CHEMILUMINESCENCE DURING THE OXIDATION OF HISTAMINE BY POTASSIUM BROMATE ACTIVATED WITH TERBIUM

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The chemiluminescence (CL) observed during the oxidation of amines by peroxides has been investigated since the end of the last century [1-3]. This has enabled many data to be obtained on the mechanism of reactions between peroxides and amines [2].

In particular, it has been found that excited species are formed with a fairly high yield (up to 0.7%) during the stages of the reaction involving the participation of peroxy radicals $RO_2^{\cdot}$ and that the carbonyl compounds which are formed during the oxidation of amines are carriers of excitation energy [3]. Chemiluminescence during the oxidation of amines by compounds not belonging to the peroxide class such as, for example, the CL accompanying the oxidation of amino acids by potassium permanganate has been studied less [4].

In [5] we reported the observation of CL in yet another reaction of this type, in the oxidation of histamine by potassium bromate in aqueous solution. In the present paper more complete information is given concerning the mechanism of the formation and the nature of the excited species in this reaction. The choice of histamine as the reductant in the chemiluminescent reaction was due to the important role played by this biologically active amine in vital processes and the possibility of developing a straightforward method for its determination in blood and tissues.

EXPERIMENTAL

The apparatus used to record the CL was similar to that described in [6]. The oxidation reaction began after the addition of the histamine solution to a cell containing a sulfuric acid solution of $KBrO_3$. The solution in the cell also usually contained activator ions. A Hitachi MPF-4 spectrofluorimeter was used to investigate the photoluminescence of the terbium ions, and an apparatus based on an LGI-21 laser was employed to measure the lifetimes of the excited states of the molecules. All experiments were carried out at $\sim$20°C. The cp grade $KBrO_3$ was additionally purified by recrystallization from doubly distilled water, and the H_2SO_4 was distilled until there was no measureable absorption in the UV region ($\geqslant$200 nm). The cp grade lanthanide sulfates and the histamine dihydrochloride from the firm E. Merck AG and the remaining reagents (all cp grade or better) were employed without further purification.

DISCUSSION OF RESULTS

Effect of Activators on the Chemiluminescence. As was reported in [5], the CL during the oxidation of histamine was recorded in the presence of an activator, Tb^{3+} ions. A typical kinetic plot of the CL intensity is shown in Fig. 1. The spectral composition of the CL corresponds to the emission from excited Tb^{3+} ions. In the absence of an activator the emission intensity does not exceed the sensitivity level of the recording instrument ($2 \cdot 10^4$ photons/sec). This made it difficult to obtain reliable information on the spectral composition and kinetics of the nonactivated CL. An increase in CL intensity in the presence of the activator, without any change in its kinetics, would suggest that the activator solely acts as an energy acceptor. We were unable to compare the activated and unactivated CL, and it was therefore necessary to consider other possible reasons for its enhancement.

According to [7], $KBrO_3$ in concentrated HNO_3 solutions oxidizes Tb^{3+} to Tb^{4+}. However, the efficiency of this oxidation falls off sharply as the acid concentration decreases. Under our experimental conditions (0.02-0.75 mole/liter H_2SO_4) there was no evidence for any

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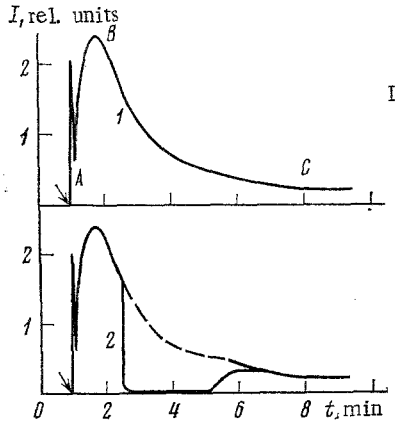


Fig. 1

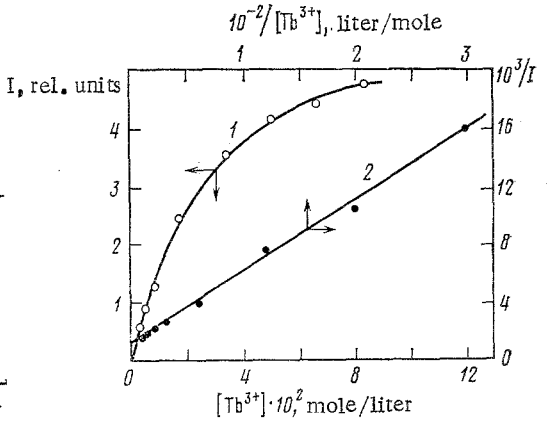


Fig. 2

Fig. 1. Kinetic curves for the intensity of the CL without an inhibitor (1) and with the addition of 10^{-4} mole/liter of hydroquinone during the course of the reaction (2). The moments when the reaction started and when the hydroquinone was added are shown by means of the arrows. $[KBrO_3]_0 = 1.9 \cdot 10^{-1}$, $[C_5H_9N_3]_0 = 2 \cdot 10^{-4}$, $[H_2SO_4] = 7 \cdot 10^{-1}$, and $[Tb^{3+}] = 2 \cdot 10^{-2}$ mole/liter, 20°C.

Fig. 2. The dependence of the CL intensity at the maximum B on the kinetic curves on the concentration of Tb^{3+} ions (1) and its linear anamorphism (2). $[C_5H_9N_3]_0 = 8 \cdot 10^{-4}$, $[KBrO_3] = 2 \cdot 10^{-1}$, $[H_2SO_4] = 7 \cdot 10^{-1}$ mole/liter, 20°C.

change in the valence state of the terbium as is also suggested by the absence of CL in control experiments (without the histamine). Furthermore, Tb^{3+} ions could speed up an oxidation reaction on account of the formation of complexes with histamine, for example. In this case, the practical absence of nonactivated CL could also be explained by the very low rate of the uncatalyzed oxidation reaction, since the CL intensity is directly proportional to the rate of the chemical reaction [1].

It may turn out that the excitation of the terbium ions is solely associated with specific catalytic steps and bears no relation to the formation of the excited state products in the uncatalyzed reaction. In order to choose between these possibilities we carried out a series of experiments with the addition of the activator to the reaction mixture at different intervals of time after the start of the reaction. It was found that the interaction of terbium ions with histamine has no significant effect on the rate of oxidation. For instance, the CL intensity curves recorded after the introduction of the activator with delays lying within the time interval BC in Fig. 1 agree within the limits of experimental error with the corresponding part of the control curve for the CL intensity which was observed in an experiment with preintroduction of the activator.

After delays in the introduction of the terbium ions corresponding to the segment AB, small deviations from the control curve were initially observed which were subsequently smoothed out. These deviations are possibly associated with complex formation between histamine and Tb^{3+} ions, but this only has a small effect on the oxidation of histamine by potassium bromate.

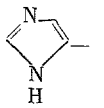
Hence, it may be assumed in a first approximation that Tb^{3+} ions solely act as energy acceptors. Without giving the details of the mechanism of the formation of the excited products (P*), a scheme may be written which solely describes the energy transfer process and the emission of light:

$$RCH_2CH_2NH_2 + KBrO_3 \rightarrow P^* + \text{products} \quad (1)$$

$$P^* \rightarrow P,\ P + h\nu_p,\ \text{products} \quad (k_d) \quad (2)$$

$$P^* + Tb^{3+} \rightarrow P + \overset{*}{Tb}{}^{3+} (k_t) \quad (3)$$

$$\overset{*}{T}b^{3+} \rightarrow Tb^{3+} + h\nu_{Tb} \qquad (4)$$

R = 

According to this scheme, the CL intensity (I) obeys the equation

$$\frac{I_0}{I} = 1 + \frac{k_d}{k_t}[Tb^{3+}]^{-1} \qquad (5)$$

where I_0 is the limiting value of I as $[Tb^{3+}] \to \infty$. It can be seen from Fig. 2 that the dependence of the CL intensity on the concentration of the activator is linearized when plotted in the coordinates of this equation. From the slope of this line, we find the ratio of the rate constants for the deactivation of the reaction product P* and for energy transfer, k_d/k_t = 0.04 mole/liter. If the diffusion-controlled value for the rate constant in water of $7 \cdot 10^9$ liter·mole^{-1}·sec^{-1} is taken as the limiting value of k_t, we obtain an estimate of the lower limit for the mean lifetime of the product P* in solution of $\tau = 1/k_d = 3.6 \cdot 10^9$ sec. Since the main contribution to k_d comes from nonradiative deactivation processes, i.e., quenching, the radiative lifetime τ_r of the product P* must be much greater. In order to estimate the quenching efficiency, we made use of the ratio of the limiting intensity of activated CL (I_0) to the sensitivity of the recording apparatus and obtained the value $\tau_r \geqslant 2 \cdot 10^{-4}$ sec.

The existence of unactivated CL was only successfully recorded when its intensity was enhanced by carrying out the oxidation in a deoxygenated solution. It was found that the intensity of activated CL also increased somewhat upon the removal of the dissolved oxygen, although $*Tb^{3+}$ ions are not quenched by oxygen. Hence, oxygen is a quencher of the product P*, which is the primary emitter of CL. This fact and the relatively large value of τ_r led us to conclude that the excited state of P is a triplet state. Estimation of the energy of this excited state of the primary emitter carried out by changing the activators did not contradict this conclusion. For instance, CL is also observed upon the introduction of Dy^{3+} ions and, moreover, its kinetics are the same as those when the activation is brought about by terbium ions and the ratio of the CL intensities approximately corresponds to the ratio of the luminescence quantum yields for these ions. No CL was observed when Gd^{3+} was introduced as the activator, although the luminescence quantum yield for this ion is no smaller than that for Tb^{3+}. Hence, k_t using activation of Gd^{3+} ions is much smaller than in the case of terbium and dysprosium ions. The most likely reason for this is the localization of the P* energy level between the excited luminescent levels of Dy^{3+} and Gd^{3+} (Fig. 3).

The triplet absorption band of carbonyl compounds corresponding to an $n \to \pi^*$ transition lies in this energy region [8]. A band due to vibrations of this group is revealed in the IR spectrum of the reaction products after separating them by extraction with butanol. The facts which have been laid out lead one to propose that a compound with a C=O group in the triplet-excited state is in fact formed during the course of the reaction.

Kinetics and Mechanism of Chemiluminescence. Amines are usually oxidized to the corresponding nitro compounds. However, in a number of cases such as, for example, under the action of various different oxidants, Ce^{4+}, $K_2S_2O_8$, and $KMnO_4$, on amino acids, deamination occurs [9-11]. The amino acid corresponding to histamine — histidine — is readily decarboxylated and deaminated [9-11]. Histamine is also deaminated during enzymatic oxidation in tissues [12]:

$$RCH_2CH_2NH_2 \xrightarrow[\text{diamineoxidase}]{+O_2 + H_2O} RCH_2CH{=}O \qquad (6)$$

It is obvious that deamination with the formation of ammonia and imidazolylacetaldehyde (IAA) is also the main process in the reaction of histamine with potassium bromate:

$$RCH_2CH_2NH_2 \xrightarrow{+BrO_3^- + H^+} RCH_2CH{=}O + NH_3 + \text{products} \qquad (7)$$

Obviously, H_2O and bromine compounds in the lower oxidation states will be among the reaction products since reaction of the bromate ion usually proceeds to Br^-. At the same time, BrO_2, BrO_2^-, $BrO^\cdot$, Br^-, and Br_2 are possibly formed as intermediate products [13]. The presence of Cl^- ions in solution can lead to the formation of BrCl.

The appearance of Br_2 and BrCl leads to the bromination of the histamine or its reaction products in the side chain and in the imidazole nucleus. The bromination of imidazole with

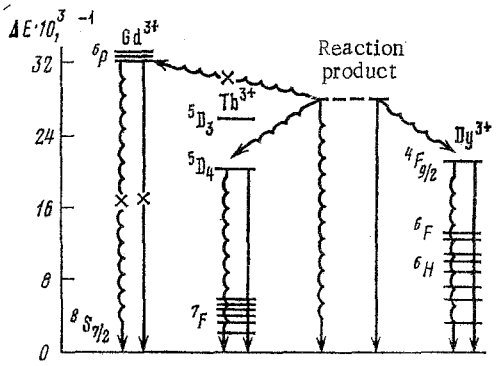


Fig. 3. Energy level scheme illustrating the process of energy transfer from the excited reaction product onto various different activators. Solid lines indicate radiative transitions; wave-like lines represent nonradiative transitions.

TABLE 1. Effect of $[KBrO_3]$ and $[C_5H_9N_3]$ on the Consumption of the Intermediate Product during the Oxidation of Histamine ($[H_2SO_4]$ = 0.73 mole/liter)

$[C_5H_9N_3]_0$	$[KBrO_3]_0$	k_2', sec^{-1}	$k_2=k_2'/[KBrO_3]$, liter·mole^{-1}·sec^{-1}
mole/liter			
$1{,}25\cdot10^{-3}$	$1{,}87\cdot10^{-2}$	$1{,}9\cdot10^{-3}$	$1{,}0\cdot10^{-1}$
$1{,}25\cdot10^{-3}$	$1{,}25\cdot10^{-1}$	$1{,}3\cdot10^{-2}$	$1{,}0\cdot10^{-1}$
$1{,}87\cdot10^{-4}$	$1{,}25\cdot10^{-1}$	$9{,}4\cdot10^{-3}$	$0{,}75\cdot10^{-1}$

Br_2 has been described in [14], and the bromination of histamine and serotonin by BrCl in [15]. The efficiency of this reaction is dependent on the pH of the medium and other conditions. However, according to our postulate, CL solely arises during the initial steps of the oxidation.

For instance, spectrophotometric monitoring of the Br_2 absorption band has shown that, during the time when CL is observed (30-40 min), no free Br_2 is revealed in the solution (less than $2\cdot10^{-5}$ mole/liter) and its appearance is only recorded 2-3 h after the start of the reaction. Furthermore, there is no CL during the direct bromination of histamine by Br_2 and BrCl in acid solutions. In addition, we found that Br^- ions quench the CL strongly while Cl^- ions quench the CL to a lesser extent. It seems most likely that the CL reflects the formation of the excited IAA molecules (reaction 7). The observation of weak CL activated by terbium ions during the oxidation of histamine by Ce^{4+} ions is evidence in favor of this.

The kinetics of chemiluminescence reflect the occurrence of a number of consecutive stages leading to the formation of the excited product. Several parts have been separated in Fig. 1: an initial brief flash of light, the growth of the emission up to a maximum, and a decay over a long period in which the presence of a second weak maximum is noticeable.

The complex form of the curve may be associated with the quenching of the primary emitter or the activator of the chemiluminescence by reactants and reaction products. At high concentrations of the activator almost all the excited molecules transfer energy to the activator, and only the processes involved in its quenching are of significance. We have studied the possible reactions involved in the quenching of $^*Tb^{3+}$ by all of the substances investigated in this work and, additionally, have monitored the intensity of the photoluminescence of the terbium ions during the course of the reaction. When this was done, no effect of the reactants or the reaction products on the photoluminescence yield of the terbium ions was revealed. Consequently, the kinetics of the CL is in fact due to the stepwise nature of the oxidation process.

The introduction of a typical inhibitor of free-radical reactions — hydroquinone — leads to a pronounced reduction in the intensity of the CL, although the emission is restored after

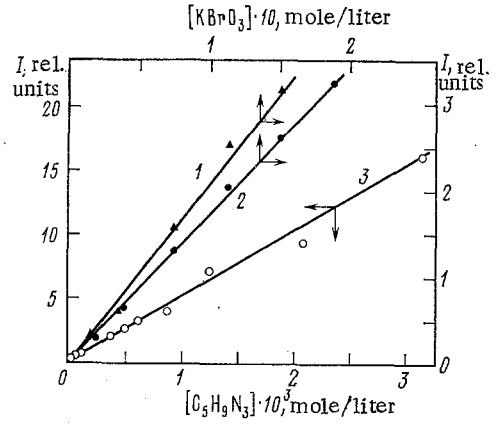


Fig. 4. The dependence of the CL intensity at the maximum B on the kinetic curves on the concentrations of $KBrO_3$ (1, 2), and histamine (3). $[Tb^{3+}] = 1.2 \cdot 10^{-2}$ mole/liter, $[H_2SO_4] = 1.2 \cdot 10^{-1}$ mole/liter for line 1 and $6.2 \cdot 10^{-1}$ mole/liter for lines 2 and 3. $[C_5H_9N_3]_0 = 6.2 \cdot 10^{-4}$ mole/liter for lines 1 and 2 and $[KBrO_3]_0 = 1.9 \cdot 10^{-1}$ mole/liter for line 3.

a certain time (see Fig. 1). It is obvious that this restoration of the CL is associated with the consumption of the inhibitor. It is possible that the oxidation process also includes steps involving radicals which play an important role in CL. It also appeared that the reaction is heterogeneous. The addition of finely ground glass during the course of the reaction with the aim of increasing the overall surface area of the walls led to a bright flash after which the emission became on a higher level than before the addition of the glass, although the condition under which the light was recorded worsened at the same time. It seems likely that the initial flash, the intensity of which is poorly reproducible, is associated with a heterogeneous process involved in the formation of reactive species from the histamine and BrO_3^-. It is possible that a complex formed from protonated histamine molecules and a BrO_3^- ion enters into reaction with BrO_3^-. We have not succeeded up to now in explaining the nature of the excited species responsible for the initial flash. At the same time, the changes in the kinetics of the CL on the ABC segment (see Fig. 1) which occur when the concentrations of histamine, BrO_3^-, and H_2SO_4 are varied do in fact suggest that this segment of the curve describes the kinetics of the reaction between histamine and $KBrO_3$.

The presence of the maximum B on the CL intensity curve indicates that an intermediate product X is formed in the reaction; i.e., the emission arises as the result of the formation of IAA* molecules in consecutive reactions: $C_5H_9N_3 + KBrO_3 \rightarrow X \rightarrow IAA^*$. The CL intensity is proportional to the rate of the second step and "follows" the concentration of the intermediate product, the dependence of which on time is a curve with a maximum [16] (for simplicity, the second weak maximum on the decaying part of the intensity curve is not considered). From the shape of this curve it may also be concluded that the formation of X is more rapid than its consumption. This enabled us to analyze the kinetics of the CL on these parts of the kinetic curve separately. It was found that the kinetics obey a first-order rate law on the part of the curve BC when there is an excess of BrO_3^-. The time required to reach the maximum and the first-order rate constant on the decaying part of the curve are independent of the initial histamine concentration but vary as the concentration of $KBrO_3$ is changed. At the same time, the $K/[KBrO_3]$ ratio remains constant (Table 1); i.e., the consumption of X is a pseudounimolecular process. The time required to reach the maximum is inversely proportional to the concentration of BrO_3^-. These data allow one to explain the kinetic curve by means of a scheme of consecutive-parallel reactions:

$$C_5H_9N_3 + KBrO_3 \xrightarrow{k_1} X \quad (8)$$

$$X + KBrO_3 \xrightarrow{k_2} IAA^* \quad (9)$$

With an excess of BrO_3^-, we shall have two consecutive first-order reactions ($k_1' = k_1[KBrO_3]$, $k_2' = k_2[KBrO_3]$), the kinetic features of which have been studied in [16]. In particular, the

TABLE 2. Effect of Sulfuric Acid on the Rate of the Consecutive Stages in the Oxidation of Histamine ($[C_5H_9N_3]_0$ = $1.25 \cdot 10^{-3}$, $[KBrO_3]_0 = 6.12 \cdot 10^{-2}$ mole/liter)

$[H_2SO_4]$, mole/liter	k_1	k_2
	liter · mole^{-1} · sec^{-1}	
0,023	$5,9 \cdot 10^{-2}$	$5,5 \cdot 10^{-3}$
0,15	$4,9 \cdot 10^{-1}$	$1,6 \cdot 10^{-2}$
0,65	1,1	$6,9 \cdot 10^{-2}$

time required to reach the maximum t_m is solely determined by the ratio of the rate constants for the first and second reactions:

$$t_m = \frac{\ln (k_2'/k_1')}{k_2' - k_1'} = \frac{\ln (k_2/k_1)}{[KBrO_3](k_2 - k_1)} \quad (10)$$

and must not depend on the concentration of the histamine. The CL intensity is proportional to the rate of the second reaction, $I = \eta k_2 [X][KBrO_3]$ (η is the proportionality constant), and must depend on the concentration of the histamine and the $KBrO_3$. For example, at the point B at which the rates of the first and second reactions are equal, we have

$$k_1 [C_5H_9N_3][KBrO_3] = k_2 [X][KBrO_3] \text{ or}$$

$$[X] = \frac{k_1}{k_2} [C_5H_9N_3]$$

The time t_m is independent of the concentration of histamine and hence we obtain $[X]_m = \theta [C_5 \cdot H_9N_3]_0$. Allowing for the fact that when there is a large excess of BrO_3^- its concentration barely varies, we obtain a linear dependence for the CL intensity on the initial concentration of both the histamine and the $KBrO_3$:

$$I_m = \eta k_2 \theta [C_5H_9N_3]_0 [KBrO_3]_0 = \varkappa [C_5H_9N_3]_0 [KBrO_3]_0 \quad (11)$$

These dependences are observed experimentally (Fig. 4). By determining the constant k_2' from the part of the curve BC and solving Eq. (10), k_1' and k_1 can be calculated. The dependence of the rate constants for reactions (8) and (9) determined in this manner on the concentration of H_2SO_4 is shown in Table 2. As $[H_2SO_4]$ is increased, the rates of both reactions speed up, which is in accord with the assumption concerning the participation of BrO_3^- in both stages and with the data on the effect of $[H_2SO_4]$ on the rate of oxidation–reduction reactions of this ion [17].

By measuring the total amount of light emitted during the reaction with the aid of a standard light source and assuming that it corresponds to the complete oxidation of histamine to IAA, we shall estimate the excitation yield: $\eta_{exc} = 5 \cdot 10^{-8}$ excited molecules per oxidized molecule of histamine. This value should be considered as a lower limit for η_{exc} in the still unknown elementary step. We note that, in spite of the small value of η_{exc}, activated CL enables one to determine down to 10^{-5} mole/liter of histamine in a sample volume of 1 ml. The detection limit is easily lowered by using a more sensitive light detector and an activator with a photoluminescence quantum yield close to unity. The high sensitivity and technical simplicity of the chemiluminescence monitoring of the reaction being studied means that it may be recommended as the basis for the determination of histamine.

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CONCLUSIONS

1. We have detected and investigated chemiluminescence (CL) during the oxidation of the biologically active amine, histamine, which can be used for analytical purposes.

2. The primary emitter of the chemiluminescence, which is most probably imidazolylacetaldehyde, is formed in the triplet state with an energy in the range from 2.60 to 3.98 eV.

3. Tb^{3+} ions do not accelerate the oxidation of histamine but activate the chemiluminescence via an energy transfer mechanism.

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KINETICS AND MECHANISM OF HYDROLYSIS OF LACTAMS IN AQUEOUS H_2SO_4 SOLUTIONS

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Lactams, like other amides, are subject to hydrolysis by the catalytic action of acids. Kinetic and mechanistic studies of the acid hydrolysis of lactams are of interest in evaluating their stability in acid solutions and in establishing the nature of the catalytic activity of acids and the relationship between the structure and reactivity of amides. A detailed kinetic study of lactam hydrolysis was published quite recently [1]. Data on the hydrolysis of ε-caprolactam at 97°C in aqueous solutions of $HClO_4$ and H_2SO_4 were presented in [2]. The work reported in [3-5] was devoted to the determination of the relative hydrolysis rates of lactams with different numbers of atoms in the ring.

The present work has been aimed at investigating the hydrolysis of γ-butyrolactam, δ-valerolactam, ε-caprolactam, and enantholactam in aqueous H_2SO_4 solutions at elevated temperatures, in order to establish the mechanisms of the equilibrium and the limiting stages.

EXPERIMENTAL

The pure grade γ-butyrolactam was distilled twice under vacuum. The fraction with bp 133°C at 12 mm was taken, corresponding to the literature data [6]. The pure-grade ε-caprolactam was recrystallized twice from ethanol and dried for one day over P_2O_5, mp 68°C (compare [6]). The cp grade δ-valerolactam, mp 39°C, and the cp grade enantholactam, mp 39°C, were kindly furnished to us by staff members of the Chemistry Department at Moscow State

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