leuco indigo-disulfonate	2.8	13	4.9	0.63	1:2.2
Same	Same	5.4	27	4.8	1.3	1:2.1
Same	leuco indigo-tetrasulfonate	2.6	15	4.7	0.70	1:1.85
Azobenzene-monosulfonate	leuco indigo-disulfonate	5.0	43	5.6	2.4	1:1.05
Azobenzene-disulfonate	Same	2.8	33	4.2	1.4	1:1

The Rate of the Irreversible Reduction of the Azo Dyes

(a) **The Effect of Dilution.**—The method of following the rate of the irreversible reduction was similar to that described in the previous papers. A weighed amount of the solid azo dye was added to a solution of an equimolecular mixture of the oxidized and reduced forms of the reagent contained in the usual type of cell in an atmosphere of nitrogen. The equimolecular mixture of oxidized and reduced reagent was prepared by titrating the oxidized form of the reagent to the "mid-point" of the titration curve with titanous chloride. The cell of about 100 cc. capacity was equipped with a mechanical stirrer, a bright platinum and platinized platinum electrode and suitable tubes for introducing nitrogen and the titrating solution from a buret; the solid dye was contained in a capsule suspended above the liquid in the cell and was dropped into the solution by turning a glass rod. A saturated potassium chloride bridge connected the cell with a saturated calomel electrode. Unless otherwise stated, all measurements were made at 23° ± 2°, and the solvent was 0.2 N hydrochloric acid ($P_H = 0.76$). The concentrations of the reduced and oxidized forms of the reagent were 0.0010–0.0012 M and an amount of azo dye was introduced such that its concentration was 0.0020–0.0025 M. The reagents were all of such a nature that each mole contained 2 reducing equivalents; as 4 equivalents are involved in the total irreversible reduction (see above), there was a 4 to 1 excess of azo dye at the start of each experiment.

It is obvious that the rate of change of potential of the cell after the introduction of the dye will be a function of the speed of the irreversible reduction of the azo compound. Since the potential of the cell (referred to the normal hydrogen electrode) is given by Equation 2, the potential at time t when the fraction S of the reduced form of the reagent has been oxidized will be given by Equation 3, since initially $E = E_0'$ and [reduced] = [oxidized].

$$E \text{ (potential of cell)} = E_0' - 0.030 \log ([\text{reduced}]/[\text{oxid.}]) \qquad (2)$$

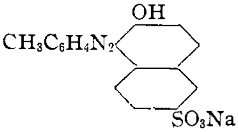
$$(E)_t = E_0' - 0.030 \log [(1-S)/(1+S)] \qquad (3)$$

The change of potential at a given time, $((E)_t - E_0')$, can thus readily be translated into the fraction of reduced reagent oxidized or the extent of the reaction at that time. (This calculation is conveniently done graphically from a curve constructed from Equation 3.)

If the irreversible reaction between the reducing agent (which we shall designate by BH_2) and the azo dye were di- or trimolecular we should expect that on diluting the solution the rate would decrease greatly (the *ratio* of BH_2 to dye being kept constant). As the results summarized in Table IV show, the rate of the process is only slightly affected by the total concentration and, indeed, in a few instances is slightly more rapid in the more dilute solution. These slight changes are undoubtedly connected with the slight changes with dilution in the value of the normal potential of the reagent (and possibly the reversible step). We have found a change from 0.001 to 0.0001 *M* solution with certain of the reagents to cause a change of several millivolts in the value of E_0'. Such effects are for our present purposes negligible; the rate of the irreversible reduction is essentially independent of dilution. We may conclude, therefore, *that some monomolecular reaction controls the rate of the entire process.* According to our hypothesis this monomolecular reaction is Step *b* of the mechanism outlined above.

Table IV

The Effect of Dilution on the Rate of Reduction of Certain Azo Dyes in 0.2 *N* HCl at 23° by Certain Reversible Systems

Dye	Reagent	Total molar concn. of dye	Fraction of reduced reagent oxidized (*S*) in		
			10 min.	15 min.	30 min.
Orange II	Leuco indigo-tetrasulfonate	0.02	...	0.38	0.62
		.002	...	.38	.70
	Leuco indigo-disulfonate	.002	0.94	.96	...
		.0002	.96	.98	...
Same	Leuco indigo-trisulfonate	.002	.32	.44	.66
		.0002	.55	.70	.85
Same	Leuco indigo-tetrasulfonate	.002	...	.20	.38
		.0002	...	.30	.45

The ratio of concentrations of oxidized and reduced forms of reagent and of dye in each experiment was 1:1:2.

(b) The Determination of Apparent Reduction Potential (A. R. P.).— In most of our experiments the potential of the electrodes was recorded

5, 15 and 30 minutes after the addition of the solid dye to the well-stirred mixture; the potentials of both electrodes were almost always within 1 millivolt of each other. Duplicate experiments with a number of different compounds showed that the change of potential with time was usually reproducible within a few millivolts. The fraction of reducing agent oxidized, S, may be calculated as explained above from the recorded change in potential, and thus the constant of the rate of the monomolecular reaction according to Equation 4 (t being in minutes).[6]

$$k = (1/t)\ 2.30 \log [1/(1-S)] \tag{4}$$

To illustrate the method a few typical results are given in Table V, but only the values of $k \times 10^2$ at 5, 15 and 30 minutes for each reagent employed with each dye are given in the complete summary (Table VI).

On the whole, the values of k calculated for the different time intervals are surprisingly consistent when one remembers that the reproducibility of the results is not greater than ±1 millivolt and a 20% reaction corresponds to only 5 mv. change. The probable significance of the decreasing values of k with time noted with many compounds will be discussed later. With certain compounds a difficulty was encountered in that after the addition of the solid dye there was an immediate change of potential of several millivolts corresponding to *oxidation* of the reagent. After this initial fall in potential, the potential then rose regularly, corresponding to the reduction. This effect was noticeable only with certain compounds and disappeared when the total concentration was diminished. It was not due to the introduction of a *solid* phase as it also occurred when a solution of the dye was added. We do not believe that this anomalous change in potential corresponded to a chemical reaction, but rather to some effect of the added component (dye) on the potential of the reagent (similar to a salt effect). To some extent this anomalous fall in potential makes the rates calculated for the 5-minute period uncertain.

TABLE V

ILLUSTRATING THE CALCULATION OF THE RATE OF THE REACTION FROM THE CHANGE IN POTENTIAL

Reagent: equimolar mixture of indigo-trisulfonate and leuco compound. Solvent: 0.2 N HCl. Temp., 23 ± 2°. Concn. of dye: 0.002 M. Concn. of reducing agent: oxidized form, 0.001 M; reduced form, 0.001 M.

Dye No. (See Table VI)	Rise in potential (mv.) 5 min.	15 min.	30 min.	Fraction of reagent oxidized (S) 5 min.	15 min.	30 min.	$k \times 10^2$ 5 min.	15 min.	30 min.
24	2	11	23	0.08	0.40	0.70	1.0	3.5	4.0
20	(−2)	17	33	...	.58	.85	...	6	6
18	7	24	37	.26	.73	.90	6	9	7
16	50	95	115	.95	>.99	>.99	65	?	?

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[6] Since the experimental errors in determining S are necessarily large, only approximate calculations were made by means of a convenient nomogram.

TABLE VI

DETERMINATION OF THE A. R. P. OF CERTAIN AZO DYES IN 0.2 *N* HCl AT 23 ± 2°

(Compounds arranged in order of decreasing A. R. P.)

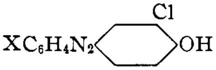
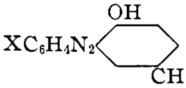
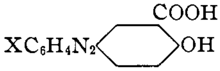
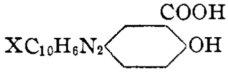
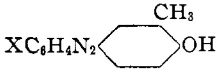
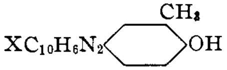
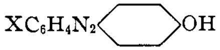
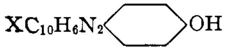
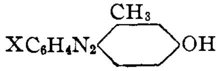
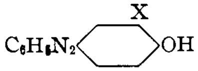
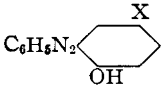
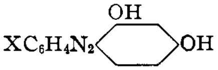
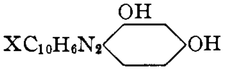
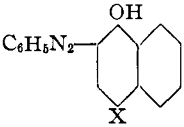
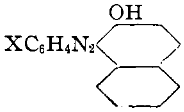
No.	Formula of Dye[a]	Reaction constant with Reagent B $(E_0') = +0.375$ $k \times 10^2$			Reaction constant with Reagent A $(E_0') = +0.425$ $k \times 10^2$			A. R. P. volts (H_2 electrode = 0)
		5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	
1		25	17	11	..	1.5	1.6	+0.435
2		11	8	11	..	0.8	1.5	+ .435
3		11	11	7	..	.6	1.0	+ .425
4		5	8	8	..	1.0	1.3	+ .425
5		30	21	..	..	1.0	1.0	+ .425
6		30	28	..	..	0.8	0.4	+ .415
7		16	13	11	..	1.0	.5	+ .415
8		12	10	7	..	..	.5	+ .415
9		12	10	7	..	...	<0.1	+ .410
10		7	5	4.5	..	...	< .1	+ .400
11		4.5	2.2	2.0	..	...	< .1	+ .390
12		3	2.5	1.8	..	...	< .1	+ .390
13		2	1.5	1.7	..	...	< .1	+ .385
		Reagent D $(E_0') = 0.293$			Reagent C $(E_0') = 0.325$			
14		>100 with Reagent E			12	9	7	+ .360
15		>100 with Reagent E			5	3	4	+ .345

TABLE VI (*Continued*)

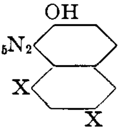
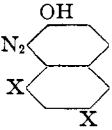
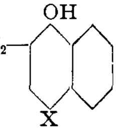
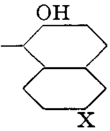
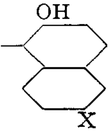
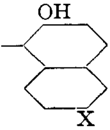
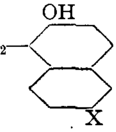
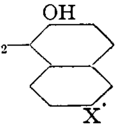
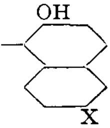
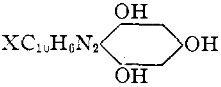
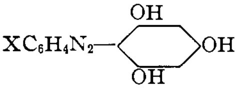
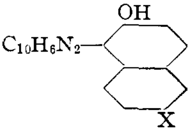
No.	Formula of Dye[a]	Reaction constant with Reagent D (E'_0) = 0.293			Reaction constant with Reagent C (E'_0) = 0.325			A. R. P. volts (H_2 electrode = 0)
		5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	
16	$C_6H_5N_2$ 	65	..	..	5	3.5	4	+0.345
17	$CH_3C_6H_4N_2$ 	>100 with Reagent E			3	4	4	+ .345
18	$CH_3C_6H_4N_2$ 	6	9	7	2	3	3	+ .345
19	$C_6H_5N_2$ 	2	7	7	..	3.5	2.5	0.340
20	$CH_3C_6H_4N_2$ 	..	6	6.5	3	2.5	1.8	.335
21	$XC_{10}H_6N_2$ 	40 and 28 with Reagent E			..	1.5	1.5	.335
22	$CH_3OC_6H_4N_2$ 	..	2.5	2.0	..	1.0	1.0	.325
23	$ClC_6H_4N_2$ 	..	2.5	3.5	..	0.8	0.9	.325
		Reagent E (E'_0) = 0.245			Reagent D (E'_0) = 0.293			
24	$(O)ClC_6H_4N_2$ 	62	..	..	..	3.5	4.0	.315

Table VI (*Concluded*)

No.	Formula of Dye[a]	Reaction constant with Reagent E (E_0') = 0.245			Reaction constant with Reagent D (E_0') = 0.293			A. R. P. volts (H_2 electrode = 0)
		5 min.	15 min.	30 min.	5 min.	15 min.	30 min.	
25		23	21	..	not tried			0.300
26		16	10	7	..	2.5	1.8	.305
27		10	7	7	not tried			.280

To save space the duplicate determinations made in many instances as well as the experiments with reagents where $k \times 10^2 > 100$ have been omitted as have also a number of experiments with reagents where $k \times 10^2 < 0.1$. The results of all these experiments were in perfect accord with the data given above. The following results with Reagent E were also obtained: No. 18, $k \times 10^2 = 65$; No. 19, $k \times 10^2 = 65$; No. 20, $k \times 10^2 = 30$; No. 21, $k \times 10^2 = 48$; No. 22, $k \times 10^2 = 50$; No. 23, $k \times 10^2 = 50$.

[a] The following abbreviations have been used in the table: X = SO_3Na; unless otherwise specified, the substituents in the benzene ring are *para* and in the naphthalene ring in the 4 position with respect to the azo linkage. The reagents employed were equimolar mixtures of the oxidized and reduced forms of the following substances: A, naphthoquinone; B, chloranilic acid; C, potassium indigo-tetrasulfonate; D, potassium indigo-trisulfonate; E, sodium indigo-disulfonate. In every case the concentrations were: leuco compound = oxidized compound =0.001 *M;* dye =0.002 *M* (calculated from the purity of the material as determined by titration; compare Table IX). The values for E_0' for the reagents employed were from the results published from this Laboratory and from those of Clark [*Pub. Health Reports,* **38**, 1669 (1923)].

Because of the experimental difficulties mentioned above, we have laid most weight on the values of k determined at the 15- and 30-minute periods, unless the reaction was so rapid that more than 95% had reacted at these times. In general we have not attempted to estimate the rate when the change in potential was more than 50 mv., which corresponds to about 95% reaction. Such large changes were noted only with reagents whose potentials were so far below the A. R. P. of the compound that a very rapid reaction was to have been expected.

It is convenient to define the apparent reduction potential as being the potential (E_0') of the reagent which under the specified condition will cause a 20–30% reduction in 30 minutes. This corresponds to a value of $k \times 10^2$ of 1. Such a critical reagent coincided with a reducing agent actually used in only a few instances. In all others the potential of this hypothetical reagent (and thus the A. R. P.) was calculated on the assumption that a change of potential of 40 mv. corresponded to a change of k of 10 fold;

that is, diff. pot. of reagents = 0.04 log k_1/k_2. This empirical approximation is discussed from a theoretical standpoint later. No attempt has been made to evaluate the A. R. P. more accurately than ±5 mv., and in some cases the error may be ±10 mv.

The Relative Rates of Reduction with Different Reagents

According to our hypothesis the rate of the entire irreversible reduction is controlled by the amount of hydrazo compound formed by the rapid reversible interaction of reagent and dye. From the usual electrochemical relationships we can write for this equilibrium Equation 5 (at 23°) where $(E_0')_{\text{azo}}$ is the normal potential of the hypothetical azo-hydrazo system and $(E_0')_{\text{B}}$ the normal potential of the reagent system BH_2 and B.

$$(E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log \left(\frac{[\text{hydrazo}]\ [\text{B}]}{[\text{azo}]\ [\text{BH}_2]} \right) \tag{5}$$

If we start with the following concentrations: $[\text{B}] = [\text{BH}_2] = C$ and $[\text{azo}] = 2C$ and let S be the fraction of BH_2 oxidized to B by the irreversible reduction that has taken place up to time t_1, we have the following resulting concentrations, noting that 2 moles of BH_2 per mole of azo compound are involved in the entire process: $[\text{B}] = C + CS$; $[\text{BH}_2] = C - CS$; $[\text{azo}] = 2C - 0.5\ CS$. For the equilibrium which then practically instantaneously adjusts at time t_1 we can write Equation 6a by substitution in Equation 5 and letting X be the fraction of BH_2 oxidized by virtue of *this* equilibrium and, therefore, $X(C-CS)$ the concentration of hydrazo compound formed in this instant of time by this equilibrium.

$$(E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log \frac{[X(C - CS)]\ [(C + CS) + X(C - CS)]}{[2C - 0.5CS - X(C - CS)]\ [(C - CS) - X(C - CS)]} \tag{6a}$$

$$\text{or} \quad (E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log \frac{X(1 - S)(1 + S + X - XS)}{(2 - 0.5S - X + XS)\ (1 - S - X + XS)} \tag{6b}$$

If X is less than 0.1 we can write an approximate equation (6c) without much error.

$$(E_0')_{\text{azo}} - (E_0')_{\text{B}} = 0.030 \log X + 0.030 \log \frac{(1 + S)}{(2 - 0.5S)} \tag{6c}$$

If we employ two different reagents of potential $(E_0')^1_{\text{B}}$ and $(E_0')^2_{\text{B}}$ and consider the value of X over the range where S is the *same* (for example, 0–50% reacted in both cases) we arrive at Equation 7.

$$(E_0')^2_{\text{B}} - (E_0')^1_{\text{B}} = 0.030 \log X_1 - 0.030 \log X_2 \tag{7}$$

Here X_1 and X_2 are the amounts of hydrazo compound formed by virtue of the reversible interaction of the reagents whose potentials are $(E_0')^1_{\text{B}}$ and $(E_0')^2_{\text{B}}$, respectively.

Since the concentration of hydrazo compound undergoing the *relatively slow* monomolecular change is $X(C-CS)$, we can write Equation 8 and, assuming X to be constant, Equation 9.

$$dc/dt = k'x(C - CS) \qquad (8)$$

$$k = k'X = (2.30/t) \log (1/(1 - S)) \qquad (9)$$

According to our theory the cleavage of the hydrazo compound controls the rate of the entire process; therefore, combining Equations 7 and 9 we have Equation 10. This relates the rates k_1 and k_2 with the potential $(E'_0)^1_B$ and $(E'_0)^2_B$ of the reagents employed.

$$\frac{(E'_0)^2_B - (E'_0)^1_B}{0.03} = \log \left(\frac{k_1}{k_2}\right) \qquad (10)$$

From the data previously presented (Table VI) the ratios of k_1 to k_2 can be calculated for several reagents. These values of k_1/k_2 must be regarded only as approximations because of the experimental difficulties referred to. In Table VII a summary of such calculations is given; the extreme values of k_1/k_2 and the average value are recorded for comparison with the ratio calculated from Equation 10. It is evident that they are in most instances considerably smaller than the theoretical values; indeed, the empirical equation Diff. in pot. = 0.04 log k_1/k_2 used in calculating the A. R. P. is a closer representation of our average results than Equation 10.

TABLE VII

RELATIVE RATES OF REDUCTION

Reagents	$(E'_0)^1_B - (E'_0)^2_B$, volts	Range of values of k_1/k_2 Calcd. (Eq. 10)	found from data given in Table VI
(A) Naphthoquinone (B) Chloranilic acid	0.050	46	6–56 Av. 20
(C) Indigo-tetrasulfonate (D) Indigo-trisulfonate	.032	11	2–12 Av. 4
(D) Indigo-trisulfonate (E) Indigo-disulfonate	.048	40	6–15 Av. 9

This can be partially explained by the fact that in most instances the values of k_1 and k_2 were determined over different ranges—10–30% for the weaker reducing agent, 60–90% for the stronger. Calculations from Equation (6c) show that the value of X is not strictly constant over the whole range (as assumed in Equations 7–10) but when 80% had reacted is about one-half the value when 10–20% has. It would, therefore, be fair in most cases to double the value of k_1/k_2 found; the agreement is then somewhat better. However, even with this correction it can be claimed only that the relative rates with two reagents is of the order of magnitude of that calculated on the basis of our theory. As a first approximation to a quantitative correlation between the potentials of the reagents and the rates, we consider this satisfactory.

The extent of the reversible step must be slight even with reagents that cause fairly rapid reduction ($k \times 10^2 = 25$) because not more than a millivolt immediate change of potential takes place when the dye is introduced into the reagent. This point was tested in a few experiments in which a solution of the dye was employed and the rate noted from the first 30 seconds. We can therefore state that X is less than 0.05 with such reagents as cause rapid reduction and is less than about 0.02 when $k \times 10^2 = 1$ and $(E_0')_B$ is the apparent reduction potential. How much smaller than this X may be, we have no way of estimating. From the apparent reduction potentials given in Table VI and the assumption that $X = 0.01$, with the critical reagent, we can calculate the potential of the reversible step $[(E_0')_{azo}]$ from Equation 6c, taking S as 0.2. For the simpler substances with two benzene rings (Nos. 1–8) this gives a value for $(E_0')_{azo}$ (taking the A. R. P. as +0.425) of +0.356 at P_H 0.76 or E_0^0 (normal hydrogen ion) = +0.401. A comparison with the values of the known azo-hydrazo system (Table II) shows that this is a very reasonable value. On the same basis from Equation 9, k', the constant for the decomposition of the hydrazo compound, would be about 1, which corresponds to a half life of about 40 seconds.

The experiments we have performed differ in one respect from the usual procedure for reducing an organic substance. To increase the accuracy of the method we have employed a considerable excess of the dye; ordinarily, one employs some excess of reducing agent. In two experiments we introduced such a quantity of dye into an equimolecular mixture of reduced and oxidized reagent that the following ratios of materials were initially present: oxid.reagent: red.reagent: dye: :1:1:0.33. Since 2 molecular proportions of reagent are required in the process, when the reduction of the dye is complete under these conditions 66% of the reducing agent would be oxidized. This corresponds to a potential change of 21 mv.; therefore, the observed change of potential divided by 21 gives the extent of the reaction at the time when the potential is recorded. From this the rate of the monomolecular reaction can be calculated as usual. With indigo-tetrasulfonate and compounds Nos. 18 and 16 (Table VI), the following values of k were obtained: No. 18, $k \times 10^2 = 1.3$; No. 16, $k \times 10^2 = 1.0$. These values are to be compared with average values of 2.7 and 4, respectively, obtained by the usual procedure involving excess of dye (Table VI). It is obvious that for practical purposes the A. R. P. determined by our usual method could be employed for predicting the action of an excess of a reagent without much error. An equation similar to 6c can be easily derived for this case, and it can be calculated that the reaction constant should be about one-fifth of that observed with the excess of dye. This calculated change ($^1/_5$) is of the same order of magnitude as the change we have found ($^1/_2$ to $^1/_4$).

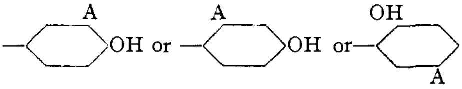
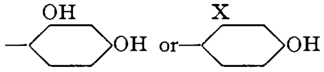
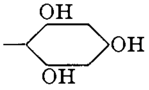
The Relation between Structure and A. R. P.

One definite generalization concerning the relation between structure and A. R. P. can be made on the basis of the data given in Table VI. *The structure of the aromatic nucleus carrying the hydroxyl group is the de-*

termining factor. Slight variations in A. R. P. are found with variation in the other aromatic nucleus (the one written on the left) but with a few exceptions these are not much greater than the experimental uncertainty (±5 mv.). Thus the following pairs of substances are similar in regard to the nucleus carrying the OH group but otherwise differ considerably, yet their respective A. R. P.s are within 10 mv. of each other: Nos. 3, 4; 5, 6; 7, 8; 12, 13; 16, 17; 20, 21; 25, 26. The greatest influence of substituents in the other nucleus is 25 mv. between compounds 19 and 24; this appears to be due to the introduction of a chlorine atom in the *ortho* position. The series, Nos. 19–24, show slight but probably definite changes that indicate an effect of substituents in this non-hydroxyl ring but this is clearly a second-order effect. The same predominant influence of the ring carrying the hydroxyl group is seen in the fact that the 27 compounds may be divided into the following groups *solely on the basis of the structure of this nucleus.*

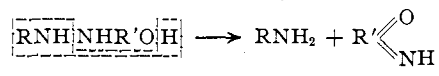
Table VIII

Relation of A. R. P. to Structure

Compounds falling in class	A. R. P.	Structure of nucleus carrying OH group
I Nos. 1–9	+0.435–0.410	 A *not* SO_3H or OH
II Nos. 10–13	+ .400– .385	 X = SO_3H
III Nos. 14–24	+ .360– .315	Naphthalene ring with or without SO_3H groups; coupled α or β
IV Nos. 25–26	+ .300– .305	

It is particularly striking that all the compounds having the hydroxyl group on a naphthalene ring fall in Class III, although all the other classes include compounds containing the sulfonated or unsulfonated naphthalene nucleus as the *other* aromatic group.

This rather surprising effect of the group R′ in the general formula RN = NR′OH finds a ready explanation in terms of our hypothesis. The decomposition of the hydrazo compound according to our view involves the elimination of a hydrogen atom from the hydroxyl group together with the group RNH– and therefore it would be expected that the nature of R′ would be very influential in determining the rate of this reaction (k',



$$\boxed{RNH\boxed{NHR'O}H} \longrightarrow RNH_2 + R'{\overset{\displaystyle \nearrow O}{\underset{\displaystyle \searrow NH}{}}}$$

Equations 8 and 9) and therefore, the A. R. P. According to this view, the *chief cause* of the difference between the compounds would be in the value of k.' Of course, the nature of *both* rings would be expected to change to some extent the potential of the reversible step, but this might well be of secondary importance in determining the final rate. It should be pointed out that if the hydroxyl (or amino) group is in the *meta* position the elimination reaction cannot proceed and such compounds (which we have not included in this study) yield relatively stable hydrazo compounds.

Some difficulty is encountered in applying our mechanism to the reduction with cleavage of azo compounds containing the group $-OR$ or $-NR_2$ in the *para* position. We have evidence that under certain conditions such compounds may be reduced to stable hydrazo compounds. We hope to deal in a later paper with this aspect of the problem as well as a further study of the effect of hydrogen-ion concentration, and temperature.

Experimental Part

Preparation and Analysis of Dyes.—The dyes were all prepared by the usual procedure of diazotization and coupling in aqueous solution. In most cases the coupling was accomplished by adding the diazonium salt solution to a solution of the naphthol or phenol in the equivalent amount of sodium hydroxide and one molecular proportion of sodium carbonate. Special procedures were used for regulating the alkalinity in the coupling of phloroglucinol with sulfanilic acid and in coupling with phenol. The dye was salted out with sodium chloride, separated by centrifuging, washed thrice with small amounts of water in the centrifuge cups and finally sucked as dry as possible on a Büchner funnel. Wherever possible, the compounds were further purified by recrystallization from 75% alcohol; this was done with the compounds marked in Table IX with (R). All the compounds were powdered, dried for three hours at 110° and kept in a vacuum desiccator over sulfuric acid.

Great pains were taken in the purification of all the intermediates used in the preparation of these dyes as it was felt that this would give the best assurance that the resulting dyes would be homogeneous. Where possible the intermediates were purified by fractional distillation at atmospheric pressure or at 20 mm. The sulfonated compounds were purified by repeated recrystallization or, in certain cases, through the special procedure recommended for the purpose (for example, *N* and *W* salt through the zinc salt).

As a result of all these precautions we felt confident that the dyes contained very little organic impurity; the presence of a certain amount of inorganic salt is practically unavoidable. The purity of each dye in terms of its oxidizing power was determined by titration in warm solution with titanous chloride in the usual manner, the disappearance of color being taken as the end-point. The titanous chloride was standardized against iron, and a sample of Orange II purified by repeated crystallization was found to be 99.7% pure on this basis. In calculating the results of these titrations it was assumed that the material that did not oxidize titanous chloride was inert inorganic salt and the only substance involved in the titration reaction was the dye in question.

The following table lists the dyes according to the number used to designate them in Table VI, the components used in preparing them and the purity as determined by titration. In calculating the amount of dye to be used in the experiments recorded in this paper, the values for the purity given in this table were employed; it was assumed that the rest of the material was inert inorganic salts.

TABLE IX

SHOWING THE MODE OF PREPARATION AND THE PURITY OF DYES

Compound No. (See Table VI)	Components (RNH$_2$ diazotized and coupled with ROH)	Purity as determined by TiCl$_3$, %
1	Sulfanilic acid + *o*-chlorophenol	(R) 98.0
2	Sulfanilic acid + *p*-cresol	(R) 95.3
3	Sulfanilic acid + salicylic acid	75.0
4	Naphthionic acid + salicylic acid	60.6
5	Sulfanilic acid + *o*-cresol	(R) 98.6
6	Naphthionic acid + *o*-cresol	(R) 88.8
7	Sulfanilic acid + phenol	(R) 99.5*
8	Naphthionic acid + phenol	(R) 92.4
9	Sulfanilic acid + *m*-cresol	(R) 97.2
10	Aniline + sodium-*o*-phenolsulfonate	82.4
11	Aniline + sodium-*p*-phenolsulfonate	86.4
12	Sulfanilic acid + resorcinol	(R) 99.6*
13	Naphthionic acid + resorcinol	78.3
14	Aniline + Nevile and Winther's salt	90.1
15	Sulfanilic acid + naphthol	(R) 99.7
16	Aniline + G salt	(R) 87.5
17	*p*-Toluidine + G salt	(R) 94.2
18	*p*-Toluidine + Nevile and Winther's salt	88.3
19	Aniline + Schaeffer's salt	95.0
20	*p*-Toluidine + Schaeffer's salt	90.2
21	Naphthionic acid + Schaeffer's salt	79.9
22	*p*-Anisidine + Schaeffer's salt	(R) 95.8
23	*p*-Chloro-aniline + Schaeffer's salt	73.8
24	*o*-Chloro-aniline + Schaeffer's salt	88.7
25	Naphthionic acid + phloroglucinol	96.5
26	Sulfanilic acid + phloroglucinol	83.0
27	α-Naphthylamine + Schaeffer's salt	79.2

The compounds which it was possible to purify further by recrystallization are indicated by the sign (R). The anhydrous dye obtained by drying at 110° for several hours was analyzed except in two cases indicated by an asterisk, where hydrated material was titrated, water of crystallization determined and the results were expressed in terms of anhydrous substances.

Summary

1. The oxidation-reduction potential of the system azobenzene-disulfonate–hydrazobenzene–disulfonate has been measured in 0.2 *N* hydrochloric acid. The system is strictly reversible and the usual electrochemical equations are applicable.
2. The rate of *irreversible* reduction of certain azo dyes has been found to be essentially independent of the dilution, indicating that the rate-controlling step is a monomolecular reaction.
3. The reduction of the type of azo dye studied (*ortho*- or *para*-hydroxy-azo compound) involves complete cleavage of the molecule even with very "mild" reducing agents. The potential of the reagent and *not* the specific nature of the reagent determines the speed of this irreversible reduction.
4. The apparent reduction potentials (A. R. P.) of 27 carefully prepared and purified hydroxy-azo dyes have been measured at 23° in 0.2 *N* hydrochloric acid. The nature of the aromatic nucleus carrying the hydroxyl group seems to be the most important factor in determining the A. R. P. No exception to the validity of the electrochemical formulation of *this type of irreversible reduction* has been found.
5. A mechanism has been suggested that is in accord with all the qualitative information available. Certain approximate equations based on this mechanism lead to values for the relative rates of reduction with two reagents that are of the same order of magnitude as those found experimentally.

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NOTE

Benzohydrylamine from Benzophenone Oxime.—This year, for at least the fourth time,[1] it was reported that benzophenone oxime may be reduced to benzohydrylamine by sodium and alcohol. The other three accounts in chronological order are given by Noyes,[2] by Konowalow[3] and by Jones and Hurd.[4]

Beilstein fails to mention the preparation of benzohydrylamine by this method. Undoubtedly, therefore, when it is again needed in an investigation, this method of preparation will again be "rediscovered" and reported in the literature. Quite independently about four years ago, the author learned of Professor Noyes' priority. When approached about it at that time, Dr. Noyes graciously waved aside the suggestion that the omission of reference to his article be rectified in a Note. It is now sub-

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[1] Billon, *Compt. rend.*, **182**, 470 (1926).

[2] Noyes, *Am. Chem. J.*, **15**, 545 (1893).

[3] Konowalow, *Chem. Zentr.*, **72**, 1002 (1901).

[4] Jones and Hurd, THIS JOURNAL, **43**, 2438 (1921).