

before for aniline. At 35° in some buffers reaction was so fast that a blank was determined in order to establish the initial iodine titer. All runs were conducted at least in duplicate and agreed usually within 1-2%.

DATA FOR SOME TYPICAL RUNS

THE IODINATION OF PHENOL IN WATER

phenol 0.007948 *M*, KI 0.12 *M*, KH₂PO₄ 0.016 *M*, Na₂HPO₄ 0.008 *M*, NaCl 0.14 *M*, $\mu = 0.3$, *T* = 25°

Time, min.	0.02 Thio-sulfate, ml.	<i>k</i> (liters mole ⁻¹ min. ⁻¹)	Time, min.	0.02 <i>M</i> thio-sulfate, ml.	<i>k</i> (liters mole ⁻¹ min. ⁻¹)
0	1.966		0	1.966	
13	1.762	(1.074)	12	1.778	1.067
23	1.630	1.048	24	1.613	1.062
37	1.454	1.062	35	1.476	1.065
47	1.342	1.067	46	1.350	1.073
57	1.244	1.063	56	1.250	1.070
68	1.152	1.048	67	1.156	1.057
84	1.020	1.054	77	1.072	1.058
94	0.946	1.057	91	0.966	1.058
Av.		1.057	Av.		1.064

The catalytic constants for secondary phosphate were obtained by the method of least squares with the omission of one point which fell obviously too far from the line.

Since in acetate buffers the reactions were very slow the iodide ion concentration was changed from 0.12 to 0.08 *M*. Recalculated to 0.12 *M* (*i.e.*, multiplied by 0.0064/0.0144) *k*_{0²⁵} for phenoxide ion becomes 3.15 × 10³ and *k*_{0³⁵} 9.2 × 10³, which agrees well with the constants for the uncatalyzed phenoxide ion reaction in phosphate buffers. Only a few acetate buffer ratios were used and the data for acetate buffer are less accurate than those for phosphate, particularly since difficulties were encountered in reproducing exactly the *pH* of the buffer. The values for *k*_{Ac⁻} at 25° and 35° are approximately 8.3 × 10⁴ and 29 × 10⁴ for phenoxide ion. The approximate activation energy (*E*_{Ac⁻}) is therefore 22.8 kcal.

In Table III are listed the rate constants obtained when

the initial concentrations are varied; they show the second order nature of the reaction. Table IV records some data which show that an increase in ionic strength from μ 0.3 to 0.5 decreases the rate by about 20%.

TABLE III

THE IODINATION OF PHENOL WITH DIFFERENT CONCENTRATIONS OF REACTANTS AT 25°

KI 0.12 *M*, KH₂PO₄ 0.06 *M*, Na₂HPO₄ 0.01 *M*, NaCl 0.09 $\mu = 0.3$

Molarity of phenol × 10 ³	Molarity of iodine × 10 ³	<i>k</i> (liters moles ⁻¹ min. ⁻¹)
3.99	1.99	4.45 ^a
7.99	1.96	4.05
12.0	1.97	4.15
16.0	1.97	4.03
7.99	1.00	4.07
7.99	3.96	4.36 ^a
16.0	3.96	4.06

^a The product precipitated during the reaction.

TABLE IV

THE EFFECT OF IONIC STRENGTH ON THE RATES OF IODINATION OF PHENOL

Phenol 0.008 *M*, Iodine 0.002 *M*, KI 0.12 *M*
 KH₂PO₄ 0.08 *M*, KH₂PO₄ 0.03 *M*,
 Na₂HPO₄ 0.01 *M*, Na₂HPO₄ 0.01 *M*

μ	<i>k</i> (liter moles ⁻¹ min. ⁻¹)	μ	<i>k</i> (liter moles ⁻¹ min. ⁻¹)
0.3	0.324	0.3	0.786
.4	.292	.4	.706
.5	.265	.5	.646

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Sensitized Catalysts. II. The Ascorbic Acid Method

BY HUGO J. KAUFFMANN

Ascorbic acid accelerates the catalytic oxidation of dyes with hydrogen peroxide in acidic solution. Dyes of different kinds show this effect, methyl orange being especially suitable and applicable under various conditions. Efficient catalysts are cupric and ferric salts. Hydrogen peroxide can be replaced by potassium persulfate. Oxygen is an inhibitor. Ethers and alcohols in the presence of ascorbic acid act as sensitizers. In the absence of ascorbic acid, they are inhibitors. The efficiency of a sensitizer increases with its concentration. The sensitization is due to the reduction of the catalyst and, presumably, to subsequent formation of free hydroxyl. The sensitization can be interpreted as an activation of the sensitizer brought about by free hydroxyl.

As shown in the first communication,¹ the catalytic oxidation of acid indigo carmine solutions by hydrogen peroxide or a persulfate can be greatly accelerated by many organic substances. Organic compounds, such as benzene or its sulfonates, which do not reduce ferric ions and which accelerate with ferric as well as with cupric salts as catalyst, have been called sensitizers.

Because with other dyes or other colored substrates, benzene, and the various sensitizers, act as regular inhibitors, the sensitizing effect seems to be connected with the particular constitution of the indigo. The kinetics of the process has been found to be complicated, but one essential fact can be stated: The described sensitization is an

autoxidation of the indigo solution induced by the percompound and highly accelerated by the sensitizer.

As to the organic compounds which reduce ferric salts, an exceptional behavior of ascorbic acid was observed, best demonstrated by comparing it with phloroglucinol. The latter is an inhibitor, retarding the indigo oxidation, especially at high hydrogen ion concentration. Ascorbic acid, on the contrary, is an excellent accelerator for other dyes also. However, what is more significant, dyes such as methyl orange are in the presence of ascorbic acid not only easily oxidizable, they now respond to sensitizers. Another substance, which like ascorbic acid stimulates sensitization, is pyrogallol, but its stimulating effect is less drastic and very limited.

(1) H. Kauffmann *THIS JOURNAL*, **69**, 899 (1947).

The Sensitizing Process

Character of the Ascorbic Acid Effect.—Solutions of methyl orange in dilute sulfuric acid, containing hydrogen peroxide and kept in Pyrex bottles in the dark at 25°, do not lose their color even after months. Addition of ferric sulfate causes slow bleaching, the slower the lower the pH. Methyl alcohol inhibits the bleaching process.

Addition of ascorbic acid thoroughly changes the picture. The inhibition ceases completely, giving way to a sudden decolorization in a few seconds. A solution of 5×10^{-5} mole of methyl orange, 1 mole of methyl alcohol, 10^{-1} mole of hydrogen peroxide and 10^{-4} g. atom of iron in 1 liter of 0.1 *N* sulfuric acid requires 14 days for bleaching. Stirring 100 mg. of ascorbic into 100 ml. of this solution accomplished the bleaching in as short a time as 8 seconds. The now colorless solution stays highly active for several minutes and quickly oxidizes new quantities of methyl orange. 2,6-Dichloroindophenol, the customary reagent, indicates that ascorbic acid is still present after one hour.

Considering the reducing power of ascorbic acid, it may appear doubtful as to whether this decolorization of methyl orange is actually an oxidation. As an azo dye, methyl orange might be reduced to colorless products, but it could be stated that in acid solutions, ascorbic acid alone, or in the presence of ferric salts, is incapable of reducing methyl orange. Other dyes than methyl orange become decolorized in the same manner and, in this connection, the behavior of methylene blue is of particular interest. If alone, ascorbic acid reversibly reduces methylene blue to its leuco compound, but with the addition of hydrogen peroxide and a ferric salt, the dye is irreversibly destroyed.

Hydrogen peroxide can be replaced by potassium persulfate. Although it was not yet possible to isolate definite reaction products, there can be no doubt any more that the process in question is a true oxidation. Certainly, the reducing power of ascorbic acid is the indispensable condition, not for attacking the dye, however, but for attacking the ferric salt. The ferrous ions formed, upon their reaction with the percompound, are the initiator of the oxidation.

Reasonable as this interpretation appears, the function of the methyl alcohol remains an enigma. Without it, the ascorbic acid effect, although still strong, is weaker. Stirring 100 mg. of ascorbic acid into 100 ml. of the above mentioned solution, but without methyl alcohol, extinguishes the red color in 26 seconds instead of 8 seconds, leaving the solution slightly yellowish. Without ascorbic acid, the bleaching time amounts to 6 days.

The Efficiency Quotient.—As provisional and empirical measure of the accelerating power of methyl alcohol or any other sensitizer, a quotient *Q*, defined by the equation

$$Q = 100 \frac{T_a - T_s}{T_a} \quad (1)$$

may be used. T_a is the bleaching time in the absence and T_s in the presence of a sensitizer. *Q* may be called the efficiency quotient. A *Q* of 100 means highest sensitization. High values of *Q* are obtained with ethers and primary and secondary alcohols.

There are three ways to prolong the time required for the bleaching process, thus making possible more accurate measurements. One way is to diminish the iron concentration to as low as 10^{-5} or 10^{-6} g. atom per liter. The second way is to increase the concentration of the sulfuric acid. Even in 4 *N* acidic solution, although the reactions are much slower, the sensitization is very obvious. The third way is to use phosphoric acid instead of sulfuric acid.

The end-point of the bleaching of the methyl orange is fairly sharp, provided ascorbic acid is present in large excess and the catalyst in very small quantities. Otherwise, the red color turns yellow and the bleaching process is slowed down, without distinct end-point. In such cases, an efficiency quotient can be given.

The first experiments were performed by stirring the calculated number of milliliters of an ascorbic acid solution quickly into a solution of the other constituents. This moment was taken as the starting point. During the reaction the mixture stood without any agitation. Tables I and II give some of the results.

Influence of Oxygen.—Two specific reactions take place in such solutions. The one reaction is the autoxidation of the ascorbic acid, the other is the oxidation of the dye. It depends on the partial pressure of the oxygen which of the

TABLE I

10^{-5} mole of methyl orange, 10^{-1} mole of hydrogen peroxide, 1 mole of methyl alcohol and 10^{-2} mole of ascorbic acid per liter at 25–26°

H_2SO_4 , <i>N</i>	(Fe) $\times 10^{-3}$ g. atom/liter	Bleaching time in sec.		Efficiency, <i>Q</i>
		Without	With CH_3OH	
0.10	1	402	255	36
.10	2	214	122	43
.10	3	148	78	47
.10	4	115	55	52
.10	5	86	40	53
1.00	100	85	12	86
1.00	200	50	5.5	89

TABLE II

10^{-5} mole of methyl orange, 10^{-1} mole of H_2O_2 , 1 mole of methyl alcohol and 2.5×10^{-2} mole of ascorbic acid in 1 liter of 0.01 *N* H_2SO_4 at 25–26°

(Cu) $\times 10^{-4}$ g. atom/liter	Bleaching time in sec.		Efficiency, <i>Q</i>
	Without	With CH_3OH	
1	355	99	72
2	214	55	74
3	166	44	73
4	139	36	74
5	122	31	75
10	93	25	73
20	72	21	71

two reactions predominates. *Oxygen protects the dye against oxidation.* In nitrogen, the dye oxidation proceeds very quickly, very much quicker than in air, whereas in oxygen it stops almost entirely. The same solution which in nitrogen can be bleached within a few minutes shows in oxygen in the same time only slight decrease in color. Even after days the solutions are often still red, the ascorbic acid being consumed meanwhile.

The degree of dye protection depends on the amount of catalyst. The protection is high if the amount of catalyst is low, with iron as low as 10^{-6} g. atom per liter and with copper as low as 10^{-5} . With large amounts of iron, the dye oxidation is so quick that on preparing the solutions an almost immediate decolorization takes place, whether oxygen is present or not. In the example given above to demonstrate the character of the ascorbic acid effect, oxygen is the cause that the high activity disappears within some minutes. Nitrogen restores the activity.

The Effect in Nitrogen.—To study the stimulating action of the ascorbic acid, the autoxidation has to be suppressed. This can best be done by bubbling nitrogen through the solution. The method suffers from the inconvenience that many good sensitizers, such as methyl alcohol or ethyl ether, are too volatile to give quantitative results.

Looking for non-volatile sensitizers which are readily soluble in water, polyhydric alcohols were tested. Sorbitol, mannitol and inositol were found ineffective, but pentaerythritol was found to be a good sensitizer. Before using, the substance was twice recrystallized from a 3% sulfuric acid solution and three times from water. Spectrographic analysis showed that no iron was present, and copper less than 0.001 p.p.m.

The nitrogen used was Linde nitrogen. It was washed with a 10% sodium hydroxide solution and with water, the last gas washing flask being in the same thermostat as the solution to be tested. The trace of oxygen in the nitrogen was not removed, because in the presence of a percompound and a catalyst the gas becomes contaminated with oxygen anyhow. For all experiments of one group, the nitrogen from the same cylinder was used. In several cases, the nitrogen was treated with an alkaline pyrogallol solution, but without visible advantage.

The solutions to be tested were in gas washing flasks, which had in their top a trap carrying a small vial with the ascorbic acid. The whole system was rinsed with a vigorous stream of nitrogen which entered through the trap, flowed from there downwards and then bubbled through the solution. After 10 minutes rinsing with nitrogen, the trap was pulled and the vial fell into the solution. The ascorbic acid dissolved very rapidly, but to make sure that nothing was

left undissolved in the vial, the flask was shaken a few seconds. By this arrangement, all experiments were well reproducible.

In all cases, ascorbic acid, as tested with 2,6-dichloroindophenol, was still present in large amount after the dye was bleached. Tables III and IV show that the efficiency of pentaerythritol increases with increase of its concentration.

TABLE III

EXPERIMENTS IN NITROGEN AT 25°, WITH SULFURIC ACID
10⁻¹ mole H₂O₂, 10⁻⁶ mole methyl orange, 10⁻⁶ g. atom Fe and 10⁻² mole ascorbic acid per liter 0.50 N H₂SO₄

Pentaerythritol, moles/liter × 10 ⁻³	Bleaching time in nitrogen in sec.	Efficiency, Q
..	810	..
5	324	60
10	193	76
20	126	84
30	104	87
40	90	89
50	74	91

TABLE IV

EXPERIMENTS IN NITROGEN AT 25° WITH PHOSPHORIC ACID
10⁻¹ mole H₂O₂, 10⁻⁶ mole methyl orange, 10⁻⁶ g. atom Fe and 10⁻² mole ascorbic acid per liter of 2 M H₃PO₄

Pentaerythritol, moles/liter × 10 ⁻³	Bleaching time in nitrogen in sec.	Efficiency, Q
..	1242	..
5	593	52
10	448	64
20	293	76
30	235	81
40	198	84
50	170	86

Formation of Hydrogen Peroxide.—Autoxidizing ascorbic acid generates hydrogen peroxide not only with copper, as is known, but also with iron as catalyst.² The first evidence was produced in an indirect way. Acidic solutions of ascorbic acid containing only ferric sulfate and *no* percompound were treated with air or oxygen and later tested for their bleaching power.

Table V shows some examples. The solutions were treated for 60 minutes with oxygen. Then the dye was added and nitrogen bubbled through. The color disappeared rather rapidly, proving that an oxidizing agent was present.

TABLE V

60 minutes pretreatment with oxygen at 25°, 10⁻² mole of ascorbic acid, 10⁻⁶ g. atom of Fe and 10⁻⁶ mole of methyl orange per liter

H ₂ SO ₄ , N	Bleaching time in nitrogen in minutes
0.01	39.2
.02	15.4
.03	13.0
.04	10.0
.05	8.6
.10	9.0
.40	8.8
1.00	8.7
2.00	13.5

Very instructive is the behavior of indigo carmine. Any pretreatment is in this case superfluous and no nitrogen is necessary. Bubbling oxygen through an acidic indigo solution in the presence of ferric ions and ascorbic acid brings about a quick bleaching, as can be seen from Table VI. The indigo oxidation is suppressed by the oxygen dissolved;

(2) Barron, DeMeio and Klempner, *J. Biol. Chem.*, **112**, 631 (1936), state that solutions of ascorbic acid, containing iron, buffered to pH 4.15 and 6.28, do not consume oxygen.

in return, the indigo autoxidation is promoted by the hydrogen peroxide formed (see Introduction).

TABLE VI

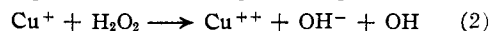
EXPERIMENTS WITH INDIGO CARMINE
10⁻⁶ mole of indigo, 10⁻² mole of ascorbic acid and 10⁻⁵ g. atom of Fe per liter at 25°

H ₂ SO ₄ , N	Bleaching time in oxygen in minutes
0.10	26.9
.20	18.4
.40	12.3
.50	10.8
1.00	9.2

The direct detection of the hydrogen peroxide formed is easy, if strongly acidic solutions are used. A solution of 10⁻³ mole of ascorbic acid and 10⁻³ g. atom iron per liter 1 N sulfuric acid was treated for 3 hours with oxygen. Upon titration with potassium iodide and 0.1 N sodium thiosulfate, 58.5% hydrogen peroxide was found, calculated on ascorbic acid added. Increasing the oxygen pressure raised the yield. Using air to replace oxygen decreased the yield to 27.5%.

The Autoxidation.—The great similarity between the iron and the copper effect indicates that in both cases the processes are analogous. The formation of hydrogen peroxide is for the kinetics of the sensitization of secondary significance as long as this percompound is present beforehand.

The autoxidation with copper as catalyst has been carefully investigated by several authors.³ They show that ascorbic acid AH₂ first forms an intermediate CuA which then decomposes, splitting off cuprous ions. However, as autoxidation produces hydrogen peroxide simultaneously, it can be expected that according to the equation



free hydroxyls are formed, as in the analogous reaction with ferrous ions. Taking into account the experience with methyl orange, it is easy to demonstrate that *autoxidizing acidic solutions of ascorbic acid really develop oxidation power.*

Since oxygen on the one hand is necessary, but on the other hand protects the dye, the oxidation effects are limited.⁴ Small quantities of oxygen give the best results, and sensitizers increase the effect. Table VII shows results of such experiments. Air was bubbled for two minutes through a 0.001 N sulfuric acid solution in which 10⁻⁶ mole of CuSO₄ and 10⁻⁵ mole of methyl orange per liter and the sensitizer were dissolved. One hundred ml. of this pretreated solution was shaken with 176.1 mg. of ascorbic acid for a few seconds and allowed to stand undisturbed.

TABLE VII

Sensitizer	Mole of sensitizer per liter	Bleaching time in minutes	Efficiency Q of sensitizer
.....	..	107	..
Methyl alcohol	1.0	32	70
Pentaerythritol	0.1	34	68

In another experiment, 100 ml. of a 0.001 N sulfuric acid solution containing 10⁻⁴ mole CuSO₄, 1.0 mole of methyl alcohol and 10⁻⁵ mole of methyl orange were shaken with 352.2 mg. of ascorbic acid in a 250-ml. mixing cylinder for 30 seconds. On standing afterwards without any agitation, bleaching took place within 3.0 minutes. If the shaking was uninterrupted, the bleaching time was much longer, namely, 27.3 minutes.

Experiments with oxygen gave similar results. A solution of the same composition but containing instead of methyl alcohol, 0.1 mole of pentaerythritol, treated in a gas washing flask for 30 seconds with oxygen and 352.2 mg. of ascorbic acid, was bleached afterwards within 3.5 minutes. With oxygen treatment uninterrupted, the bleaching time was 63 minutes.

(3) A. O. Dekker and R. G. Dickinson, *THIS JOURNAL*, **62**, 2165 (1940); E. Silverblatt, A. L. Robinson and C. G. King, *ibid.*, **65**, 137 (1943).

(4) Induced oxidation of lactic acid has been studied by W. P. Jorissen and A. H. Belinfante, *Rec. trav. chim.*, **55**, 374 (1936).

Sensitization without Ascorbic Acid.—Experiments were made to obtain sensitization by iron without the aid of ascorbic acid. The necessary ferrous salt, instead of being generated in the solution itself, was used as such. The acidic solution of methyl orange containing ferrous sulfate and methyl alcohol was violently stirred and hydrogen peroxide was added all at once. Marked sensitization took place if the solution was strongly acidic, the concentration of the hydrogen peroxide high, and that of the ferrous salt low. Detailed description will be published in a later paper, but one example is given here. Ten ml. of 1 *M* hydrogen peroxide, poured into 100 ml. of 1 *N* sulfuric acid containing per liter 5×10^{-4} mole of ferrous ammonium sulfate, 1 mole of methyl alcohol and 10^{-6} mole of methyl orange, decolorizes the red solution instantaneously. If no methyl alcohol is present, the color stays red.

An objection to these experiments may be raised in that they are made in air and that therefore peroxy derivatives of the alcohol may be formed which bring about the bleaching. To counter this objection, a method working in nitrogen was developed. Taking potassium persulfate instead of hydrogen peroxide, the same equipment as for the ascorbic acid method was used. The flask with the trap contained the acidic dye solution with the ferrous salt and the methyl alcohol. The persulfate used was twice recrystallized and was in the vial in the trap. The whole system was flushed with nitrogen. After dropping the vial, the flask was shaken by hand. The bleaching started immediately and was complete within a few seconds, often before all persulfate was dissolved. For a solution of the above composition, 0.40 g. of persulfate was used. If no methyl alcohol was present, no bleaching took place, and the solution was still red even after five hours.

Such experiments were made with various dyes. Using methyl alcohol, indigo carmine was instantly oxidized to the yellow isatin sulfonate. Without methyl alcohol, the solution remained blue.

Very interesting was the behavior of methylene blue. In the presence of methyl alcohol, not only oxidation but also reduction of the dye took place. After dropping the vial and shaking, the blue color disappeared instantaneously only to come back, although weaker, within a few seconds. The factors which control the competition between oxidation and reduction are under investigation.

Discussion

Thorough and important investigations about the influence of ferrous ions on the oxidation of organic substances with hydrogen peroxide have been made by I. M. Kolthoff and A. I. Medalia⁵ and by J. H. Merz and W. A. Waters.⁶ Their findings form a good basis for the explanation of the ascorbic acid effect.

Under the combined influence of ferrous ions and the percompound methyl alcohol or another sensitizer RH forms a radical R which has reducing power. Such organic free radicals reduce mercuric chloride to mercurous chloride, as Merz and Waters have shown for several organic compounds. These free radicals are probably also the cause of the

(5) I. M. Kolthoff and A. I. Medalia, *J. Polymer Sci.*, **4**, 377 (1949); *THIS JOURNAL*, **71**, 3777, 3784, 7789 (1949).

(6) J. H. Merz and W. A. Waters, *J. Chem. Soc., Suppl. Issue No. 1*, 515 (1949).

reduction of methylene blue to the leuco compound, observed in the experiments without ascorbic acid.

The accelerated dye oxidation cannot be based on such a radical which has reducing power. Peroxy derivatives of this radical such as ROO or ROOH as causes are excluded, since oxygen is not necessary and can be replaced by nitrogen. An increase of free hydroxyls by reactions such as $R + H_2O_2$ or $R + Fe^{+++}$ is likewise excluded, as can be shown clearly by mathematical analysis. This leads to the conclusion that, besides the radical R, another short lived substance appears in the solution. The assumption that R is formed by the reaction $RH + OH$ in one single step, is obviously too simple. This reaction seems to proceed *via* an intermediate which has oxidizing power.

Two concepts can be considered. One is: the first step in the impact of a free hydroxyl with an organic molecule is not removal of a hydrogen atom, but removal of an electron. RH is transformed into RH^+ . This cation is now the true oxidizing agent. It oxidizes by taking up an electron and reverting to its original state.

The other concept is related and is as follows: the free hydroxyl forms an addition product with the organic compound and the addition product $RH + OH$, besides decomposing, can react with hydrogen ions reversibly, giving $RH^+ + H_2O$.

The ideal sensitization would be a process in which no decomposition of the sensitizer takes place, only an oscillation between RH and RH^+ . The chain rupture $OH + Fe^{++}$ is suppressed, because it is supplanted by the main reaction $OH + RH$. The suppression of the chain ruptures and therefore the sensitization is the more perfect the higher the concentration of the sensitizer.

Ascorbic acid is much more readily oxidizable than methyl orange. In the described experiments, however, the dye is oxidized long before the ascorbic acid is consumed. This abnormal behavior is not found if instead of hydrogen peroxide or persulfate another oxidizing agent is used. If ascorbic acid is titrated with ceric sulfate and methyl orange, the behavior is normal and the attack of the dye takes place only when all ascorbic acid is oxidized.

The abnormal behavior indicates that the true oxidizing agent is not the free hydroxyl itself but the intermediate AH_2^+ formed from it. This intermediate cannot oxidize ascorbic acid, because such an attack would mean only an exchange of the positive charge. A sensitizer would be a substance whose activated state RH^+ is stable enough to be transferred on the ascorbic acid.

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