

Reduction of Dyes by Free Radicals in Solution. Correlation between Reaction Rate Constants and Redox Potentials

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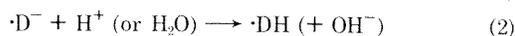
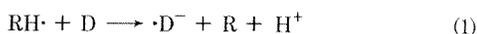
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The reactions of some free radicals (RH·) with a number of organic dyes (D) have been examined in aqueous solutions using the fast-reaction technique of pulse radiolysis. The radicals studied include ·CH₂OH, (CH₃)₂·COH, NH₂·CHCOO⁻, ·C-OH (C = cytosine), ·TH (TH₂ = dihydrothymine), and ·CH₂⁻ and were produced by reaction of the substrates with OH radicals. The dyes used were Crystal Violet, Safranin T, Phenosafranin, Indigo Di- and Tetrasulfonate, Methylene Blue, Thionine, Indophenol and 2,6-Dichloroindophenol. The electron transfer reaction, RH· + D → R + ·D⁻ + H⁺ (*k*₁), were determined by following the bleaching kinetics of the dyes at the wavelengths where they absorb. The rates were found to increase monotonically with increase in the redox potential *E*_m of the dyes examined. Similarly the efficiencies (expressed in percentage) of these reactions were obtained and found to be markedly dependent upon the *E*_m values of the dyes in the range from -0.357 to +0.217 V. These results are discussed and the suggestion made that this correlation represents the dependence upon Δ*E*_m, the difference in the redox potentials of the donor radical and the acceptor dyes.

Introduction

Organic dyes are an important class of compounds which usually can undergo both oxidative and reductive processes. Various aspects of the photochemistry² and radiation chemistry of dyes³ and the role of dyes in photodynamic action and photosensitization reactions⁴ have been reviewed recently. For example, the reaction which leads to the photoreduction of an excited dye molecule by a substrate usually involves an electron or hydrogen atom transfer from the reducing agent to the dye. In these cases, free radicals (or odd valent unstable species) are produced in solution and these can undergo subsequent redox reactions with the dye molecules. This work deals with the nature of these reactions in aqueous solutions.

The fast-reaction technique of pulse radiolysis was used to produce certain free radicals, under conditions such that these radicals were the only species reacting with the various dyes present in solution. From the "bleaching" kinetics of the colored dyes (D) used, it was possible to determine the reaction rate constants of process 1



where RH· is the free radical and ·DH and ·D⁻ the semiquinone radical and radical anion of the dye (D). The *k*₁ values obtained have been correlated with the redox properties of the various dyes studied.

Experimental Section

The pulse radiolysis set-up used has been described elsewhere.^{5,6} Single pulses of 2.3-MeV electrons and ~30-nsec durations were used. Dosimetry was carried out⁵ using KCNS solutions.

Fresh solutions were prepared just previous to use and considerable care was taken to minimize the exposure to light of the dyes in aqueous solutions. A synchronized shutter was used (open for ~2-5 msec) to reduce exposure of the solution to the monitoring light from the 450-W

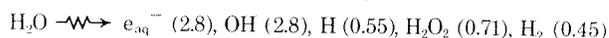
xenon lamp and, in addition, appropriate cut-off filters were employed.

Most of the dyes used were supplied by J. T. Baker Co. and the rest from Eastman Chemicals. Glycine was obtained from Calbiochem and the pyrimidines from Cyclochemicals. Solutions were buffered using perchloric acid, potassium hydroxide, and 1 mM phosphates or tetraborate.

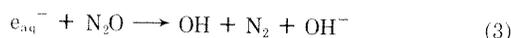
The redox potentials of the dyes were obtained from the literature.⁷ *E*_m values refer to the redox potential at the stated pH used.

Results and Discussion

The radiation chemistry of water produces



where the values in parentheses are the *G* values (yield produced per 100 eV of energy absorbed by the water). The experiments were carried out in N₂O-saturated aqueous solutions to convert the hydrated electrons into OH radicals



where *k*₃ = 8.0 × 10⁹ M⁻¹ sec⁻¹ (ref 8). The concentrations of the dyes and substrates were also kept low such that >90% of the e_{aq}⁻ reacted according to reaction 3.

Organic dyes are known to polymerize in aqueous solution with increase in the concentration of the dye (see, e.g., ref 9). The radiation dose was therefore kept very low, ~70-200 rads/pulse, in order not to exceed the concentration of the dyes above 25 μM, and at the same time ascertain complete reaction between the free radicals produced and the dyes. These low doses also reduced the extent of radical-radical reaction under these experimental conditions to <5%.

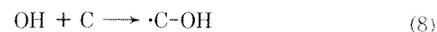
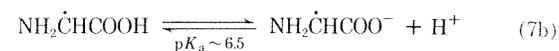
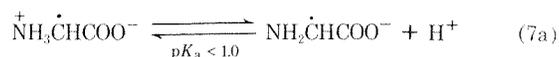
Five organic free radicals were studied in detail, and were produced from the reaction of the substrates with OH radicals



TABLE I: Reaction Rate Constants and Efficiencies (%) of One-Electron Reduction of Dyes by Free Radicals in Aqueous Solution

No.	Dyes ^a	E_m, V^b	pH	Wavelength monitored, nm		-CH ₂ OH		(CH ₃) ₂ COH		NH ₂ CHCOO ⁻		Cytosine ·C-OH		·TH ^c	
				k	%	k	%	k	%	k	%	k	%	k	%
1.	Crystal Violet	-0.357	7	525	4	2.3	84	1.2	56	F	10	14	H		
2.	Safranin T	-0.289	7	520	12	2.8	86	1.6	60	F	17	22	H		
3.	Phenosafranin	-0.254	7	520	22	3.2	82	1.9	66	F	g	0.9	H		
4.	Indigo Disulfonate	-0.199	9	610	1.9	4.0	88	2.8	71	F	55	1.2	H		
4'	Indigo Disulfonate	-0.125	7	610	2.0	4.0	88	4.0	88	F	81	g	H		
5.	Indigo Tetrasulfonate	-0.046	7	610	3.0	4.2	89	4.2	78	F	84	2.3	H		
6.	Methylene Blue ^c	+0.011	7	580	3.4	4.4	91	3.7	86	F	85	2.7	H		
7.	Thionine ^d	+0.031	8	600	2.6	4.2	88	3.2	85	F	84	2.7	H		
8.	Indophenol	+0.083	9	610	3.1	4.0	86	g	87	F	88	g	H		
9.	2,6-Dichloroindophenol	+0.217	7	600	3.2	4.4	88	3.6	87	F	88	3.4	H		

^a Unless stated otherwise, 25 μM concentration of dyes was used. ^b From ref 7, at 25°. ^c 10 and 20 μM and doses of 70–150 rads/pulse. ^d 20 μM . ^e Rate constants, k , given in $10^{-9} M^{-1} sec^{-1}$ units, and reversibility, R, of the dyes are indicated as F (fully reversible) and H (half-reversible, i.e. 50% of the dye is regenerated). ^f Produced from reaction of OH radicals with dihydrothymine. ^g Thermal reaction between substrate and the dye apparently occurs.



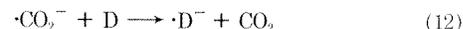
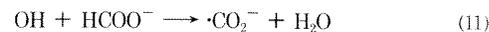
where C = cytosine and TH₂ = dihydrothymine. These radicals had previously been studied: $\cdot CH_2OH$,⁵ $(CH_3)_2\dot{C}OH$,⁵ $NH_2\dot{C}HCOO^-$,¹⁰ $\cdot C-OH$,¹¹ and $\cdot TH$.¹¹

The rates of reaction 1 were determined by following the "bleaching" or "disappearance" kinetics of the dyes at the appropriate wavelengths where they absorb. From the pseudo-first-order kinetics observed, dependent upon [dye], the second-order k_1 rates were calculated. These values for reaction of the free radicals with various dyes (triphenylmethane, azine, thiazine, and quinoneimine dyes) are given in Table I. These can be seen to be in the range 8.0×10^8 – $4.4 \times 10^9 M^{-1} sec^{-1}$.

The log k_1 values have been plotted for each radical as a function of the redox potential, E_m , of the dyes, and can be seen in Figure 1. In addition to the five radicals mentioned above, the rates of reaction of $\cdot CO_2^-$ radicals with various dyes, previously determined and summarized in ref 3, are plotted as a function of the E_m of the dyes in Figure 1. To these values have been added our own determined rates for these and some other dyes.

In all these cases, the log k_1 vs. E_m plots start levelling off at the higher redox potentials of the dyes, with k_1 values close to the expected near-diffusion-controlled rates. Similar results and dependence of the rates of electron transfer reactions from free radicals to a large number of quinones upon the redox potentials of the quinones have recently been observed.¹²

The efficiency of reaction 1, based on the extent (percentage) of bleaching of the dyes by the various radicals, was also determined. This was obtained based on 100% efficiency for the bleaching of the dyes on reaction with e_{aq}^- or $\cdot CO_2^-$ radicals



with $k_{10} \sim 1-5 \times 10^{10} M^{-1} sec^{-1}$ and $k_{12} \sim 1.6-5.0 \times 10^9 M^{-1} sec^{-1}$. These $-\Delta OD$ of the dyes based on reactions 10 or 11, equivalent to 100% bleaching efficiency, were obtained immediately before the experiment under otherwise identical experimental conditions of dosimetry, pH, wavelength, and slit widths on the double monochromators. The percentage efficiencies for the transfer of an electron from the free radicals to the dyes are given in Table I. For each radical a marked dependence of the percentage efficiency for the reduction of the dyes can be observed on going from one dye to the other. These approached 100% with dyes having $E_m > 0.01 V$.

Following the bleaching of the dyes from the reaction with free radicals, the degree of reversibility of the dye was monitored on the oscilloscope about 15 sec after the electron pulse. With all the free radicals examined, except with $NH_2\dot{C}HCOO^-$, ~50% of the concentration of the bleached dye was regenerated. This 50% reversibility is consistent with a disproportionation reaction of the dye

TABLE II: Rate Constants, k , for the Reaction of Organic Radicals with Dyes in Aqueous Solution

Dyes, D ^a	Donor radical, RH·	pH	$k(\text{RH} \cdot + \text{D})$, M ⁻¹ sec ⁻¹ ^b
Fluorescein (500).	CH ₃ CHOH	10.8	4.5 × 10 ⁸
	Thymine (·T-OH)	10.8	5.7 × 10 ⁸
	Uracil (·U-OH)	10.8	6.0 × 10 ⁸
	Cytosine ^d	9.2	1.5 × 10 ⁹
Crystal Violet (520)	·CO ₂ ⁻	7.0	1.5 × 10 ⁹ (1.7 × 10 ⁹)
	Thymine (·T-OH)	10.8	1.3 × 10 ⁹
	Uracil (·U-OH)	10.8	1.5 × 10 ⁹ (1.7 × 10 ⁹)
	Thymine ^d	5.4	2.4 × 10 ⁹
Indigo Disulfonate (610)	·CO ₂ ⁻	7.0	2.0 × 10 ⁹ (2.1 × 10 ⁹)
	Histidine ^c	7.0	1.1 × 10 ⁹ (1.3 × 10 ⁹)
	Riboflavin (·RF ⁻)	10.8	5.0 × 10 ⁸
Toluidine Blue (610)	Riboflavin (·RF ⁻)	10.8	6.0 × 10 ⁸
Methylene Blue (660, 580)	Riboflavin (·RF ⁻)	10.8	6.2 × 10 ⁸
	Lipoate (·RSSR ⁻)	7.5	1.0 × 10 ⁹
Indophenol (610)	·CO ₂ ⁻	9.0	2.8 × 10 ⁹ (2.7 × 10 ⁹)
	Thymine (·T-OH)	10.8	2.0 × 10 ⁹
	Histidine ^c	9.0	1.6 × 10 ⁹ (1.0 × 10 ⁹)
2,6-Dichloroindophenol (600)	·CO ₂ ⁻	7.0	3.5 × 10 ⁹ (3.6 × 10 ⁹)
	Riboflavin (·RF ⁻)	10.8	6.2 × 10 ⁸
	Histidine ^c	7.0	1.1 × 10 ⁹ (1.1 × 10 ⁹)

^a Values in parentheses are wavelengths monitored (in nm). ^b Rates determined by following "bleaching" kinetics of the dye at appropriate wavelengths; values in parentheses were determined by following formation kinetics of the reduced dye semiquinone radical, usually at 400 nm. ^c OH adduct. ^d e_{aq}⁻ adduct.

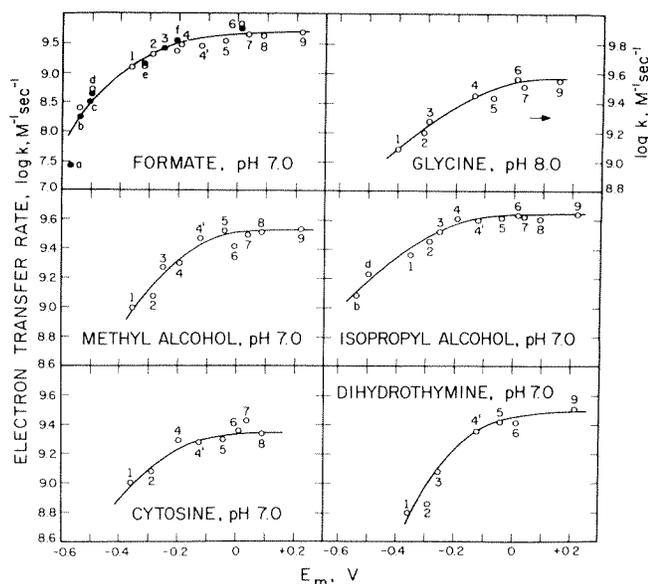
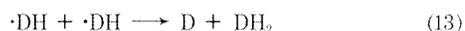


Figure 1. Dependence of $\log k_1$, the rate of electron transfer, from free radicals to various dyes in aqueous solutions as a function of the redox potential, E_m , of the dyes. Donor radicals used are $\cdot\text{CO}_2^-$, $\text{NH}_2\text{CHCOO}^-$, $\cdot\text{CH}_2\text{OH}$, $(\text{CH}_3)_2\text{COH}$, $\cdot\text{C-OH}$, and $\cdot\text{TH}$. The dyes used corresponding to the numbers are given in Table I. In addition, the letters are a, Fluorescein; b, Rhodamine B; c, Acridine; d, Eosin Y; e, NAD^+ ; and f, Riboflavin. The data represented by \bullet were taken from ref 3, and \circ symbols were determined in this work. Total dose ~ 200 rads/pulse, corresponding to a $[\text{radical}] = 1.2 \mu\text{M}$.

semiquinone radical (or radical anion)



where DH_2 is the leuco dye. Almost complete reversibility was observed from reaction of the dyes with the $\text{NH}_2\text{CHCOO}^-$ radical. These results are not easy to explain and would appear to indicate a reduction of the sub-

strate by the dye semiquinone radical. Alternatively, dehydroglycine may be produced from the reaction of $\text{NH}_2\text{CHCOO}^-$ with the dyes, and this unstable product could be reoxidized either by reaction with $\cdot\text{DH}$ or with DH_2 .

The rate constants for the reaction of a number of organic free radicals with some other dyes in aqueous solutions have been determined in the course of this work. These rates are presented in Table II. Most of these rates are in general agreement with the postulate that electron transfer rates increase with increase in the redox potential $\Delta E = E_D - E_{\text{RH}}$. The somewhat lower observed rate k_1 for the riboflavin radical $\cdot\text{RF}^-$ cannot be explained at present.

Conclusions

The above results show a strong dependence of the electron transfer reaction from free radicals, to a number of organic dyes or acceptors, upon the redox potential of the acceptors. The potential ranged from E_m values of -0.357 to $+0.217$ V at pH 7.0. This dependence was observed based on both the efficiencies and the rates of the electron transfer processes. While the results here have been correlated on the basis of the redox potential of the acceptor only, it is clear that such a dependence should be based on the difference between the redox potentials of the donor radical and the acceptor. Work is currently in progress¹³ to determine the redox potentials of these donor free radicals in aqueous solution.

References and Notes

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