mostat temperature (constant to ±0.05°). A 25-ml. portion of the solution was withdrawn, added to 25 ml. of standard sodium hydroxide at the same temperature, and titrated conductometrically in an erlenmeyer cell[19] against standard hydrochloric acid in 50% dioxane.

A sample of 2,2-dimethylethylenimine weighing 1.3319 g. was diluted with dioxane to 50 ml. A 25-ml. portion of this solution was added to the remaining solution of benzoic acid in dioxane and the time recorded. At appropriate intervals 25-ml. samples of the reaction mixture were withdrawn and treated as the benzoic acid solution had been. The time of withdrawal was considered to be when half the sample was added to the sodium hydroxide solution. The accuracy was ±0.5 minute. The reaction mixture was kept under a slight nitrogen pressure and samples were taken by increasing the nitrogen pressure to fill the pipet.

The rates gives in Table II were determined by plotting $1/(a - 2b) \ln (a - 2X)/(b - X)$ against time in minutes where a is the original acid concentration, b is the original imine concentration and X the amount of benzoic acid used in forming the benzamide. A value for the rate was calculated for each recorded interval of time from the equation

$$kt = \frac{1}{a - 2b} \ln \frac{a - 2X}{b - X} - \frac{1}{a - 2b} \ln \frac{a}{b}$$

where the value for the second term is the intercept of the curve as calculated by the method of least squares. Average deviations from the calculated rates were determined and the slopes were calculated by the method of least squares.

The ρ-values were then obtained by plotting the accepted σ-values[20] for the various substituents against log k (Fig. 1). The slopes of these curves are the respective ρ-values + 1.66 and +1.50.

Acknowledgment.—The authors are indebted to John O. Edwards for valuable suggestions and discussions on the kinetic studies reported here.

PROVIDENCE, R. I.

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[19] C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

[20] Ref. 3, p. 188.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Rate of Ferrous–Ferric Exchange in D_2O[1]

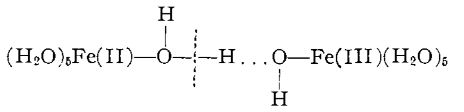
BY J. HUDIS AND R. W. DODSON

RECEIVED OCTOBER 25, 1955

The rate of the ferrous–ferric electron exchange reaction has been measured in heavy water solvent as a function of perchloric acid concentration at constant ionic strength. As in light water, the acid dependence indicates two reaction paths involving ferric ion and hydrolyzed ferric ion, respectively. The specific rate constants are each lowered by a factor of *ca.* 2 in D_2O. The result supports the idea of a hydrogen "atom transfer" mechanism for electron exchange.

Introduction

Previous measurements[2] of the rate of the ferrous–ferric electron exchange in aqueous perchlorate media have shown that the rate law is expressible as $R = k_1(\mathrm{Fe}^{++})(\mathrm{Fe}^{+++}) + k_2(\mathrm{Fe}^{++})(\mathrm{FeOH}^{++})$, and that the specific rate constant, k_2, for the path involving hydrolyzed ferric ion is about 1000 times that for the path involving unhydrolyzed ferric ion. In order to account for the exceptionally high rate of the Fe^{++}–FeOH^{++} reaction it has been suggested[3] that a mechanism of hydrogen atom transfer might be particularly favorable in this case.



$$(\mathrm{H_2O})_5\mathrm{Fe(II)}\!-\!\overset{\mathrm{H}}{\mathrm{O}}\!-\!\vdots\!-\!\mathrm{H}\ldots\underset{\mathrm{H}}{\mathrm{O}}\!-\!\mathrm{Fe(III)}(\mathrm{H_2O})_5$$

It has also been found[2,4] that FeCl^{++}, $\mathrm{FeCl_2}^{+}$, FeF^{++}, $\mathrm{FeF_2}^{+}$ and $\mathrm{FeF_3}$ all exchange with ferrous ion at rates equal within an order of magnitude to that of the (Fe^{+++}) reaction. Hydrogen atom transfer has been suggested[4] as a feature common to all these reactions.

To investigate the hypothesis of a hydrogen transfer mechanism we have studied the rate of the ferrous–ferric exchange in heavy water solvent under conditions which were otherwise comparable to those of some of the earlier experiments.

Experimental

The experimental procedure followed was similar to that used in previous iron exchange work.[2,4] α,α'-Dipyridyl was used to complex the Fe(II), thereby stopping the reaction. The Fe(III) fraction was then removed immediately by precipitation of $\mathrm{Fe(OH)_3}$ with $\mathrm{NH_4OH}$. Fe^{55} obtained from the Atomic Energy Commission at Oak Ridge was the radioactive tracer used, and the 5.9 kev. Mn X-rays emitted were detected either by means of a scintillation counter or a Geiger–Mueller counter. All reagents, including the radioactive tracer, were purified as earlier described.[4] The heavy water (~99% D_2O) was obtained from the Stuart Oxygen Co., San Francisco.

Each exchange solution was prepared by the addition of small volumes of the relatively concentrated reagent solutions (H_2O) to a sufficient volume of D_2O to bring the final volume to 10.0 ml. The ionic strength was adjusted to 0.55 *f* with weighed amounts of sodium perchlorate. Eight 0.8-ml. samples were withdrawn from the reaction mixture for exchange points; two 1.0-ml. aliquots were taken for iron analyses; and the remaining solution was used to check the D_2O/H_2O ratio present at the end of the experiment. The sample taken for the determination of the D_2O/H_2O ratio was doubly vacuum distilled and the refractive index of the purified sample measured with an Abbe type refractometer.[5] All D_2O/H_2O analyses indicated that at the end of the experiment the mole fraction of D_2O was greater than 0.90 ± 0.05. The refractive index measurements were reproducible to ±3% and the difference between the refractive indices of pure D_2O and pure H_2O agreed with the literature value to ±5%. Any error in the refractive index analysis due to H_2O^{18} enrichment of the D_2O would be small, since the samples measured were high in D_2O content and were analyzed by comparison with 99% D_2O. No correction was applied to the rate data to normalize results to 100% D_2O.

The reaction mixtures were made up in such a way that the ferrous concentration was approximately twice the ferric concentration. The exact concentration of total iron was determined by reducing an aliquot of the mixture, adding α,α'-dipyridyl, and measuring the optical density with a Beckman spectrophotometer. Since the reaction has been

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 869 (1952).

[3] R. W. Dodson, *ibid.*, **56**, 852 (1952); R. W. Dodson and N. Davidson, *ibid.*, **56**, 866 (1952), remarks in discussion at the 1952 ACS Symposium at Notre Dame.

[4] J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953).

[5] G. N. Lewis and D. B. Luten, *ibid.*, **55**, 5061 (1933).

shown[2,4] to be first order in the total concentration of each oxidation state the over-all rate constant is given by

$$\frac{R}{(\mathrm{FeII})(\mathrm{FeIII})} = k = \frac{0.693}{t_{1/2}[(\mathrm{FeII}) + (\mathrm{FeIII})]}$$

where R is the rate and $t_{1/2}$ the half-time of the exchange.

All experiments were run at 7.1 ± 0.1° in order to compare the results directly with those of Silverman and Dodson. The experimental procedure and apparatus were checked by measuring the rate of the iron exchange in H_2O. The observed rate constants agreed with those given by Silverman and Dodson to ±3%.

Results and Discussion

The experimental data are given in Table I.

TABLE I

DEPENDENCE OF RATE ON ACID CONCENTRATION IN D_2O–$DClO_4$–$NaClO_4$ MIXTURES

$(DClO_4)$, f	(FeII) + (FeIII) $f \times 10^3$	$t_{1/2}$, sec.	k, mole^{-1}-l.-sec.$^{-1}$
0.55	1.68	300	1.37
.27	1.56	240	1.85
.18	1.62	190	2.3
.13	1.54	145	3.1
.107	1.57, 1.54	116, 107	3.8, 4.2
.092	1.48	107	4.4
.082	1.54	100	4.5
.057	1.55	70	6.4

According to the rate law previously given the rate may be expressed as

$$R = k(\mathrm{FeII})(\mathrm{FeIII}) = (\mathrm{FeII})(\mathrm{FeIII})\left[k_1 + \frac{k_2K_1}{(\mathrm{H}^+)}\right]$$

where K_1 is the hydrolysis constant

$$K_1 = \frac{(\mathrm{FeOH}^{++})(\mathrm{H}^+)}{(\mathrm{Fe}^{+++})}$$

That the results of the work in D_2O also show this type of acid dependence may be seen from Fig. 1, in which k is plotted against $1/(D^+)$ and a straight line is obtained. The ordinate intercept yields directly the value of k_1. The slope of the line is equal to the product k_2K_1. The value of K_1 in D_2O at ionic strength 0.55 has been found[6] to be 1.2×10^{-3} at 21° by spectrophotometric measurements. The value in H_2O at ionic strength 0.50 has been determined[7] as 1.6×10^{-3} at 25°. Taking the heat of hydrolysis as 12.3 kcal./mole,[8] one finds that the constant is 1.2×10^{-3} in H_2O at 21°. The lack of a deuterium isotope effect on the hydrolysis constant is of interest in view of the fact that the ionization constant of water itself is one-fifth that for D_2O.[9] The hydrolysis equilibrium in D_2O evidently is worthy of further study.

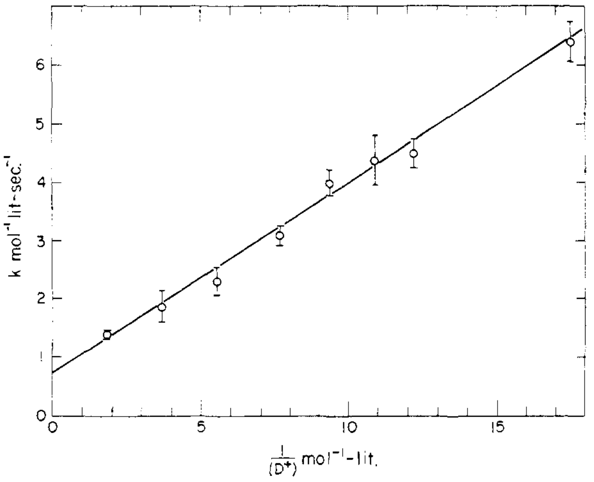

Fig. 1.—Specific rate *versus* reciprocal acid concentration.

For the present calculation of k_2 we estimate K_1 at 7.1° to be 4.3×10^{-4}, assuming the heats of hydrolysis are the same in D_2O and H_2O. (If the heat of hydrolysis were 1 kcal. greater in D_2O, as is the heat of ionization of water,[9] the hydrolysis constant at 7.1° would be about 10% less than the value assumed here.)

The values of k_1 and k_2 found are 0.7 and 765 mole^{-1}-l. sec.$^{-1}$, respectively, which may be compared with the Silverman and Dodson values of 1.4 and 1430 mole^{-1}-l. sec.$^{-1}$. The values of the rate constants in D_2O are each one half the values in H_2O within the experimental error.

There is no question but that the electron exchange rate is reduced by changing the solvent from light water to heavy water. Since the dielectric constants of H_2O and D_2O are essentially identical (85.3 *vs.* 85.0 at 7°),[10] the effect of the alteration on the electrostatics of the reaction must be negligible. The viscosity of D_2O is about 20% greater than that of H_2O at room temperature. This difference should reduce the encounter frequency[11,12] by about 20% in D_2O, an effect substantially smaller than that observed in the present experiments. Hence we take the view that the observed decrease in rate indicates that the activated complex contains hydrogen and that the rate determining step involves the motion of a hydrogen atom or ion.

The fractional decrease in the rate constant is the same for each of the two reaction paths. Hence, this work does not support the idea that the high specific rate of the reaction with hydrolyzed ferric ion is due to the occurrence of hydrogen transfer *uniquely* in this reaction path. This feature appears common to both paths.

The maximum kinetic isotope effect of the substitution of deuterium for hydrogen has been estimated[13] as a factor of 18. This corresponds to the extreme case that the hydrogen atom is free (unbonded) in the activated complex. Observed effects show a wide range.[14] The effect here is of the same order of magnitude as those in the reaction between water and the alkali metals[14] (k_H/k_D = 1.4–2.6 at room temperature).

The body of experimental knowledge about the rates of electron exchange reactions in aqueous media is by now rather extensive. In a rather large number of systems involving one electron exchange the specific rates are all about the same order of magnitude, and the correspondence also seems to apply separately to the heats and entropies of activation. The feature common to all of the systems is the solvent, water; and a view has been

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(6) J. Hudis and M. Wolfsberg, to be submitted for publication.

(7) A. S. Wilson and H. Taube, This Journal, **74**, 3509 (1952).

(8) E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

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(11) J. Q. Umberger and V. K. LaMer, *ibid.*, **67**, 1099 (1945).

(12) E. Montroll, *J. Chem. Phys.*, **14**, 202 (1946).

(13) J. Bigeleisen, *Science*, **110**, 14 (1949).

(14) See, *e.g.*, K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

expressed that the rate determining step involves the direct participation of the solvent in the reaction.[15,16] The results herein reported are compatible with this view.

We wish to thank Drs. J. Bigeleisen and M. Wolfsberg for their interest and helpful discussions.

(15) This point has been discussed in a paper by R. W. Dodson, presented at the New York meeting of the National Academy of Sciences, November, 1954.

(16) Hydrogen atom transport from ferrous ion *via* a water bridge also has been proposed by W. L. Reynolds and R. Lumry, 128th Meeting of the American Chemical Society, Minneapolis, 1955, Abstract 141-R.

UPTON, LONG ISLAND, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Long-Lived States in Photochemical Reactions. I. Photoreduction of Eosin

BY GERALD OSTER AND ALBERT H. ADELMAN[1]

RECEIVED AUGUST 15, 1955

A mechanism for the photoreduction of Eosin Y with allyl thiourea is presented which necessitates the postulation of a long-lived excited state of the dye. Extensive quenching of this metastable state by dye in the ground state is shown to occur. Kinetic and quenching data are used to evaluate the extent to which the unexcited dye, reducing agent, potassium iodide and *p*-phenylenediamine interact with the metastable excited state of the dye. Further, these data are used to calculate an approximate lifetime of the long-lived excited state which was found to be about fifty thousand times greater than that of the first excited singlet state.

Introduction

Long-lived or metastable states of excited dye molecules have been postulated to account for the phosphorescence of dyes dissolved in highly viscous media.[2] For fluorescein, at least, paramagnetic studies have identified this state to be the lowest triplet state.[3] Perrin and his students have performed semi-quantitative experiments whose results indicate that such long-lived states play a role in photochemical reactions.[4] These workers found that potassium iodide in small concentrations sufficient to quench the *phosphorescence* (of millisecond duration) in glycerol will strongly inhibit the photobleaching of the dye although the fluorescence is quenched to only a slight extent. Long-lived states of chlorophyll have been postulated to account for the decrease in over-all quantum yield of photobleaching with increase in concentration of this substance in methanol.[5] The kinetics of oxidation of allyl thiourea in acetone using ethyl chlorophyllide as the sensitizer[6] has been interpreted in terms of a long-lived state of the sensitizer.[7]

The present work is concerned with the photoreduction of eosin to the leuco form in aqueous medium using allyl thiourea as the hydrogen donor. As will be shown, the kinetics of this reaction requires the postulation of a long-lived species (probably free radical in nature) of the dye. Other work by us further substantiates this postulate.[8]

Experimental

Materials.—Eosin Y (tetrabromofluorescein-C.I.768) in the form of the disodium salt was obtained from Allied Chemical and Dye Corporation. The sample is 94% pure, the remaining 6% consisting mainly of salt additives. Allyl thiourea (Fisher C.P. grade) was recrystallized from acetone. Nitrogen (Airco prepurified) was further treated to remove traces of oxygen by passing over hot copper filings. The copper was periodically regenerated with hydrogen at elevated temperatures. Potassium iodide and *p*-phenylenediamine hydrochloride were Fisher C.P. grade.

Procedure.—All the solutions were made up in $^1/_{15}$ M phosphate buffer at *p*H 7.0. The solutions were placed in a cell 1 cm. in thickness and 5 × 5 cm. in cross-section and which was provided with a cover which allowed nitrogen to be passed through the solution to both stir the solution and to prevent contact with atmospheric oxygen. The solutions were flushed with nitrogen 15 min. prior to and during the irradiation. The cell was illuminated with a 500-watt tungsten lamp TDC slide projector (stabilized with a Sola constant voltage transformer) at a distance of 20 cm. An interference filter with maximum transmission at 518 mμ (band width 10 mμ) was placed between the light source and the cell. The transmittances of the solutions were measured with an Aminco photometer unit[9] (in conjunction with a highly dense neutral filter) and recorded continuously on a Leeds and Northrup Speedomax Type G recorder.

The absolute intensity of the light falling on the reaction cell was determined with a calibrated thermopile (Eppley Laboratories, Inc.) having a sensitivity of 0.039 microvolt per microwatt of radiant energy falling on one square cm. and the voltage was read on a galvanometer (Leeds and Northrup, type 2430-D with a sensitivity of 5×10^{-4} microamp. per mm.) in series with the thermopile and a 3200 ohm precision resistor.

Fluorescence measurements were carried out in an Aminco light scattering apparatus[9] using the 436 mμ line of mercury and placing a complementary yellow glass filter before the photomultiplier tube. Spectra of the dye solutions were determined in a Beckman model DU spectrophotometer.

Results and Discussion

The sodium salt of eosin in the phosphate buffer obeys Beer's law in the concentration range employed in the present work. The maximum in the spectrum is at 518 mμ with a molar extinction coefficient of $\epsilon_{\max}$ 7.25×10^4 liters per mole. The area $\int \epsilon d\nu$ of the spectral curve plotted against frequency in the visible range is 7.84×10^{18} liters per mole per sec.

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(1) Eastman Kodak Fellow.

(2) For review, see P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, Ch. 5, Sec. E.

(3) G. N. Lewis, M. Calvin and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949); M. Kasha, *Chem. Revs.*, **41**, 401 (1947).

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(7) J. Weiss, "Symp. Soc. Dyers and Colourists," Manchester, 1949, p. 135.

(8) Another paper in this series will be submitted for publication to THIS JOURNAL and will be presented in greater detail in the forthcoming Ph.D. thesis of A. H. Adelman.

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