deactivation reaction: $Fe^{2+}_{aq}{}^{*} + Fe^{2+}_{aq} \longrightarrow 2Fe^{2+}_{aq}$

molecular hydrogen formation: $Fe^{2+}_{aq}{}^{*} + H^{+}_{aq} + Fe^{2+}_{aq} \longrightarrow 2\,Fe^{3+}_{aq} + H_2 + OH^-$

Besides, the reaction of the "molecular" formation of hydrogen is not consistent with the oxygen effect on the reaction mechanism.

The pronounced effect of oxygen on the rate of the photochemical oxidation is important for the elucidation of the primary photochemical process. This effect may be applied as a diagnostic criterion for hydrogen atom formation by the dissociation of the excited state. As in the case of the radiation-chemical oxidation of the ferrous ion, it appears that the photochemical system fulfills the prediction of the free radical theory where competitive scavenging reactions of the hydrogen atoms by two different solutes occur. The quantitative agreement between the photochemical and radiation-chemical results provides an additional support for the proposed mechanism. Comparison with the reactions of atomic hydrogen[11] indicates that in both systems in acid solution H atoms as such are involved.

Kinetic data derived from radiation-chemical and photochemical experiments may be compared. The application of a homogeneous kinetic treatment is justified at relatively low rates of radical formation and moderately low scavenger concentrations. This assumption is consistent with some experimental kinetic data on the reactions of hydroxyl radicals in aqueous solutions.[14,23,24]

The investigation of the photochemistry of oxygen-containing solutions yields the result that at relatively low O_2 concentrations (up to $\sim 10^{-4}$ *M*) the direct effect of oxygen on the excited state of the ferrous ion is negligible.

(23) T. J. Sworski, *J. Am. Chem. Soc.*, **79**, 3655 (1957).

(24) F. S. Dainton and T. J. Hardwick, *Trans. Faraday Soc.*, **53**, 333 (1957).

THE PHOTOCHEMICAL EVOLUTION OF HYDROGEN FROM AQUEOUS SOLUTIONS OF FERROUS IONS. PART II. EFFECT OF CHANGING pH

By Joshua Jortner and Gabriel Stein

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel

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The photochemistry of the ferrous ion in the presence and in the absence of oxygen was investigated in the pH region 0.35–3.0. The pH dependence of the initial quantum yield up to pH 2.5 in the presence and absence of oxygen is interpreted as arising from the dependence on H^+ ion concentration of the rate of introduction of H atoms into the bulk. This results in the dependence of the quantum yield on $\sqrt{[H^+]}$. A mechanism to account for this is proposed. Another pathway leading to the pH independent formation of H atom also is postulated. The oxidation and reduction processes of the H atoms thus formed are investigated and it is shown that the oxidation of Fe^{2+} by H atoms may proceed by way of a hydride intermediate. Specific velocity constants are derived. The results of the photochemical experiments are correlated with those obtained in radiation chemistry.

In Part I the photochemistry of aqueous Fe^{2+} solutions at a constant low pH was investigated. It was shown that the excited state of the ferrous ion yields H atoms. However, the mechanism of this photochemical formation of hydrogen atoms in ionic solution is not yet well established, and the role of H^+ ions in this process is still a matter of controversy.[1–4]

The evidence in favor of the oxidation of ions such as Fe^{2+} [5,6] or Cr^{2+} [4] by H atoms is conclusive. Again the actual oxidation mechanism is not yet finally established. The results of Rigg and Weiss[7] on the pH dependence of the quantum yield in the photoöxidation of the ferrous ion were interpreted as due to the participation of the H_2^+ molecule ion in the oxidation of the ferrous ion by H atoms.[8] These results were not confirmed by Lefort and Douzou.[9] Recently the pH dependence of the initial quantum yield in the photoöxidation of the chromous ion was demonstrated[4] and for Fe^{2+}, it was reconfirmed.[8]

As the basic oxidation mechanism by H atoms still is in doubt, further work on this subject appeared desirable.

Results

The experimental technique was described in Part I. The evaluation of the initial photoöxidation rates was facilitated by the introduction of the correction for the inner filter effect. The pH dependence of the molar extinction coefficient of the ferric ion and the values of *B* in H_2SO_4 solutions are given in Table I. The absorption of the ferrous ion was found to be independent of pH. When 0.02 *M* Na_2SO_4 was added to each of these solutions *B* remained unchanged.

Photochemistry of Aerated Solutions.—The photoöxidation of aerated ferrous sulfate solutions was investigated at different values of pH. From these experimental results the values of $[Fe^{3+}]_c$—the concentrations of the ferric ion corrected for the inner filter effect—were obtained from the relation

$$[Fe^{3+}]_c = [Fe^{3+}]_t + \frac{B}{2}\,[Fe^{3+}]_t^2 \qquad (I)$$

These data are presented in Fig. 1. From Fig. 1

(1) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1113 (1938).

(2) J. Franck and R. L. Platzman, "Farkas Memorial Volume," Jerusalem, 1952, p. 21.

(3) J. Franck and R. L. Platzman, *Z. Physik*, **138**, 411 (1954).

(4) E. Collinson, F. S. Dainton, and M. A. Malati, *Trans. Faraday Soc.*, **55**, 209 (1959).

(5) J. Weiss, *Nature*, **165**, 728 (1950).

(6) T. Rigg, G. Stein, and J. Weiss, *Proc. Roy. Soc.* (London), **A211**, 375 (1952).

(7) T. Rigg and J. Weiss, *J. Chem. Phys.*, **30**, 1194 (1952).

(8) E. Hayon and J. Weiss, *J. Chem. Soc.*, 3866 (1960).

(9) M. Lefort and P. Douzou, *J. Chim. Phys.*, **53**, 536 (1956).

TABLE I

MOLAR ABSORPTION COEFFICIENTS OF Fe^{2+} AND Fe^{3+} IN H_2SO_4 SOLUTIONS AT 2536 Å.

Values of B calculated for $[Fe^{2+}] = 2 \times 10^{-2}$ mole^{-1} l.

$[H_2SO_4]$, N	$\epsilon_{Fe^{3+}}$ mole^{-1} l. cm.$^{-1}$	$\epsilon_{Fe^{2+}}$ mole^{-1} l. cm.$^{-1}$	B, mole^{-1} l.
0.80	2850	14.9 ± 0.2	9450
.088	2800	15.1 ± 0.2	9250
.033	2750		9000
.0088	2620	15.0 ± 0.2	8700
.0017	2300		7600

the initial yields were calculated, and are presented in Fig. 2. Inspection of these results indicates that up to pH 2.6 the photoöxidation rates in aerated solutions are independent of the ferric ion concentration (after introduction of the correction for the inner filter effect). At pH 3, deviation from linearity is observed (curve 9, Fig. 1), indicating the existence of additional inhibition effect of the ferric ion.

The mechanism of the photoöxidation reaction will be presented by the following scheme (keeping the notation used in Part I): excitation (1), deactivation of the excited state (2), and hydrogen atom formation (3).

The hydrogen atoms formed may react by oxidation of the ferrous ion, or by the reduction of ferric ion or oxygen (reactions 4, 5, and 10).

In these equations the nature of the actual ferric ion species reacting is not specified. It may, for example, be one of the hydrolysis products, *e.g.*, the $Fe^{3+}\ OH^-$ ion pair. The hydroperoxy radical may act by the oxidation of three additional ferrous ions by the Haber–Weiss mechanism[10] as in reaction 11. HO_2 or its conjugate base O_2^- also may act as a reducing agent for the ferric ion (reaction 14).

The rate of formation of the ferric ion will be

$$\frac{d[Fe^{3+}]}{dt} = \frac{k_3 I_a}{k_2 + k_3}\left\{1 + \frac{k_4[Fe^{2+}] - k_5[Fe^{3+}]}{k_4[Fe^{2+}] + k_5[Fe^{3+}] + k_{10}[O_2]} + \frac{k_{10}[O_2](3 - k_{14}[Fe^{3+}]/k_{11}[Fe^{2+}])}{(1 + k_{14}[Fe^{3+}]/k_{11}[Fe^{2+}])(k_4[Fe^{2+}] + k_5[Fe^{3+}] + k_{10}[O_2])}\right\} \qquad \text{(II)}$$

Evidence from radiation chemistry[11,12] indicates that the rate constants ratio k_{14}/k_{11} is pH dependent and at pH 2.7, $k_{14}/k_{11} = 0.3$. Thus for the initial photoöxidation stages under our experimental conditions, the contribution of the competition for the HO_2 radical by the ferric ion can be neglected. Equation II then is reduced to the form

$$\frac{d[Fe^{3+}]}{dt} = AI_a \left\{\frac{2 + k_4[Fe^{2+}]/k_{10}[O_2]}{1 + (k_4[Fe^{2+}]/k_{10}[O_2]) + (k_5[Fe^{3+}]/k_{10}[O_2])}\right\} \qquad \text{(III)}$$

From Fig. 1 it appears that the third term in the denominator can be neglected up to pH 2.7.

At pH 3.05, the rate constant ratio k_5/k_{10} was determined from the experimental results of curve 9 of Fig. 1. Equation III will be written in the form

$$\frac{d[Fe^{3+}]}{dt} = \frac{(1 + G)AI_0}{(1 + B[Fe^{3+}])(G + H[Fe^{3+}])} \qquad \text{(IV)}$$

where

$$G = 1 + \frac{k_4[Fe^{2+}]}{k_{10}[O_2]}$$

$$H = \frac{k_5}{k_{10}[O_2]}$$

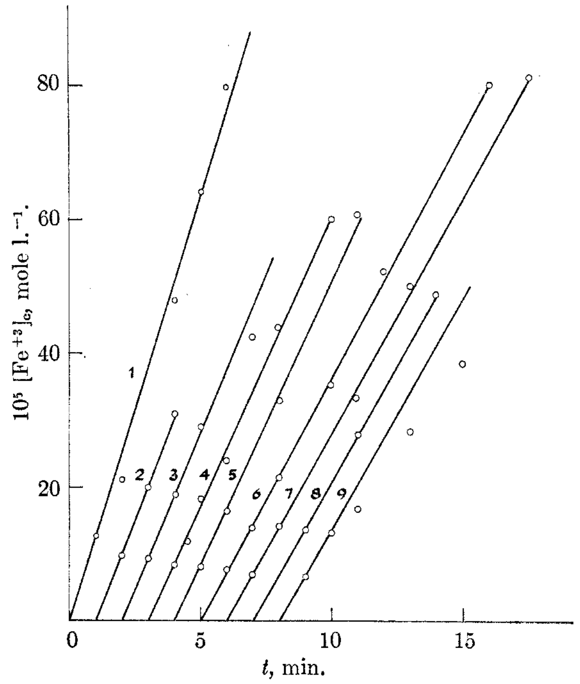

Fig. 1.—Photoöxidation curves of air-saturated ferrous sulfate solutions, corrected for the inner filter effect: $[Fe^{2+}] = 0.0204$ mole l.$^{-1}$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$. Curves are shifted along the time axis.

Curve	pH
1	0.60
2	0.85
3	1.20
4	1.45
5	1.55
6	1.85
7	2.35
8	2.65
9	3.05

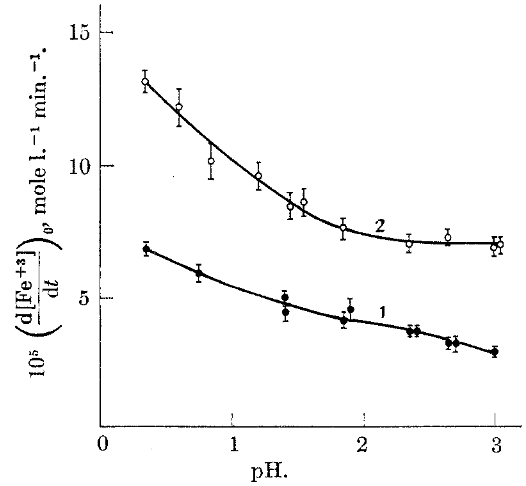

Fig. 2.—pH dependence of initial photoöxidation yields: 0.0204 M Fe^{2+} solutions; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$: (1) evacuated solutions, (2) air-saturated solutions.

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(10) F. Haber and J. Weiss, *Proc. Roy. Soc.* (London), **A147**, 332 (1934).

(11) A. O. Allen, V. D. Hogan, and W. G. Rothschild, *Radiation Res.*, **7**, 603 (1957).

(12) W. G. Rothschild and A. O. Allen, *ibid.*, **8**, 101 (1958).

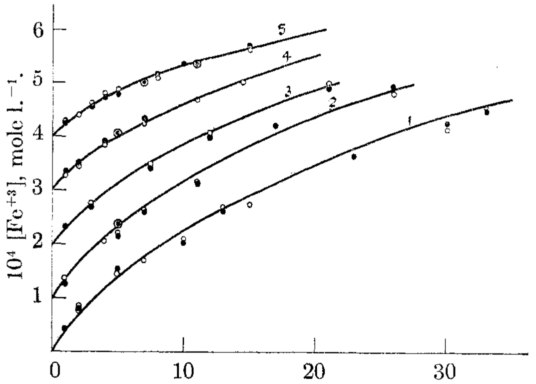

Fig. 3.—The photoöxidation curves of evacuated ferrous sulfate solutions: $[Fe^{2+}] = 0.0204$ mole l.$^{-1}$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$.

Curve	pH
1	1.40
2	1.85
3	2.35
4	2.65
5	3.00

Solid curves calculated from eq. VIII: ●, Fe^{3+} determination; ○, H_2 determination.

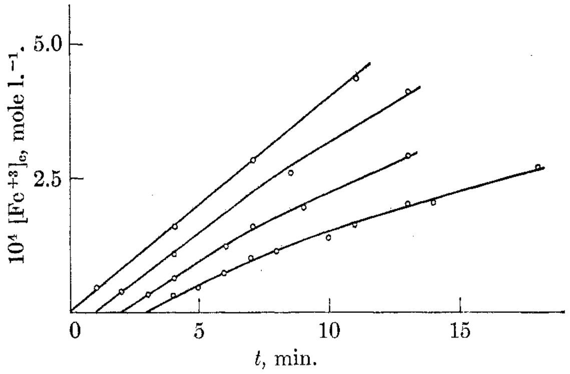

Fig. 4.—The photochemical curves in evacuated solutions corrected for the inner filter effect.

Curve	pH
1	1.85
2	2.35
3	2.65
4	3.00

Integration of eq. IV leads to the result

$$[Fe^{3+}] + \frac{B}{2}[Fe^{3+}]^2 + \frac{H}{2G}[Fe^{3+}]^2 + \frac{BH}{3G}[Fe^{3+}]^3 = AI_0\left(1 + \frac{1}{G}\right)t \quad (V)$$

Hence we calculated

$$\Delta = AI_0\left(1 + \frac{1}{G}\right)t - [Fe^{3+}] - \frac{B}{2}[Fe^{3+}]^2 \quad (VI)$$

and hence k_5/k_{10} was determined.

The results of these calculations are presented in Table II. It will be seen later that the ratio k_{10}/k_4 is only slightly pH dependent. The value of $k_{10}/k_4 = 10^3$ was used in the present calculations.

Photochemistry in Evacuated Solutions.—The photochemical oxidation curves of evacuated solutions are presented in Fig. 3. From the experimental results corrected for the inner filter effect (Fig. 4) the initial yields were obtained.

TABLE II

THE DETERMINATION OF THE RATIO k_5/k_{10} AT pH 3.05 FROM PHOTOCHEMICAL DATA IN AERATED SOLUTIONS

$[O_2] = 2.63 \times 10^{-4}$ mole l.$^{-1}$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$

t, min.	$10^4[Fe^{3+}]$, mole l.$^{-1}$	$10^4[Fe^{3+}]_c$, mole l.$^{-1}$	$10^4\Delta$, mole l.$^{-1}$	H, mole l.$^{-1}$	$\frac{k_5}{k_{10}}$
1	0.555	0.680			
5	1.71	2.96	0.44	1780	0.5 ± 0.2
7	2.10	3.87	0.77	1750	0.5 ± 0.1

At pH values above 2.0 an additional retarding effect of the ferric ion is observed. To ascertain the extent to which the increase of the concentration of the ferric ion is responsible for the decrease of the rate, the nature of this additional inhibition effect of the ferric ion has to be considered. Attributing the retarding effects to the inner filter effect and to the reduction of the ferric ions by hydrogen atoms (reaction 5), if the recombination reaction of hydrogen atoms (reaction 6) can be neglected, the kinetic equation will be

$$\frac{d[Fe^{3+}]}{dt} = \frac{AI_0}{(1 + B[Fe^{3+}])(1 + D[Fe^{3+}])} \quad (VII)$$

where $D = k_5/k_4[Fe^{2+}]$.

Integration of eq. III, assuming that the change in $[Fe^{2+}]$ can be neglected, yields the result

$$[Fe^{3+}] + \frac{B + D}{2}[Fe^{3+}]^2 + \frac{BD}{3}[Fe^{3+}]^3 = AI_0t \quad (VIII)$$

The initial rates were calculated from initial slopes of the curves in Fig. 4 and the value of AI_0 was obtained. Using eq. I and VIII we get

$$\delta = AI_0t - [Fe^{3+}]_c = DF \quad (IX)$$

where $F = {}^1/_2\,[Fe^{3+}]^2 + (B/3)[Fe^{3+}]^3$.

Linear plots of δ *vs.* F were obtained and from these D was determined. Thus we obtained $k_5/k_4 = 16 \pm 4$ at pH 2.35 and 40 ± 6 at pH 2.65. At pH 3.0 agreement with the experimental results was obtained by setting $k_5/k_4 = 100$. Using these values we could calculate theoretical curves to represent the dependence of the quantum yield on pH and on $[Fe^{3+}]$. The theoretical curves drawn in Fig. 3 are in good agreement with the experimental results.

Additional experiments were carried out in the presence of 0.1 M sulfate. In the experiments previously described the pH was varied simultaneously with sulfate ion concentration. These photochemical results were obtained by irradiation at constant dose, and by introduction of the appropriate correction for the inner filter effect. These results are presented in Table III.

It appears that in the presence of sulfate ion, the same trend of decrease in the quantum yield with increasing pH is observed. However, in the presence of the sulfate ion, the initial quantum yield in the pH region 2–2.5 is higher than in its absence. A similar effect was observed by Rigg and Weiss.[7] Addition of 0.4 M Na_2SO_4 caused an increase of the oxidation yield of ferrous ion by atomic hydrogen.[13]

Our experimental results in evacuated solutions (Fig. 2) clearly indicate that the initial oxidation

[13] G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959).

TABLE III

EFFECT OF THE SULFATE ION ON THE INITIAL PHOTOÖXIDATION YIELDS

$[Fe^{2+}] = 0.204\ M$; irradiation time $t = 5$ min.

$[H_2SO_4]$, N	$[Na_2SO_4]$, mole l.$^{-1}$	pH	$10^4 I_0$, einstein l.$^{-1}$ min.$^{-1}$	$10^4[Fe^{3+}]$, mole l.$^{-1}$	$2 \times 10^4[H_2]$, mole l.$^{-1}$	$\frac{[Fe^{3+}]_c}{I_0 t}$
0.030	..	1.90	4.59	1.39	1.42	0.100
.030	0.10	2.07	3.73	1.20	1.19	.111
.008	..	2.40	4.59	1.18	1.14	.081
.015	0.10	2.42	3.73	1.18	1.15	.108
.004	..	2.70	4.59	1.07	1.05	.070
.008	0.10	2.65	3.73	1.13	1.16	.097

yield is pH dependent. This result confirms the experimental data of Rigg and Weiss,[7] who showed that a 50% drop of the initial yield at pH 2.7 relative to pH 0.35 is observed. However, our interpretation of these results is different. On the other hand, Lefort and Douzou[9] claimed that the initial yields are pH independent and that after a relatively short irradiation period a decrease of the yield of the ferric ion with increasing pH is observed. The inhibition effect of the ferric ion, observed by these workers in the pH region up to 2.2, probably is due to the inner filter effect. Inspection of eq. VIII indicates that for 1% conversion, the reduction reaction is negligible as long as $k_5/k_4 < 10$, *i.e.*, up to pH 2.2.[12] This conclusion also is confirmed by our experimental results. Thus it appears that in the pH region investigated by Lefort and Douzou the back reaction 5 is of minor importance. The decrease of the yield below 1% conversion has to be attributed only to the decrease of the initial yield. These arguments might have been invalidated if an efficient deactivation reaction of the excited state would occur by

$$Fe^{2+*} + Fe^{3+}OH^- \longrightarrow Fe^{2+} + Fe^{3+}OH^-$$

The efficiency of this reaction would increase with increasing pH, due to the increase of the fraction of the hydrolyzed ferric ion. However, our experimental results *in vacuo* do not confirm this hypothesis. The inhibition effect of the ferric ion up to pH 2.0 can be interpreted adequately by the correction for the inner filter effect. This conclusion also is consistent with the results in aerated solutions.

Effect of Variable Oxygen Concentrations.—The determination of the ratio of the rate constants for the competitive reactions between oxygen and ferrous ions for hydrogen atoms is important for the elucidation of the oxidation mechanism by hydrogen atoms. Solutions of 0.02 M ferrous sulfate were irradiated at constant dose at various O_2 concentrations. These experiments were performed at pH 2.4 ($H_2SO_4 = 0.0055\ N$). From these results corrected for the inner filter effect, the initial yields were obtained. The results were treated according to the relation

$$\frac{1}{(A_{O_2} - A)I_0} = \frac{1}{AI_0} + \frac{k_4}{k_{10}AI_0}\frac{[Fe^{2+}]}{[O_2]} \qquad (X)$$

where AI_0 and $A_{O_2}I_0$ are the initial yields *in vacuo* and in the presence of O_2. This equation can be deduced from eq. XI of part I.

The experimental results plotted according to this relation (Fig. 5) yield $AI_0 = (0.35 \pm 0.03) \times 10^{-4}$ mole l.$^{-1}$ and $k_{10}/k_4 = 1500 \pm 400$ at pH 2.4. This result indicates a relatively small pH effect on the ratio of these rate constants, in agreement with the radiation chemical data.[12,14]

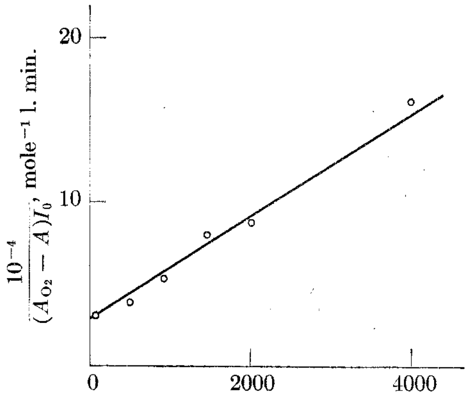

Fig. 5.—Graphical determination of the ratio k_4/k_{10} at pH 2.4 according to eq. X.

Assuming that in the pH region 2.35–2.65 k_4/k_{10} remains constant, we obtain the constants ratio presented in Table IV.

TABLE IV

THE pH DEPENDENCE OF RATE CONSTANTS RATIO FOR REACTIONS OF Fe^{2+} AND Fe^{3+} IONS

pH	$\frac{k_{H+Fe^{3+}}}{k_{H+Fe^{2+}}} = \frac{k_5}{k_4}$	$\frac{k_{H+O_2}}{k_{H+Fe^{2+}}} = \frac{k_{10}}{k_4}$	$\frac{k_{H+Fe^{3+}}}{k_{H+O_2}} = \frac{k_5}{k_{10}}$
Photochemical Data			
0.4	...	900 ± 300	
2.35	16 ± 4		(0.01)
2.40		1500 ± 400	
2.65	40 ± 4		(0.03)
3.00	(100)		
3.05			0.5 ± 0.2
Radiation Chemistry[11,12,15]			
0.4	0.081	1200 ± 300	
1.1[a]	0 50		
1.57	1.35		
2.10	7.2	1500 ± 200	0.007
2.70			0.10
Reactivity of Hydrogen Atoms[13]			
0.4	0.135		
1.3	0.87		
2.3	4.75		
2.9	50		

[a] Calculated from ref. 15.

Rate Constants Ratios as a Function of pH.—Table IV contains our results for the ratio of the

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(14) A. O. Allen and W. G. Rothschild, *Radiation Res.*, **7**, 591 (1957).

(15) J. H. Baxendale and G. Hughes, *Z. physik Chem.* (Frankfurt), **14**, 323 (1958).

rate constants of hydrogen atoms produced photochemically, with ferrous ions and with oxygen. The comparison of these data with the available experimental results from other sources[11–13,15] indicates that the agreement is reasonable.

Discussion

The Absorption Spectrum.—The first step in the mechanism of the photochemical evolution of hydrogen from aqueous solutions of ferrous ions is the formation of an excited state after the absorption of one quantum. The absorption spectrum of ferrous ion solutions between 2000 and 3000 Å. has been investigated by several workers.[16–18] Our measurements, in agreement with previous data, showed the band onset (for $\epsilon = 0.1$ mole^{-1} l. cm.$^{-1}$) at 2870 Å. (100 kcal.) and a shoulder at 2390 Å. (119 kcal.) with $\epsilon = 20$ mole^{-1} l. cm.$^{-1}$.

Hitherto this band has been assigned to an electron transfer from the ion to the solvent[17–19] similar to that proposed for the absorption spectra of anions in solutions.[2,3] Weiss[16] postulated a dissociative electron capture by a water molecule as the resulting primary chemical process. Farkas and Farkas[1] have shown that such a mechanism is not consistent with energetic data. The alternative proposed by Farkas and Farkas[1] involves electron transfer to a single water molecule. Theoretical[20,21] and experimental[22] evidence shows that a single water molecule cannot bind an additional electron. However Franck and Platzman[2,3] showed that in the case of anions the organized solvent medium in the neighborhood of the ion provides a potential well in which bound excited states may exist. Good agreement can be obtained between the experimental and the theoretical spectroscopic values calculated on the basis of such a theory.[23–25]

However when the spectrum of the positive ferrous ion was compared with theoretical calculations[26] based on a similar model in which the excited electron is bound in a potential well formed by the charge of the central ion screened by the polarized medium, no agreement could be obtained. The calculated binding energy of the electron in the excited state was about 1.2 e.v. The theoretical value of the Franck–Condon orientation strain, required to transfer the solvation configuration of the ion M^{Z+} to the configuration of the ion $M^{(Z+1)+}$ was quite different from the experimental one for this and similar positive ions examined. On the other hand, comparison with the energy levels of the gaseous ions indicated that the excited state may be related to the $3d^{n-1}4s$ state.[27,28] We suggest that such forbidden transitions may appear in aqueous solutions with relatively low ϵ values, as found for the 2390 Å. band. Unlike the case of anions, *e.g.*, iodide, where excited states pertaining to the ion itself alone are impossible, such excited states are possible in the case of cations, *e.g.*, ferrous ions. Therefore in this latter case the transition may be an essentially internal one, the participation of the solvent being less pronounced than in the case of iodide.

The absorption spectrum of Fe^{2+} at 2000–3000 Å. reveals two overlapping bands. Irradiation at 2536 Å. affects both bands and the quantum yields obtained are compound quantities. Investigation of the dependence of the quantum yield on wave length is desirable.

Primary Photochemical Processes.—The excited state formed in the primary absorption process may decay back to the ground state. In competition with this there occur processes leading to the net photochemical decomposition observed. Both in the presence and in the absence of O_2 the initial photoöxidation rate at constant light intensity decreases with increasing pH up to pH 2.5 in a parallel manner. Using for the initial rates the expressions ($I_a = I_0$)

$$\left(\frac{\mathrm{d}[\mathrm{Fe}^{3+}]}{\mathrm{d}t}\right)_0^{\mathrm{evac}} = 2\alpha I_a$$

$$\left(\frac{\mathrm{d}[\mathrm{Fe}^{3+}]}{\mathrm{d}t}\right)_0^{\mathrm{O}_2} = 2\alpha I_a\left[1 + \frac{1}{1 + \dfrac{k_4[\mathrm{Fe}^{2+}]}{k_{10}[\mathrm{O}_2]}}\right]$$

α, the fraction of excited centers leading to H atom formation was calculated from the experimental results in the pH range of 0.35 to 2.5 for evacuated solutions, and of 0.35 to 3.0 for aerated solutions. The values of $k_{10}/k_4 = 10^3$ was used over the whole range. Figure 6 shows that the values of α are identical for evacuated and air-saturated solutions over the whole pH range. Therefore at this concentration the effect of O_2 on the process in which H atoms are formed is negligible. The process by which H atoms appear in the bulk of the solution is facilitated by H^+ ions specifically.

A similar pH dependence of the quantum yield of hydrogen formation in the photoöxidation of chromous ion was attributed[4] to the formation of an ion-pair complex with anions. In ferrous ion solutions up to 0.8 N H_2SO_4 there is no spectroscopic evidence (Table I) for the formation of such a complex.

A molecular mechanism for the pH dependent formation of H_2 has been suggested[29] where the excited ion and H^+ would form a cluster which dissociates yielding H_2

$$\mathrm{Fe}^{2+}\,\mathrm{H_2O}^* + \mathrm{H}^+ \longrightarrow \mathrm{Fe}^{2+}\,\mathrm{H}-\mathrm{OH}^* \text{———} \mathrm{H}^+$$

$$\mathrm{Fe}^{2+}\,\mathrm{H}-\mathrm{OH}^* \text{———} \mathrm{H}^+ + \mathrm{Fe}^{2+} \longrightarrow 2\mathrm{Fe}^{3+} + \mathrm{OH}^- + \mathrm{H}_2$$

However such a molecular mechanism is inconsistent with the effect of oxygen on the reaction mechanism and with the fact that the initial rates at pH 0.35 are independent of Fe^{2+} concentration between 0.02 and 0.1 M.

Of the mechanisms by which atomic hydrogen may be formed in a pH dependent process a possible one is that involving the interaction of H^+

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(16) J. Weiss, *Trans. Faraday Soc.*, **37**, 463 (1941).

(17) H. L. Schlaefer, *Z. physik. Chem.* (Frankfurt) **3**, 263 (1955).

(18) F. S. Dainton and D. G. L. James, *Trans. Faraday Soc.*, **54**, 649 (1958).

(19) E. Rabinowitsch, *Rev. Mod. Phys.*, **14**, 112 (1942).

(20) J. A. Pople, *J. Chem. Phys.*, **21**, 2234 (1953).

(21) F. O. Ellison and H. Shull, *ibid.*, **23**, 2348 (1955).

(22) N. E. Bradbury and H. E. Tatel, *ibid.*, **2**, 835 (1934).

(23) G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 1086 (1959).

(24) G. Stein and A. Treinin, *ibid.*, **55**, 1091 (1959).

(25) G. Stein and A. Treinin, *ibid.*, **56**, 1393 (1960).

(26) J. Jortner, Ph.D. Thesis, Jerusalem, 1959.

(27) C. K. Jorgensen, *Acta Chem. Scand.*, **9**, 717 (1955).

(28) L. E. Orgel, *Disc. Solvay Conf.*, **10**, 289 (1956).

(29) L. J. Heidt and A. F. McMillan, *J. Am. Chem. Soc.*, **76**, 2135 (1954).

ions with the primary excited state, resulting in electron transfer[8]

$$Fe^{2+}{}_{aq}{}^{*} + H_3O^+ \longrightarrow Fe^{3+}{}_{aq} + H + H_2O$$

The low molar extinction coefficient of the ferrous ion absorption band is consistent with a relatively long lifetime of the excited state. However, fluorescence was not observed in this system and the degradation of electronic excitation energy proceeds by radiationless transition. Therefore the lifetime calculated from the area of the absorption band is only an upper limit. After a much shorter period the primary excited state already may have started on its process of radiationless decay back to the ground state.

During this process distinct intermediates may have formed in the Franck–Rabinowitch photochemical cage. For example the excited electron may become a separate entity undergoing a random walk process within the cage. H^+ in the bulk then may scavenge this electron. Alternatively an H atom may have been formed within the cage, and undergo random walk there before recombination within the cage with the positive ion. In this case the H atom may be scavenged by H^+ ions. The quantitative dependence on pH will be different in the case of direct interaction with the primary excited state from that in the case of scavenging of a distinct fragment undergoing a random walk process. Systems where efficient scavenging competes with secondary recombination of the type now considered were investigated by Noyes.[30,31] The quantum yield, α, for the introduction of radicals into the bulk of the solution in the presence of a scavenger in concentration [S] is given by

$$\alpha = \alpha_0 + 2a(\pi k_s[S])^{1/2} - \frac{4a^2k_s[S]}{\beta} + \text{—} \qquad \text{(XI)}$$

where a is a constant specifying the reaction probability of the two original partners, k_s is the rate constant of the reaction between the scavenger and one of the fragments, α_0 is the *residual yield* of fragments escaping recombination by diffusion into the bulk in a pH independent process, and β is a constant as defined by Noyes. The theoretical relation XI holds only after a period of time corresponding to the formation of two distinct chemical entities and subsequent few diffusive displacements.[30–33]

The quantitative results (Fig. 7) show that within a range of pH values $\alpha(H^+)$, the pH dependent rate of introduction of H atoms into the bulk is a linear function of $[H^+]^{1/2}$. The results can be presented by the straight line drawn in Fig. 7, given by the relation

$$\alpha(H^+) = 0.038 + 0.063\,[H^+]^{1/2} \qquad \text{(XII)}$$

The results in Fig. 7 show at higher H^+ concentration the negative deviation from the straight line expected from eq. XI. In the case of the photochemistry of the iodide ion,[34] eq. XI was obeyed very well over a wide range of pH and the results decisively favored a scavenging mechanism rather than direct interaction between H^+ and the excited state. In the present case the results in evacuated solutions are in fair agreement with the theory; in aerated solutions—particularly at low pH values—the agreement is less satisfactory. We conclude that the experimental results favor the scavenging mechanism with possibly some contribution by another reaction path which is ineffective in the case of iodide, where the primary excited state is rather different.

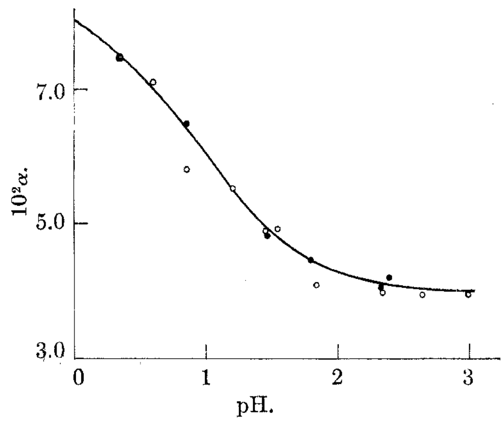

Fig. 6.—pH dependence of α: ●, evacuated solutions; ○, air-saturated solutions.

Equation XI involves the expansion of an exponential function. A rough estimation of the scavenging rate constant may be obtained if we follow Noyes' treatment and set $4a^2 = 10^{-11}$–10^{-10} sec., which is of the order of the relaxation time of the solvent molecules. With this choice we obtain $k_s = 10^7$–10^6 l. mole^{-1} sec.$^{-1}$ for the rate constant of scavenging by the H^+ ion. One likely mechanism for the formation of dissociated fragments from the primary excited state of the hydrated ferrous ion within the cage is dissociative electron capture by a water molecule in the solvation layer. This may occur during an antisymmetric vibration of a water molecule and is facilitated by coulombic repulsion of the proton by the positive central ion. In this process an H atom will be formed within the cage. The scavenging process following on this may have involved the H atom in the cage and the H^+ ion in the bulk, forming $H_2{}^+{}_{aq}$. However it was shown[35] that the velocity of formation of $H_2{}^+{}_{aq}$ is relatively low, the rate constant being of the order of 10^3 l. mole^{-1} sec.$^{-1}$. The magnitude of the rate constant k_s now obtained indicates that another possibility, namely the charge transfer process

$$\underset{\text{cage}}{\{Fe^{2+}\,OH^-\,H\}} + \underset{\text{bulk}}{H^+} \longrightarrow \underset{\text{cage}}{\{Fe^{2+}\,OH^-\,H^+\}} + \underset{\text{bulk}}{H}$$

is more likely, in which H^+ acts as an electron scavenger. The efficiency of such electron transfer processes over relatively large distances has been pointed out.[36] This pH dependent mechanism will thus cause the appearance of H atoms in the bulk of the solution.

In addition there exists a mechanism for the appearance of H atoms in the bulk independent of pH. In the pH region above 2.0 the initial quantum

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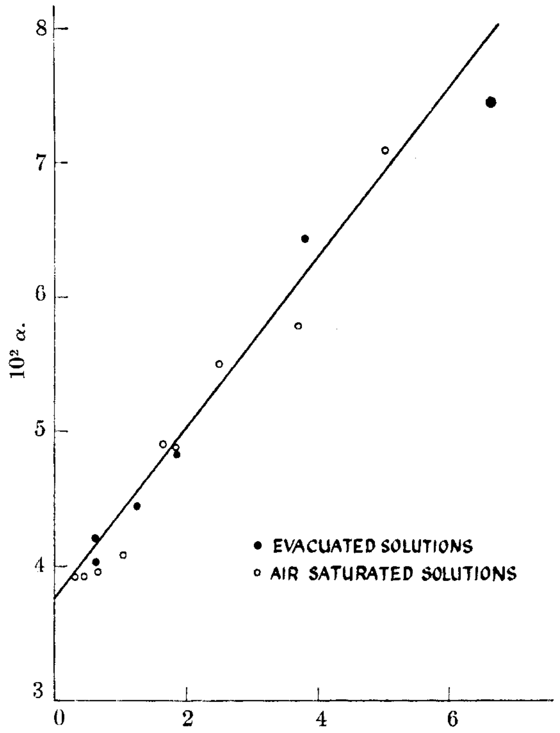
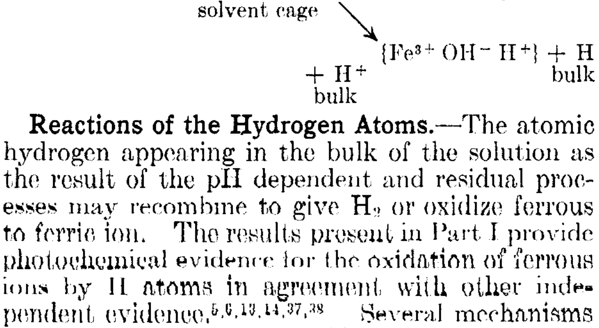


Fig. 7.—The dependence of α on $[H^+]^{1/2}$: ●, evacuated solutions; ○, air-saturated solutions.

yield in aerated solution, determined solely by the yield of H atoms, remains constant. This *residual yield* is then the fraction of H atoms which escape the back reaction by diffusion into the bulk. The full mechanism suggested for the introduction of H atoms into the bulk is therefore



Reactions of the Hydrogen Atoms.—The atomic hydrogen appearing in the bulk of the solution as the result of the pH dependent and residual processes may recombine to give H_2 or oxidize ferrous to ferric ion. The results present in Part I provide photochemical evidence for the oxidation of ferrous ions by H atoms in agreement with other independent evidence.[5,6,13,14,37,38] Several mechanisms have been proposed for this oxidation process. Weiss[5] postulated the intermediate formation of $H_2^+{}_{aq}$. Uri[39] considered the possibility of H atom abstraction from the hydration sphere of the ferrous ion. The original suggestion of Ethier and Haber[40] was of a triple collision between H, H^+_{aq}, and Fe^{2+}_{aq}. Recently experiments with atomic hydrogen showed[41,42] that the mechanism of oxidation may be different for different acceptors. Iodide is oxidized by way of the mechanism involving intermediate $H_2^+{}_{aq}$ formation, while ferrous ions may be oxidized in a pathway involving a hydride complex intermediate between the ferrous ion and atomic hydrogen.

The photochemical results in deaerated solution show a decrease of the oxidation yield with increasing pH at pH 2.5, while in aerated solutions in this region the yield remains constant. Therefore the additional pH effect is not due to the change in the rate of introduction of H atoms into the bulk. It may well be due to a competition between a pH dependent oxidation process and recombination

$$2H \longrightarrow H_2 \qquad (6)$$

Treatment of the results according to the $H_2^+{}_{aq}$ mechanism, assuming steady state kinetics, gives for the initial photoöxidation yield

$$\left(\frac{d[Fe^{3+}]}{dt}\right)_0 = \alpha I_0 + V[H^+]^2 \left\{\left(1 + \frac{2\alpha I_0}{V(H^+]^2}\right)^{1/2} - 1\right\} \qquad \text{(XIII)}$$

where

$$V = \frac{k_{15}{}^2}{2k_6}\left(\frac{k_{17}[Fe^{2+}]}{k_{16} + k_{17}[Fe^{2+}]}\right)^2$$

involving the velocity constants of the reactions

$$H + H^+_{aq} \underset{k_{16}}{\overset{k_{15}}{\rightleftarrows}} H_2^+{}_{aq}$$

$$H_2^+{}_{aq} + Fe^{2+}_{aq} \xrightarrow[k_{17}]{} Fe^{3+}_{aq} + H_2$$

Our experimental results above pH 2.5 can be represented by eq. XIII by setting the value of V = 0.1 l. mole^{-1} sec.$^{-1}$. For high Fe^{2+} concentrations $V = k_{15}/2k_6$. Introducing[43] $k_6 = 10^{10}$ l. mole^{-1} sec.$^{-1}$ yields $k_{15} = 4.5 \times 10^4$ l. mole^{-1} sec.$^{-1}$ for the lower limit of the velocity constant of $H_2^+{}_{aq}$ formation. This lower limit is higher than the value of the rate constant of $H_2^+{}_{aq}$ formation obtained in experiments using atomic hydrogen.[35]

The existence of the pH dependence rules out a pH independent mechanism as proposed by Uri.[39] The results obtained for the competition between ferrous ion and oxygen for the hydrogen atoms show that the ratio of the rate constants increases only slowly over a rather wide pH range. These results agree with those obtained for the radiation–chemical system.[13,14] They rule out a triple collision mechanism of oxidation.

Treatment of the results according to the mechanism[44,45] in which first ferrous ion and atomic hydrogen form an intermediate hydride complex, which then interacts with an H^+ ion

$$Fe^{2+}_{aq} + H \underset{k_{19}}{\overset{k_{18}}{\rightleftarrows}} FeH^{2+}$$

$$FeH^{2+} + H^+ \xrightarrow[k_{20}]{} Fe^{3+}_{aq} + H_2$$

assuming steady state kinetics to apply, leads to the result

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$$\left(\frac{\mathrm{d}[\mathrm{Fe}^{3+}]}{\mathrm{d}t}\right)_0 = \alpha I_0 + \frac{k_{18}^2}{2k_6}[\mathrm{Fe}^{2+}]^2\left(\frac{[\mathrm{H}^+]}{(k_{19}/k_{20}) + [\mathrm{H}^+]}\right)^2 \tag{XIV}$$

$$\left\{\left(1 + \frac{2\alpha I_0}{k_{18}^2/2k_6[\mathrm{Fe}^{2+}]^2[\mathrm{H}^+]/(k_{19}/k_{20}) + [\mathrm{H}^{2+}]}\right)^{1/2} - 1\right\}$$

Equation XIV can be transformed to the form

$$\frac{k_{18}^2}{2k_6}\left\{\frac{[\mathrm{H}^+]}{(k_{19}/k_{20}) + [\mathrm{H}^+]}\right\}^2 = \frac{\{(\mathrm{d}[\mathrm{Fe}^{3+}]/\mathrm{d}t)_0 - \alpha I_0\}^2}{\{4\alpha I_0 - 2(\mathrm{d}[\mathrm{Fe}^{3+}]/\mathrm{d}t)_0\}[\mathrm{Fe}^{2+}]^2}$$

Analysis of the quantitative data obtained for the oxidation of ferrous ion by atomic hydrogen over a wide range of H^+ and Fe^{2+} concentrations showed[41,42] that the hydride complex mechanism gave good agreement with the experimental results, but none of the other mechanisms considered did so. This pH dependent mechanism is distinct from the triple collision mechanism over the pH range where self dissociation of the hydride complex is negligible in comparison with the interaction of the complex with H^+. According to this treatment, the value of $k_{18} = 10^5$ l. mole^{-1} sec.$^{-1}$ was obtained for the rate of formation of the ferrous–hydrogen complex. To test the consistency of the photochemical results with this mechanism, the rate constant ratio k_{19}/k_{20} is derived in Table V, using the above value of k_{18} and the value of $\alpha = 4 \times 10^{-2}$ obtained in the present series of experiments in air-saturated solutions.

TABLE V

CALCULATION OF k_{19}/k_{20} FROM PHOTOCHEMICAL DATA IN EVACUATED SOLUTION

$I_0 = 7.64 \times 10^{-6}$ einstein l.$^{-1}$ sec.$^{-1}$; $[Fe^{2+}] = 0.02$ *M*

pH	10^7 (d[Fe^{3+}]/dt)$_0$, mole l.$^{-1}$ sec.$^{-1}$	k_{19}/k_{20}
2.65	5.34	0.05 ± 0.02
3.0	4.85	0.04 ± 0.02

The value of k_{19}/k_{20} obtained from the photochemical experiments is in good agreement with the values obtained in other systems.[42,46] Thus the present photochemical results are at least consistent with the assumption that the oxidation of ferrous ions by atomic hydrogen involves, in the present system, the intermediate formation of a hydride complex.

When ferric ions are present there is competition for the available H atoms between the ferric ions, which are reduced, and the ferrous ions, which are oxidized. The variation of the rate constants in Table IV shows that those involving the reduction of ferric ions are pH dependent. The pH dependence of the ratio k_5/k_4 should be due mainly to the pH dependence of reaction 5, which proceeds mainly by

$$\mathrm{Fe}^{3+}\mathrm{OH}^- + \mathrm{H} \longrightarrow \mathrm{Fe}^{2+} + \mathrm{H_2O} \tag{5.1}$$

rather than by the reduction of the hexaaquo ferric ion or the ferric sulfate ion pair.[44] Schwartz and Hritz[47] already have considered the effect of complexing negative groups on the reduction of ferric ions by atomic hydrogen. Their experiments on the competing reduction of ferric and oxidation of ferrous ions in irradiated solutions are not consistent with the assumption of an $H_2{}^+{}_{aq}$ intermediate mechanism. However, they are consistent, as are the present results, with the hydride mechanism.

The conclusion reached as the result of the present work is therefore that the main pH dependent process in the photochemical evolution of hydrogen from aqueous solutions of ferrous ions is the one in which atomic hydrogen is introduced into the bulk of the solution. The subsequent oxidation by atomic hydrogen introduces into the photochemical process only a minor additional pH dependence. The results show that this oxidation mechanism probably may be one involving a hydride intermediate. However in this respect the photochemical results may serve at most as further support for the conclusions reached by the use of atomic hydrogen in separate experiments.

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THE ULTRAVIOLET SPECTRUM OF POLYACRYLONITRILE AND THE IDENTIFICATION OF KETENE–IMINE STRUCTURES[1]

BY R. B. BEEVERS

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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The ultraviolet spectra of polyacrylonitrile and polymethacrylonitrile show an absorption band at about 270 mμ. This has been ascribed, in polymethacrylonitrile, to ketene–imine linkages in the chain. From an examination of the ultraviolet spectrum of the ketene–imine structure prepared by the photodecomposition of 2,2′-azo-bis-isobutyronitrile it is shown that the ultraviolet absorption at 270 mμ in polyacrylonitrile cannot be due to ketene–imine linkages.

During the course of an examination of the properties of acrylonitrile polymers prepared by anionic and free radical mechanisms it was observed that absorption occurred in the ultraviolet with a maximum at about 270 mμ. Absorption was most marked for the anionic polymers (Fig. 1) but some trace of a peak at this wave length was found for all polymers examined, bearing out the observations of Schurz, Bayzer, and Stübschen.[2] The origin of the absorption has so far not been determined. Some of the polymers which absorbed strongly in the ultraviolet also showed some absorption in the

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