most of the ΔH^0 values for the heavy rare earths. The inference is that the "gadolinium break" is not primarily due to ligand-field stabilization.

It has also been suggested that the stability of the rare-earth–EDTA chelates can be explained by a change in the number of coördination positions occupied by the EDTA due to increased steric hindrance as the radii of the rare-earth ions decrease across the series.[1,5] Betts and Dahlinger[5] have interpreted their values for the entropy of chelation with EDTA as showing a change from penta-coördination to tetra-coördination. They expressed ΔS^0 in terms of the relative partial molal entropies of the ions involved. The quantity

$$\Delta S^0 = \bar{S}^0{}_{RY^-} - \bar{S}^0{}_{R^{3+}} - \bar{S}^0{}_{Y^{4-}} \qquad (6)$$

$(\Delta S^0 + \bar{S}^0{}_{R}3+)$ then provides a measure of $\bar{S}^0{}_{RY^-}$, since $\bar{S}^0{}_{Y}4-$ is a common factor. On this basis the rare-earth chelates divided into two subgroups (La to Gd and Tb to Lu) which differed from each other by more than 6 e.u. Our results show approximately the same thing. Rather than interpret this phenomenon in terms of a change from penta-coördination to tetra-coördination, we would only suggest that ΔS^0, like ΔH^0, indicates that the rare-earth chelates of EDTA fall into two series. There is, in fact, substantial evidence opposed to any abrupt change in the number of points of attachment of the chelate. Schwarzenbach and Gut[12] have pointed out that both the EDTA and the nitrilotriacetate (NTA) stability constants of the rare earths divide into two series around gadolinium. Since NTA has only four coördinating groups, it seems unlikely that the discontinuity at gadolinium is due to a change in the number of points of attachment of the chelate. Kolat and Powell's data for the acid dissociation constants of rare-earth–EDTA chelates indicate no change in the number of coördinated positions occupied by the ligand.[13]

Staveley and Randall[4] have pointed out from a study of molecular models that it is possible to arrange all six coördinating groups of EDTA around a relatively large central metal ion and still have room for the close approach of at least one water molecule. Finally, we would like to cite that recent determinations of the formation constants of simple rare-earth complexes with ligands such as acetate[14,15] and thioglycolate[15] show the same trends that are apparent in our ΔH^0 values. The constants fall into two groups with the heavy-rare-earth constants actually smaller than those for the light-rare-earths. Since the entropy terms are usually small for the formation of simple complexes, this suggests a basic trend in ΔH^0 for the rare-earth series, independent of the complexing or chelating ligand. This basic trend would be obscured in the stability constants of extremely stable chelates due to the large entropy terms involved. Such a basic trend or "natural order" has been found for the bivalent transition-metal complexes.[16]

In summary, ΔH^0 and ΔS^0 data for the formation of rare-earth-EDTA species show two series within the rare-earth series. The exact reasons for the existence of two series are not clear, but evidence indicates that the phenomenon is general for rare-earth complexes rather than being a unique occurrence in the case of EDTA-like ligands and explainable by an abrupt change in the number of points of attachment of the ligand to the central metal ions. Accurate calorimetric data are needed for other complexes and chelates of the rare earths in order to either substantiate or refute our present theories.

Acknowledgments.—The authors would like to express their gratitude to D. J. Houser for his help in the calculations used in this report.

[12] G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **39**, 1589 (1956).

[13] R. S. Kolat and J. E. Powell, *Inorg. Chem.*, **1**, 293 (1962).

[14] A. Sonesson, *Acta Chem. Scand.*, **12**, 165 (1958).

[15] J. E. Powell and R. S. Kolat, AEC Report No. IS-350.

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[CONTRIBUTION NO. 2237 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK]

Kinetics of Reaction of Nucleophilic Reagents with Naphthoquinone Imine Dyes in Alkaline Solution

BY R. L. REEVES AND L. K. J. TONG

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The kinetics of the reaction of two indoaniline dyes with OH^-, $SO_3^=$, and CN^- are in agreement with the general scheme

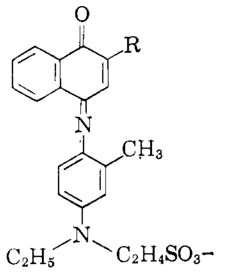
$$X + B^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z \xrightarrow{k_3} P_1 \qquad X + B^- \xrightarrow{k_4} P_2$$

where X = dye, B^- = a nucleophile, Z = a complex and the P's represent the products of irreversible reactions. The reaction with OH^- shows all the features of this general scheme, the reaction with $SO_3^=$ does not proceed beyond complex formation, *i.e.*, $k_3 = k_4 = 0$, and the reaction with CN^- leads to products without measurable presence of the complex at any stage of the reaction. Equilibrium constants and rate constants have been evaluated.

Introduction

The instability of indoaniline dyes has led us to investigate some of the reactions leading to their decomposition. Little has been reported on the chemistry of these reactions. In the following we call dye "bleaching" the decolorization arising from dark reactions and reserve the term "fading" for photochemical reactions. The present study involves a kinetic investigation of the bleaching of two naphthoquinone imine dyes in aqueous alkaline solution by reactions other than direct reduction. Studies[1] on the bleaching of triphenylmethane dyes by OH^- and by amine bases[2] provide little information for our dye system. The only investigation of quinone imine dyes reported is one in which certain indoaniline dyes were hydrolyzed in alkaline solution to indophenols.[3] These reactions are conversions from one dye to another and not the destruction of the chromophoric system.

The relatively high susceptibility of Dyes I and II to attack by the reagents studied led us to select them as model dyes so that we could achieve rapid reactions with convenient concentrations of reagents. It is thought that the principles established from the study of the models will be applicable to other naphthoquinone imine dyes.



I, R = $CONHC_2H_4SO_3^-$
II, R = $COCH_3$

In preliminary studies we found that anions such as hydroxide, sulfite and cyanide; nitrogen bases such as primary and secondary amines, ammonia, hydrazine and hydroxylamine; and thiophenols were effective bleaching agents. These reagents are all nucleophiles.

Kinetic Treatment.—The kinetics for the bleaching of the dyes follow the general scheme

$$X + B^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z \xrightarrow{k_3} P_1 \qquad (1)$$

$$X + B^- \xrightarrow{k_4} P_2 \qquad (2)$$

where X represents dye, B^- a nucleophilic reagent, Z a complex and P_1 and P_2 the product(s) of irreversible reaction(s) but not necessarily the final product(s). Depending on the nature of B^- and the particular dye, the values of k_2, k_3 or k_4 will vary, and their relative magnitudes will determine the characteristics of the bleaching reaction. It should be pointed out that either reaction 3 or reaction 4, or both, may be omitted from the scheme without destroying its adequacy to describe the bleaching of the dye. Since we do not know *a priori* whether reaction 3 or reaction 4, or both, are the irreversible reactions involved, making the assumption that either one is zero would seem arbitrary. The relative magnitudes of k_3 and k_4 could be determined, however, if we could follow either the concentration of Z or that of P_1 or P_2.

The differential equations for the scheme can be written as

$$\mathrm{d}x/\mathrm{d}t - k_2 z + (k_1 + k_4)[B^-]x = 0 \qquad (3)$$

$$\mathrm{d}z/\mathrm{d}t + (k_2 + k_3)z - k_1[B^-]x = 0 \qquad (4)$$

where x and z represent the concentrations of X and Z. For convenience, we let

$$a = k_2,\ b = k_1[B^-],\ \alpha = k_3/k_2, \text{ and } \beta = k_4/k_1$$

The solution to equations 3 and 4 is

$$x = A_1 e^{-(w+v)t} + A_2 e^{-(w-v)t} \qquad (5)$$

and

$$z = \frac{A_1}{a}[b(1+\beta) - (w+v)]e^{-(w+v)t} + \frac{A_2}{a}[b(1+\beta) - (w-v)]e^{-(w-v)t} \qquad (6)$$

where

$$w = \frac{a(1+\alpha) + b(1+\beta)}{2} \text{ and } v = \sqrt{w^2 - ab[(1+\alpha)(1+\beta) - 1]}$$

Equation 5 was fitted to the data by one of the methods described to obtain the empirical constants A_1, A_2, w and v.

The functions of the rate constants are then calculated by the equations

$$k_2 + k_3 = w - [(A_1 - A_2)/(A_1 + A_2)]v \qquad (7)$$

$$(k_1 + k_4)[B^-] = w + [(A_1 - A_2)/(A_1 + A_2)]v \qquad (8)$$

$$(1 + k_3/k_2)(1 + k_4/k_1) = \frac{w^2 - [(A_1 - A_2)/(A_1 + A_2)]^2 v^2}{v^2[1 - \{(A_1 - A_2)/(A_1 + A_2)\}^2]} \qquad (9)$$

The four rate constants cannot be determined independently by these equations; however, from them we can obtain the nucleophile-independent rates, the nucleophile-dependent rate and a measure of the partitioning of *X* and *Z*, respectively. Clearly, if either k_3 or k_4 is known, or is arbitrarily made zero, the other rate constants can be determined.

In the analysis of the data, the log of the difference of optical densities, log $(D_t - D_\infty)$, was plotted *vs.* time (for the first-order rates). If the plot did not have constant slope but appeared to be a pair of broken straight lines, with the slope of the first being greater than that of the second, an approximate value of the latter and the extrapolated intercept were obtained from the plot and used to estimate the constants in the second term of the right-hand side of equation 5. The first term $A_1 e^{-(w+v)}$ was then obtained approximately from the initial portion of the curve after subtraction of the second portion. This result was then used, in turn, to correct the second term, etc. By repeated operations, both terms can be separated, provided v/w is not too small. When the two exponential terms were nearly alike, the curves were fitted by non-linear regression by means of an IBM 705 digital computer.

Results

Reaction with Hydroxide Ion.—The kinetics of bleaching of Dye II follow equations 1 and 2 in the pH range of 10–11. Plots of ln optical density *vs.* time are shown for four pH's in Fig. 1. The extent of the initial fast reaction increases with

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[1] (a) E. S. Amis and S. E. Cook, *J. Am. Chem. Soc.*, **63**, 2621 (1944). (b) E. S. Amis and R. T. Overman, *ibid.*, **66**, 941 (1944).

[2] R. Cernatescu and M. P. Poni, *Bull. sect. sci. acad. roumaine*, **24**, 132 (1941).

[3] S. Hünig and W. Daum, *Ann.*, **595**, 131 (1955).

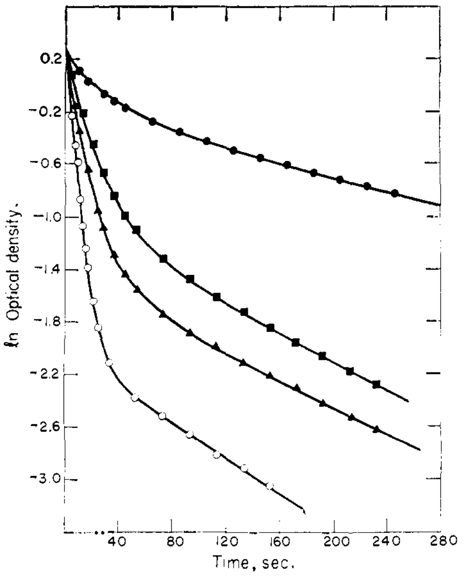

Fig. 1.—Rates of reaction of Dye II with hydroxide ion at 25°: ●, pH 10.16; ■, pH 10.69; ▲, pH 10.86; ○, pH 11.18.

[OH$^-$]. A comparison of the total rate of bleaching at pH 11.18 with a rate obtained by carrying out the reaction at pH 11.18 but measuring optical density after first lowering the pH to neutrality showed a large difference (Fig. 2). This difference indicates that large quantities of dye can be regenerated by quenching (removal of OH$^-$) during the initial rapid stages of the bleaching. The initial reaction appears to be due in part to the reversible formation of a complex that has little absorption in the region of dye absorption. That the bleaching is also accompanied by an irreversible reaction is indicated by the fact that not all the dye is regenerated on lowering the pH. Equation 5 was fitted to the optical density–time data for total bleaching by adjustment of the four parameters, as described, until the reconstituted densities agreed with the experimental values to within about 0.003 density unit throughout 90% reaction. The fact that such excellent fits are obtained shows that no reactions other than those given by equations 1 and 2 are important.

The bleaching of Dye I shows the same kinetic behavior as Dye II at [OH$^-$] greater than 0.01 *M*. At lower [OH$^-$], the initial rapid bleaching is not observed and the disappearance of I follows first-order kinetics in phosphate buffers for about 50% reaction. Beyond this point, the first-order rate constants increase with time. This increased rate of bleaching is consistent with a reduction of dye to leuco dye[4] superimposed upon the hydrolytic bleaching. The reduction is brought about by one of the products. No leuco dye could be detected during the early stages of bleaching where the first-order plots are linear. First-order rate constants determined from the initial portions of these plots increased linearly with [OH$^-$], so that $k_{\text{obsd.}} = 0.59 \pm 0.06$ [OH$^-$].[5] Therefore, in the *p*H region where the concentration of complex is immeasurably low, $k_{\text{obsd.}} = k_4[\text{OH}^-]$, if the parallel mechanism is assumed ($k_3 = 0$), and $k_{\text{obsd.}} = \frac{k_1k_3}{k_2 + k_3}[\text{OH}^-]$ if the consecutive mechanism is assumed ($k_4 = 0$). The second relationship follows from the steady-state approximation, since at *p*H 11, k_3 and $k_2 >> k_1[\text{OH}^-]$. On using either assumption and evaluating the rate constants from data obtained in highly alkaline solution by means of equation 5, a value for $k_{\text{obsd.}} = 0.64$ [OH$^-$] is obtained, which gives acceptable agreement with the measured value.

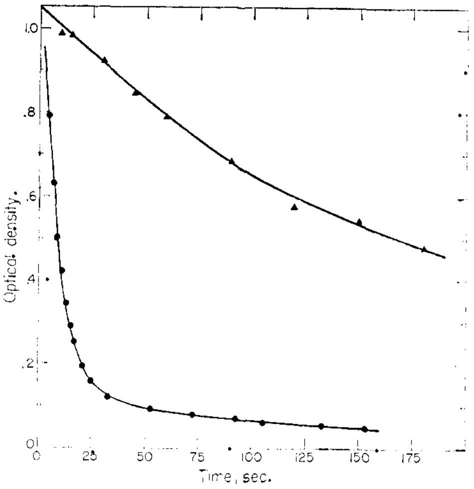

Fig. 2.—Reaction of Dye II with OH$^-$ at pH 11.18, with and without quenching: ●, density at time *t*, read without acidification; ▲, density at time *t*, read after acidification to pH 7.

The composite kinetic constants shown on the left of equations 7, 8 and 9, are summarized in Table I. The composite constants are experimentally constant.

Table I

Composite Rate Constants for the Bleaching of Dyes I and II with OH$^-$

Dye	pH	$k_2 + k_3$	$k_1 + k_4$	$\frac{(1 + k_3/k_2)}{(1 + k_4/k_1)}$
II	10.16	0.0227	81.7	1.47
II	10.69	.0202	83.3	1.63
II	10.86	.0182	80.6	1.55
II	11.18	.0191	82.3	1.66
	Mean	.0200	82.0	1.58
I	12.00	.271	1.9	1.50

The choice between the consecutive mechanism ($k_4 = 0$) and the parallel mechanism ($k_3 = 0$) cannot be made from the kinetics of dye disappearance alone. It seems reasonable to assume that either of the mechanisms, but not both, are operative. If the concentration of either the complex (Z) or the first product of irreversible reaction (P_1 or P_2) could be followed as a function of time, the two mechanisms could be distinguished. The concentration–time relationships for Dye II, complex Z, and P were calculated for pH 12.00, using the constants in Table I, and are shown in Fig. 3 for the

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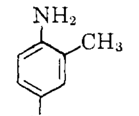
[4] Throughout this paper, a leuco dye will be strictly defined as a reduced dye differing from the parent dye only by two hydrogen atoms.

[5] All confidence limits are for 95% probability.

two mechanisms, it being assumed that $k_4 = 0$ and $k_3 = 0$, respectively. At this pH the dye is essentially completely bleached after 5 seconds. By the consecutive mechanism ($k_4 = 0$), all the bleached dye is converted to Z within 5 seconds and practically no P is present. Since P must form from Z, the accumulation of P will show a slight induction period. In the case of the parallel mechanism ($k_3 = 0$), Z and P are both formed rapidly and simultaneously, so that, after 5 seconds, the concentration of P will be approximately a third that of the original dye and will then continue to build up at a slower rate. Thus, a method that measures Z or P directly without drastically disturbing the equilibrium should permit the determination of their rate curves and differentiate the two possible mechanisms.

Product studies showed that one of the final stable products arising from attack of OH^- on the dyes is the *p*-phenylenediamine III. In the hope that III might correspond to P in the kinetic scheme, the rate of its formation was determined at pH 12.0 by oxidative coupling to form a stable blue indoaniline dye. The results are shown in Fig. 3 by the circles. As explained in the Experimental section, these values are probably high. The observed rate of formation of III does not correspond to the rate curves for P for either mechanism. It must be concluded that III probably arises from further reaction of the first product of the irreversible reaction. A choice between the two mechanisms must await a new analytical method which will measure Z directly and will not involve reversal to dye. The difference between the rate curves for the quenched and unquenched reaction (Fig. 2) cannot be used as a measure of the concentration of Z because, by equation 1, Z does not return quantitatively to dye upon acidification but partitions itself between dye and P_1, according to the magnitudes of k_2 and k_3. Although different amounts of Z will be formed by the two mechanisms, it can be shown that, according to this scheme, exactly the same amount of dye is regenerated on acidification, regardless of whether the parallel ($k_3 = 0$) or consecutive ($k_4 = 0$) mechanism is chosen.



Reaction with Sulfite Ion.—The reaction of both dyes with this nucleophile was very rapid and completely reversible. No reduction to leuco dye was observed. This corresponds to the limiting case in the general reaction scheme where $k_3 = k_4 = 0$. The absorption spectra of the complexes were quite characteristic and showed no changes on standing, provided the $[OH^-]$ was not too high. Much, but not all, of the dye could be recovered by complexing the free sulfite with a large excess of formaldehyde. As will be shown, the dye–sulfite complexes are very stable in solution, and failure to achieve complete recovery of dye with formaldehyde is due to the relative stabilities of the dye–sulfite and formaldehyde–sulfite complexes.

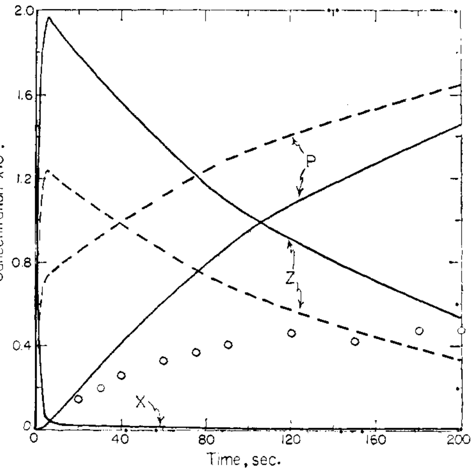


Fig. 3.—Comparison of the calculated curves for Z and P with the observed formation of III. Solid line-consecutive mechanism ($k_4 = 0$); dashed line-parallel mechanism ($k_2 = 0$); O, concn. of III.

When the concentration of Dye I and sulfite are equal ($2\text{–}5 \times 10^{-4}$ *M*), a significant concentration of dye is present at equilibrium. It is thus possible to determine K_f, the formation constant, directly from the loss of dye upon addition of sulfite and the use of the mass action relationship

$$K_f = \frac{[I]_s - [I]_e}{[I]_e\{[SO_3^=]_s - ([I]_s - [I]_e)\}} \qquad (10)$$

where the subscripts refer to the stoichiometric and equilibrium concentrations, respectively. In this way, a value of $4.8 \pm 0.5 \times 10^4$ is obtained for K_f for Dye I. In addition, K_f may also be determined by the kinetic method described below.

The rate of formation of the Dye I–sulfite complex (eq. 13) has been measured by a steady-state flow method (see Experimental). It was found that the rate is independent of *p*H in the range of 8.4–11, and is first-order in $[SO_3^=]$ and in [dye]. The results are summarized in Table II.

The rate of formation of complex with Dye II was too rapid to measure, even by a flow method. Furthermore, there was evidence that complex formation was essentially complete, even at concentrations $[II]_s = [SO_3^=]_s = 2.00 \times 10^{-4}$ *M*. The following scheme was therefore used to determine K_f kinetically

$$X + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} X\cdot OH^- \xrightarrow{k_3} P_1 \qquad (11)$$

$$X + OH^- \xrightarrow{k_4} P_2 \qquad (12)$$

$$X + SO_3^= \underset{k_6}{\overset{k_5}{\rightleftarrows}} X\cdot SO_3^= \qquad (13)$$

$$X + SO_3^= \xrightarrow{k_7} P_3 \qquad (14)$$

where X, $X\cdot OH^-$ and $X\cdot SO_3^=$ represent the dye, hydroxide complex and sulfite complex, respectively. The possibility of an irreversible reaction of $X + SO_3^=$ (eq. 14) is introduced to make the

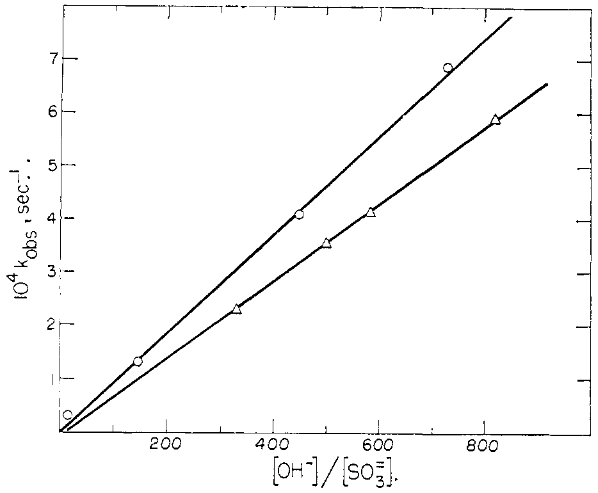


Fig. 4.—The rate of disappearance of the Dye II–sulfite complex as a function of $[OH^-]/[SO_3^=]$. ○, ionic strength = 0.09 *M*; △, ionic strength = 0.4 *M*.

scheme general. We make the further assumption that $k_5 >> k_6 >> k_1$, as suggested by qualitative evidence that the equilibrium constant (15) is large and equilibrium is rapidly established.

$$K_f = \frac{k_5}{k_6} = \frac{[X \cdot SO_3^=]}{[X][SO_3^=]} \qquad (15)$$

Since it has been shown that the reaction with OH^- can be described equally well by setting either k_3 or k_4 equal to zero, we make the simplification that $k_3 = 0$. The above scheme (eq. 11–14) and assumptions lead to low concentrations of X and $X \cdot OH^-$ so that Reactions 1 and 2 (eqs. 11) can be ignored. We have, therefore, approximately

$$\frac{d([X \cdot SO_3^=] + [X])}{dt} = \frac{d[X \cdot SO_3^=]}{dt} = -(k_4[OH^-] + k_7[SO_3^=])[X] \qquad (16)$$

$$= -\frac{(k_4[OH^-] + k_7[SO_3^=])[X \cdot SO_3^=]}{K_f[SO_3^=]} \qquad (17)$$

$$k_{obsd.} = \frac{-d \ln [X \cdot SO_3^=]}{dt} = \frac{k_4[OH^-]}{K_f[SO_3^=]} + \frac{k_7}{K_f} \qquad (18)$$

For the reaction of Dye II with OH^-, $k_4 = 29.5$ when k_3 is assumed to be zero. The rate of disappearance of $X \cdot SO_3^=$ in highly alkaline solutions was followed spectrophotometrically at 322 mμ, and linear Guggenheim plots[6] were obtained. Plots of k_{obsd} *vs.* $[OH^-]/[SO_3^=]$ from runs where the ratio $[OH^-]/[SO_3^=]$ was varied were linear (Fig. 4) and passed through the origin. Thus k_7 is zero. From the slopes of such plots the value of K_f can be computed (eq. 18) and was found to be 3.2×10^7 for $\mu = 0.09$ *M*. Application of the kinetic treatment to Dye I gave $K_f = 4.7 \times 10^4$ compared to $4.8 \pm 0.5 \times 10^4$ by direct measurement.

Reaction with Cyanide Ion.—No significant reversal of the bleaching with CN^- could be accomplished by removal of CN^- either by cyanohydrin formation with formaldehyde or by precipitation with Ag^+. This corresponds to the limiting case in the general scheme where k_1, k_2 and k_3 are zero. Treatment of bleached solutions of Dye I with persulfate restored some dye, but with a different hue (visual) from that of the starting dye. The rate of appearance of the new dye was quite discernible in contrast to the rate of oxidation of the leuco dye of I, which is immediate. This slower rate of oxidation and the change in hue suggest that if the product of CN^- bleaching is a leuco dye, it is not the leuco dye of I but a CN^--substituted leuco dye.

Table II

Rates of Formation of Dye (I)–Sulfite Complex

$[I]_s = 2.00 \times 10^{-4}$ *M*

pH	$[SO_3^=]_s$ (*M*)	$k_{obsd.}/[SO_3^=]$ (l. mole^{-1} sec.$^{-1}$)
8.38	0.0200	4.6×10^3
8.4	.0100	4.5×10^3
8.75	.0100	4.7×10^3
10.94	.0100	4.9×10^3

The bleaching of Dye I by excess CN^- closely follows pseudo first-order kinetics throughout the entire reaction. The absorption curves show an isosbestic point in the visual region during most of the bleaching. After bleaching is complete, the curve continues to change slowly in the ultraviolet region, however, and a new isosbestic point appears. Apparently, a slow reaction follows the bleaching, but it is not fast enough to affect the kinetics of bleaching. The kinetic results for I are summarized in Table III. The second-order rate constants were calculated from the observed pseudo first-order constants and the known CN^- concentrations. The latter were computed from the total CN^- added ($[CN^-]_s$), the *p*H and the pK_a for HCN which was taken to be 9.14. In all the runs, the ratio $[CN^-]/[OH^-]$ was sufficiently high to avoid competitive reaction with OH^-. The experimental constancy of the calculated second-order constants confirms the assumption that the reactive species is CN^- and not HCN.

The bleaching of Dye II by CN^- was complicated by competitive attack by OH^- in the concentration region where convenient rate measurements could be made. Since the bleaching by OH^- does not follow first-order kinetics, neither does the total bleaching by both reagents. In this situation, dye disappears by equations 1 and 2 plus an additional one for the competing nucleophile. The

$$X + CN^- \xrightarrow{k_8} P_4 \qquad (19)$$

solution of the differential equations is still given by Equation 5, but now the nucleophile-dependent term (eq. 8) is $(k_1 + k_4)[OH^-] + k_8[CN^-]$, from which k_8 is readily calculated, since $(k_1 + k_4)$ has previously been determined in the absence of CN^-. The second-order rate constants determined by fitting the rate curves to (5) are given in Table IV.

The results describe adequately the kinetic pattern for bleaching of Dyes I and II in dilute solution by nucleophilic reagents. The formulation of complete mechanisms for the reactions involved must await further studies of reaction products and their interactions. The *p*-phenylenediamine III, the leuco dyes IVa and IVb, and the 3-hydroxyl-1,4-naphthoquinone V have been isolated

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(6) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

TABLE III

RATES OF REACTION OF DYE I WITH CYANIDE AT 25°; ADDED $[CN^-]_s = 0.00445\ M$, $\mu = 0.09\ M$

pH	7.65	8.17	8.64	9.19	9.47	9.57	9.68	9.82	10.05	10.32	11.75
$10^2 k_{obsd.}$ (sec.$^{-1}$)	0.150	0.393	1.027	2.08	0.468[a]	1.60[b]	3.93	3.72	7.52[a]	4.05	4.36
k (l. mole^{-1} sec.$^{-1}$)	10.7	9.10	9.60	9.04	7.73	9.89	11.4	10.1	9.50	9.71	9.81

[a] $[CN^-]_s = 8.90 \times 10^{-4}\ M$. [b] $[CN^-]_s = 2.22 \times 10^{-3}\ M$.

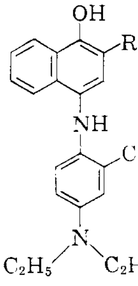
TABLE IV

RATES OF REACTION OF DYE II WITH CN^- AT 25°
ADDED $[CN^-]_s = 3.32 \times 10^{-4}\ M$; $\mu = 0.09\ M$

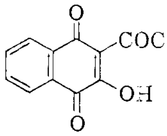
pH	$w + v\ [(A_1 - A_2)/(A_1 + A_2)]$	k_8 (l. mole^{-2} sec.$^{-1}$)	s[a]
10.20	0.0299	55.2	0.00148
9.67	.0269	57.2	.00536
8.90	.00734	55.2	.00384

[a] Standard error of the regression.

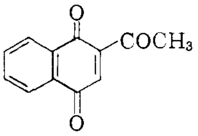
as final products. The kinetic results show that IV is not a primary product of attack by OH^- and that III probably is not. It is not known at present whether V arises from attack of OH^- on the dye or from hydrolysis of the naphthoquinone VI in basic solution. The latter reaction has been shown to occur rapidly. Quinones are formed from acid hydrolysis of indophenols.[7]



IVa, R = $CONHC_2H_4SO_3^-$
IVb, R = $COCH_3$



V

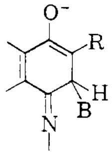


VI

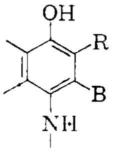
The study of products as an aid in elucidating the mechanism is complicated by the fact that results obtained on the concentrated solutions required for product isolation cannot be extended quantitatively to the very dilute solutions investigated here. Association of the dye anions begins at concentrations of dye around $10^{-4}\ M$, as indicated by deviations from Beer's law and in reaction rates that cease to rise linearly with [dye] above $10^{-4}\ M$. We believe that association leads to the formation of dye anion micelles wherein vulnerable positions in the molecule are shielded from the attacking reagent. We also have evidence that Dyes I and II form mixed micelles with cationic surfactants from the fact that the stabilities of the dyes in the presence of these surfactants are increased by several orders of magnitude over the stabilities of the monodispersed dyes. We are not certain that this self-association stabilizes the dyes equally to the various nucleophiles, since the position of attack may differ. Thus, when competition for the dye from two nucleophiles is possible, as in the case of simultaneous reaction by OH^- and CN^-, rate ratios established in dilute solution may not be valid when applied to concentrated solutions, so that it could be difficult to associate the products with the reaction giving rise to them.

Another serious difficulty arises in using product studies from concentrated solutions to determine the mechanism. Preliminary results show that in the reaction of Dye I with OH^-, a series of reactions follow the initial bleaching. One of the products is capable of reducing dye to leuco dye, so that when "nucleophilic" bleaching is slow, an apparent autocatalytic bleaching is observed. Since bimolecular reactions with products are involved, the importance of bleaching by reduction increases with initial dye concentration. These extraneous products must be distinguished from primary products arising from the nucleophilic reaction, if, indeed, any of the latter remain, before any conclusions regarding the mechanism can be drawn.

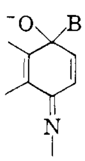
If the nucleophilic nature of these reactions is accepted, then the reagents should attack preferentially at those positions in the dye molecule where relatively low electron densities exist or can be promoted. Thus it might be expected that attack should occur at carbons 1 or 3 of the naphthalene skeleton or at the imine nitrogen. There is no reason to assume that all the reagents studied attack at the same position; the differences in their kinetic behavior suggest that they do not. Consideration of some possible consequences of attack at the various positions might be illuminating. It is expected that if initial attack occurs at carbon 3 to give an intermediate such as VII, proton loss should rapidly follow to give, irreversibly, the substituted leuco dye, VIII. A completely reversible attack at position 3 requires that the bond to the ring hydrogen never be broken. The breaking or non-breaking of this bond should not be greatly influenced by the nature of the entering group. For example, sulfite attacks the 3-position of benzoquinones and quinonediimines irreversibly to give sulfohydroquinones[8] and sulfo-*p*-phenylenediamines,[9] respectively, while cyanide attacks the 3-position of 2-aryl-1,4-naphthoquinones ir-



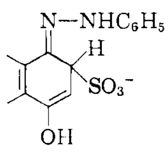
VII



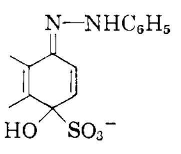
VIII



IX



X



XI

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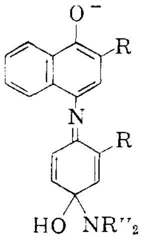
(7) M. P. H. Bayrac, *Bull. soc. chim. France*, **11**, 1129 (1894).

(8) (a) J. W. Dodgson, *J. Chem. Soc.*, **105**, 2435 (1914) and 2498 (1930); (b) J. Pinnow, *J. prakt. Chem.*, **6**, 536 (1914).

(9) (a) K. Meyer and H. Ulbricht, *Z. wiss. Phot.*, **45**, 222 (1950); (b) K. H. Bauer, *J. prakt. Chem.*, **6**, 65 (1958).

reversibly to give 2-aryl-3-cyanonaphthalene-1,4-diols.[10] It appears then that 1,4-addition of both $SO_3^{=}$ and CN^- to a quinoid system leads to an over-all irreversible reaction. On the other hand, 1,2-addition of both reagents to carbonyls is reversible.[11] These facts suggest that, in the case of the naphthoquinone imine dyes, CN^- may attack the 3-position to give a cyanoleuco dye (see above) while sulfite attacks the 1-position reversibly to give the complex IX. It is more difficult to speculate on the reversibility of attack at the imine nitrogen; OH^-, $SO_3^{=}$, and CN^- could give rise to stable diaryl hydroxylamines, aminosulfonates and cyanamides, respectively, by an irreversible reaction. It has been shown, however, that, in the sulfite addition compounds of naphthol azo dyes, the SO_3^- is not bound to azo nitrogen but to carbon. The structures X or XI have been proposed for the compounds.[12]

The attack of OH^- at the 4′-position to give an intermediate such as XII cannot be ruled out in some cases. Such an intermediate is analogous to those proposed for the deamination of quinonediimines[13] and should lead to deaminated dyes. Although deamination of some quinone imine dyes is reported by Hünig and Daum,[3] no evidence for such a reaction was obtained with the dyes studied here.



XII

Although it is recognized that cleavage of the dye molecule to give the isolated products III and V must result from attack at the 4-position by OH^- or water at some point, it is not believed at this time that initial attack by OH^- occurs at this position.

If it is postulated that reversible attack occurs at certain positions but not at others, then the parallel mechanism for bleaching by OH^- ($k_3 = 0$) is favored, *i.e.*, OH^- is attacking two positions competitively, one leading to reversible complex formation and one leading directly to irreversible reaction. We hope that product studies now in progress will answer some of these questions.

Experimental

Materials. 2-(β-Sulfoethylcarbamyl)-N-(2′-methyl-4′-(N′-ethyl-N′-β-sulfoethylamino)phenyl)-1,4-naphthoquinoneimine. (I).—A solution of analytically pure 2-(β-sulfoethylcarbamyl)-1-naphthol(0.2 mole) and 2-methyl-4-(N-ethyl-N-β-sulfoethylamino)-aniline (0.2 mole) in 8 l. of 0.125 *M* tripotassium phosphate was treated with dilute hydrochloric acid, with stirring, until the naphthol just began to precipitate. Potassium ferricyanide (0.8 mole) in 1.6 l. of water was slowly added, with vigorous stirring, to form the dye. Sufficient barium chloride in water was slowly added to precipitate the inorganic salts. Excess barium chloride was added to the filtered solution, the precipitated dye salt was collected (suction) and treated with 10 l. of hot water. The resulting mixture was filtered, the residue treated with an additional 5 l. of hot water, filtered, and the filtrates were combined. Cooling yielded 41.6 g. of dye salt (33%) which was recrystallized again from water and converted to the dipotassium salt by treatment of a hot solution with the calculated amount of potassium sulfate, filtering and evaporation. Countercurrent distribution of this material (100 stage) showed the presence of approximately 0.5% of an impurity having an absorption maximum at 675 mμ. The dye has maximum absorption at 692 mμ in the same solvent system. Repeated recrystallizations failed to free the dye from small amounts of inorganic salts, probably because of the high degree of association of the dye in concentrated solution.

2-Aceto-N-(2′-methyl-4′-(N′-ethyl-N′-β-sulfoethylamino)-phenyl)-1,4-naphthoquinoneimine. (II). To a rapidly stirred, two-phase system of 2-butanone and aqueous sodium bicarbonate containing equimolar amounts of Eastman Grade 2-aceto-1-naphthol and analytically pure 2-methyl-4-(N-ethyl-N-β-sulfoethylamino)aniline, was added, in portions, four molar equivalents of potassium ferricyanide in water. The phases were separated and the aqueous phase was re-extracted with 2-butanone to remove all the dye. The extracts were washed with sodium chloride solution (120 g./l.) and treated with 2,2,4-trimethylpentane to force out the residual water containing the dye as a separate phase. The dye was obtained by evaporation and was recrystallized from methanol. Repeated recrystallizations failed to remove all the inorganic salts.

Tests for Reversibility. (a) **Reaction with Cyanide Ion.**—Treatment of an aliquot of a stock solution of Dye I with a solution containing excess cyanide ion gave complete bleaching within several minutes. Treatment of the dye solution with cyanide ion that had previously been equilibrated with excess formalin gave no bleaching, showing that formaldehyde can remove free cyanide ion by cyanohydrin formation to a concentration too low to bleach dye effectively. Treatment of a solution of cyanide-bleached dye with the same excess of formalin failed to restore any dye. Precipitation of free cyanide with silver ion also failed to restore any dye, further demonstrating the irreversible nature of the cyanide bleaching. Addition of aqueous persulfate to a bleached solution gave a dye of different hue from that of the substrate Dye I. The rate of formation of this new dye was much less than the very rapid rate of oxidation of the leuco dye of I.

(b) **Reaction with Sulfite Ion.**—Treatment of sulfite-bleached dye solutions with excess formalin gave back up to 80% of Dye I but only small amounts of Dye II. This follows from the difference in stability constants for the two dye–sulfite complexes (see section on Results).

(c) **Reaction with Hydroxide Ion.**—An aliquot (0.49 ml.) of a 7.75×10^{-4} *M* solution of dye in water was injected from a calibrated Cornwall Luer-Lok syringe into 4.0 ml. of high-pH phosphate buffer or standardized sodium hydroxide solution. After timed intervals, 4.0 ml. of low-pH buffer was added to give a final pH of 6–7 and the optical densities of the solutions were determined. The resulting rates of the quenched reactions were considerably less than the total rates of bleaching measured at the high pH, showing that part of the bleached dye had been restored by removing hydroxide ion. No quantitative significance can be attached to the rates determined by quenching (see text).

Kinetic Measurements.—All rates were measured at 25.0° with solutions of ionic strength = 0.1 *M*. The runs were carried out under pseudo first-order conditions by having the nucleophile in constant excess or by buffering. All buffers were deaerated by bubbling with nitrogen prior to a run to prevent oxidation of any *p*-phenylenediamine or leuco dye formed. The absorption cells were tightly stoppered throughout a run and bulk reaction solutions were maintained in an atmosphere of nitrogen as nearly as possible. To test for the presence of any leuco dye formed during a run, identical parallel runs were carried out in the presence and absence of air or chemical oxidant and differences in dye densities in the two runs noted. No leuco dye was ever detected during the early stages of any reaction; it was

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(10) A. N. Grinev, A. P. Klyagina and A. P. Terent'ev, *Zhur. Obshchei Khim.*, **29**, 2773 (1959).

(11) A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2533 (1928).

(12) N. N. Woroshtzow and A. S. Tsherkasski, *J. Am. Chem. Soc.*, **58**, 2327 (1936) and preceding papers.

(13) L. K. J. Tong, M. Carolyn Glesmann and R. L. Bent, *ibid.*, **82**, 1988 (1960).

detected during the later stages of bleaching of I with OH^- at $pH < 11$, where increasing rate constants were also observed after about 50% reaction.

The disappearance of dye was measured spectrophotometrically. Very dilute solutions of Dyes I and II have absorption maxima at 685 and 675 mμ, respectively, in basic buffers. In more concentrated solutions where Beer's law is not obeyed, the maxima are shifted. The dyes obey Beer's law at concentrations below 5×10^{-5} *M*. Calibration curves were used for concentrations above this level. For the slower runs, 0.49 ml. of a solution of dye in water was injected from a calibrated syringe into 4.0 ml. of buffer contained in a 1-cm. absorption cell and the rate of bleaching plotted continuously on a Cary Recording Spectrophotometer, Model 14. For the very slow runs, a Beckman DU Spectrophotometer was employed. The fast rates were measured on a flow machine described previously,[14] using either a stopped-flow or a steady-state flow method. The former method was used to follow the rate of bleaching of I with OH^- at pH 12 and involved forcing equal volumes of a solution of dye in water and phosphate buffer from motor-driven, stainless-steel syringes into a jet mixing chamber and thence into a tube containing an absorption cell. When a steady state was established, the flow was quickly stopped and the disappearance of dye plotted continuously as a function of time on a Mosley Autograph X-Y Recorder. The steady-state flow method was used to measure the very rapid rate of complexing of I with $SO_3^=$. Equal volumes of dye in water were mixed as described with $SO_3^=$ in phosphate buffers and the steady state was established in the observation tube. The steady-state dye densities of the flowing solution were measured; the extent of reaction at the time of observing a given steady-state level was varied by changing both the flow rate and the distance between the mixing chamber and absorption cell by means of stainless-steel spacers. The reaction times corresponding to a given distance and flow rate had previously been obtained by calibration with a reaction of known rate.

The *p*-phenylenediamine (III) was determined in the presence of substrate dye by oxidative coupling with an α-naphthol to give a new indoaniline dye whose properties differed from those of the substrate. Two methods were used: (A) Coupling with 2-*n*-amylcarbamyl-1-naphthol. The formation and extraction of this dye into *n*-butyl acetate is quantitative, whereas the substrate Dye I is not extracted. For a kinetic run, aliquots of the reaction solution were quenched in a pH 9.4 phosphate buffer containing the naphthol. Excess ferricyanide solution was added and the dye extracted into a known volume of *n*-butyl acetate. The extracts were allowed to stand overnight to permit the turbidity to clear and the color from the oxidized naphthol to fade before the optical densities were determined. (B) Coupling with 2-(N-ethyl-N-3′,5′-dicarboxyphenyl)-carbamyl-1-naphthol (X). Method A was not applicable to Dye II because it is partially extracted into butyl acetate. At pH 12, II is almost completely in the form of the complex with hydroxide ion, while the indoaniline dye formed by oxidative coupling of III with X is not complexed and is stable at this *p*H. Thus the dye from X can be determined directly in solution in the presence of II at *p*H 12. For a run, 4.0 ml. of a 1.2×10^{-3} *M* solution of II in water was injected into 20 ml. of 0.06 *M* tripotassium phosphate at time zero. After timed intervals, 10 ml. of 4×10^{-3} *M* X and 10 ml. of 5×10^{-4} *M* ferricyanide were rapidly added from syringes and the optical density of 1–10 cm. layers at 665 mμ was determined immediately. A new run was initiated for each point on the rate curve. Since Method B does not quench the reaction of substrate dye, each point is probably a little high, so that the observed rate of formation of III determined by this method is high.

Formation Constants for the Dye–Sulfite Complexes.—Aliquots of concentrated solutions of I and sodium sulfite in water were mixed and diluted with phosphate buffer to give final ionic strengths of 0.1 *M* and pH 10.25. The total concentrations of dye and sulfite were equal and either 5.00×10^{-4} or 2.00×10^{-4} *M*. Every precaution had to be taken to exclude air by working in a nitrogen atmosphere. The equilibrium concentration of sulfite was calculated from the total concentration and the measured equilibrium concentration of dye. The mean of six determinations of K_f was 4.8×10^4 with standard error $= 0.16 \times 10^4$. To determine the equilibrium constants by the kinetic method, various aliquots of dye and sulfite were mixed and diluted with standard sodium hydroxide solution so that $[\text{Dye}]_s = 1.0 \times 10^{-4}$ *M* and $[SO_3^=]_s$ varied from 2×10^{-4} to 7×10^{-3} *M* with II, and from 1.0×10^{-3} to 1.0×10^{-2} *M* with I. Under these conditions, both dyes were completely complexed with sulfite. The I–sulfite complex has absorption maxima at 260 mμ ($\epsilon = 2.94 \times 10^{-4}$ and 315 mμ ($\epsilon = 1.10 \times 10^4$) and a shoulder at 360 mμ ($\epsilon = 4.82 \times 10^3$). The II–sulfite complex has absorption maxima at 236 mμ ($\epsilon = 2.24 \times 10^4$), 260 mμ ($\epsilon = 2.44 \times 10^4$), 322 mμ ($\epsilon = 9.24 \times 10^3$) and a shoulder at 360 mμ ($\epsilon = 5.74 \times 10^3$). Rates of disappearance of the complexes were followed spectrophotometrically at the 315- and 322-mμ peaks. Pseudo first-order rate constants were determined by the Guggenheim method. Plots of k_{obsd} *vs.* $[OH^-]/[SO_3^=]$ were linear and passed through the origin (Fig. 4).

Acidity Scale.—All pH measurements were made with a Beckman general-purpose glass electrode No. 1190–80 (*vs.* s.c.e.) and a Beckman pH meter, Model G. The e.m.f. as measured by this method is proportional to $-\log a_{H^+}$ for buffers of the ionic strengths used in this investigation.[15] No attempt was made to correct for liquid junction potential, as it was thought this would be small compared to the error of measurement with this meter. Throughout the discussion, the approximation is made that $14.0 - \text{pH} = \text{pOH} = -\log[OH^-]$.

Acknowledgment.—The authors acknowledge the help of Dr. D. P. Harnish of these Laboratories in performing the exploratory experiments and the isolation of the major products.

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[14] (a) W. R. Ruby, *Rev. Sci. Instruments*, **26**, 460 (1955); (b) L. K. J. Tong and M. Carolyn Glesmann, *J. Am. Chem. Soc.*, **79**, 583 (1957).

[15] R. G. Bates, "Electrometric pH Determinations, Theory and Practice," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 88.