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The Kinetics and Mechanism of the Chlorine Dioxide−Iodide Ion Reaction

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The oxidation of iodide ion by chlorine dioxide has been studied by stopped-flow techniques at $I = 1.0$ M ($NaClO_4$). The following two-term rate law was confirmed for the reaction: $-d[ClO_2]/dt = k_I[ClO_2][I^-] + k_{II}[ClO_2][I^-]^2$. The rate constants at 298 K and the activation parameters are $k_I = (1.87 \pm 0.02) \times 10^3$ M^{-1} s^{-1}, $\Delta H_I^\ddagger = 35.4 \pm 0.7$ kJ/mol, $\Delta S_I^\ddagger = -63.5 \pm 2.3$ J/(mol K), $k_{II} = (1.25 \pm 0.04) \times 10^4$ M^{-2} s^{-1}, $\Delta H_{II}^\ddagger = 36.7 \pm 1.3$ kJ/mol, $\Delta S_{II}^\ddagger = -43.2 \pm 4.6$ J/(mol K). Both the second- and third-order paths are interpreted in terms of an outer-sphere electron-transfer mechanism. The calculations based on the Marcus theory yield $k_I = 1358$ M^{-1} s^{-1} for the second-order path.

Introduction

The redox reaction between chlorine dioxide and iodide ion has been the subject of intense studies for decades.[1−4] This reaction serves as a basis for the iodometric determination of ClO_2.[5] It is also an important subset in a series of oxychlorine-based exotic reactive systems.[4,6,7]

Earlier it was suggested[2] that the oxidation of iodide ion by ClO_2 proceeds via the fast formation and subsequent slower decomposition of a transient species, ClO_2I^-. Recently a more simple kinetic behavior was reported by Lengyel et al.[4] The reaction was found to be first order with respect to both reactants. It was assumed that the rate-determining step in the overall process is a simple electron-transfer reaction between the reactants. The details of the mechanism were not discussed in that paper, and kinetic data are not available to evaluate whether the electron transfer occurs by means of an inner- or outer-sphere process. Therefore, we have designed a temperature dependent study in order to explore the intimate nature of this reaction. Preliminary results indicated a somewhat unexpected kinetic behavior, which is discussed in the present paper in detail.

Experimental Section

Chemicals. Chlorine dioxide solutions were prepared by mixing aqueous solutions of $K_2S_2O_8$ and $NaClO_2$ as described earlier.[8] The concentration of the ClO_2 stock solutions was determined spectrophotometrically by using the characteristic absorbance band[9] of ClO_2 in the near-UV−visible region (λ_{max}= 358.5 nm; $\epsilon_{max} = 1250$ $M^{-1}cm^{-1}$). $NaClO_4$ was prepared from Na_2CO_3 and $HClO_4$ and purified as detailed elsewhere.[10] Other reagents, i.e., NaI, CH_3COONa, and CH_3COOH, were analytical grade and used without further purification. All experiments were carried out in 0.04 M acetic acid/acetate buffer and at 1.0 M ionic strength set by adding appropriate amounts of $NaClO_4$.

Methods. Stopped-flow traces were recorded on an Applied Photophysics SX-17MV unit. Pseudo-first-order conditions were applied by using at least a 10-fold excess of iodide ion over chlorine dioxide ($[ClO_2] = (2.0-8.0) \times 10^{-4}$ M; $[I^-] = 0.006-0.3$ M). The reaction was monitored by following the formation of I_3^- in the 350−470 nm region. First-order rate constants were obtained by fitting the average of at least five replicate runs by using a nonlinear least squares routine provided with the stopped-flow instrument. In test experiments, the rate constants obtained at various wavelengths agreed within ±2%. Thus, most of the measurements were made at a single wavelength (400 or 410 nm). The temperature dependence of the rate constants was studied from 3 to 46 °C.

Results and Discussion

In excess iodide ion, ClO_2 is reduced to Cl^-. However, in slightly acidic to neutral solutions the reaction occurs in two, well-separated phases. In the first, fast step, chlorine dioxide is reduced to ClO_2^-. Further redox reaction between chlorite ion and iodide ion is slower by several orders of magnitude and does not interfere with the first process. Under the applied conditions, the observed kinetic traces correspond to the following overall redox reaction:

$$2ClO_2 + 2I^- = 2ClO_2^- + I_2 \qquad (1)$$

In agreement with recent results,[4] simple first-order kinetic traces were obtained, indicating that the reaction is first order with respect to ClO_2. Our observations also confirmed that the reaction rate is independent of pH. The pseudo-first-order rate constants (k_{obs}) are statistically identical in the pH 4.09−5.04 region (Figure 1). However, Figure 1 also indicates an

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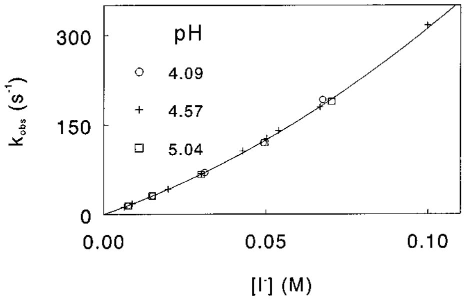

Figure 1. The pseudo-first-order rate constant as a function of iodide concentration at various pH values (25.0 °C, $I = 1.0$ M NaClO$_4$).

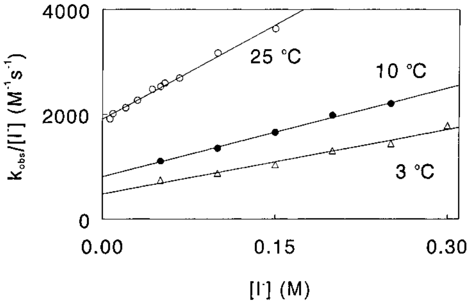

Figure 2. The plot of the data at various temperatures according to eq 4 (pH = 4.57, $I = 1.0$ M NaClO$_4$).

unexpected kinetic feature in this system. According to previous literature the reaction is first order with respect to iodide ion. This would predict a simple linear concentration dependence of k_{obs} on [I$^-$]. However, the systematic deviation from linear behavior at higher iodide ion concentrations clearly indicates a more complex kinetic pattern. The problem was investigated in an extended concentration range of iodide ion at various temperatures.

The concentration dependence of the rate constants was consistent with the following rate law:

$$-d[ClO_2]/dt = k_I[ClO_2][I^-] + k_{II}[ClO_2][I^-]^2 \qquad (2)$$

It follows that

$$k_{obs} = k_I[I^-] + k_{II}[I^-]^2 \qquad (3)$$

and eq 3 can be rearranged into the following form:

$$k_{obs}/[I^-] = k_I + k^{II}[I^-] \qquad (4)$$

The plot of the experimental data according to eq 4 is shown at three different temperatures in Figure 2. The excellent linearity of these plots confirms the above rate law.

The activation parameters of rate constants k_I and k_{II} were calculated by fitting k_{obs} data on the basis of eq 5, by using the nonlinear least squares routine of the program SCIENTIST 2.0.[11] Experimental and calculated rate constants are given in the Supporting Information. The results are listed in Table 1.

$$k_{obs} = \frac{kT}{h}e^{\Delta S_I^{\ddagger}/R}e^{-\Delta H_I^{\ddagger}/(RT)}[I^-] + \frac{kT}{h}e^{\Delta S_{II}^{\ddagger}/R}e^{-\Delta H_{II}^{\ddagger}/(RT)}[I^-]^2 \qquad (5)$$

The value of k_I is about 3 times smaller than the rate constant reported by Lengyel and co-workers;[4] however, the source of the discrepancy is not apparent. Perhaps the omission of the third-order term, i.e., the second term in eq 2, led to a higher rate constant in the earlier paper.

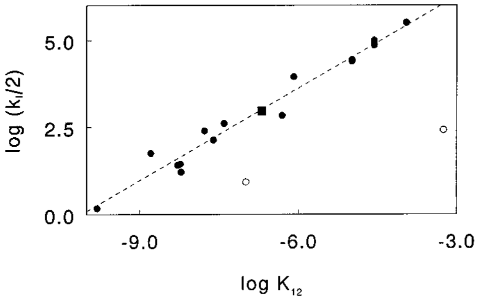

Figure 3. LFER for the second-order path of oxidation reactions of I$^-$. The oxidants are as follows: Fe(phen)$_3^{3+}$, Fe(5,6-(CH$_3$)$_2$-phen)$_3^{3+}$, Fe(4,7-(CH$_3$)$_2$-phen)$_3^{3+}$, Fe(3,4,7,8-(CH$_3$)$_4$-phen)$_3^{3+}$, Fe(bpy)$_3^{3+}$, Fe(4,4′-(CH$_3$)$_2$-bpy)$_3^{3+}$, IrCl$_6^{2-}$, IrBr$_6^{2-}$, Mo(CN)$_8^{2-}$, Os(bpy)$_3^{3+}$, Os(phen)$_3^{3+}$ (●); ClO$_2$ (■); NpO$_2^{2+}$, PuO$_2^{2+}$ (○). The data were used as given or cited in refs 13−15.

Table 1. Kinetic Results for the Oxidation of I$^-$ by Chlorine Dioxide

parameter	
k_I (M^{-1} s^{-1}) at 298 K	(1.87 ± 0.02) × 10^3
$\Delta H_I^{\ddagger}$ (kJ/mol)	35.4 ± 0.7
$\Delta S_I^{\ddagger}$ (J/(mol K))	−63.5 ± 2.3
k_{II} (M^{-2} s^{-1}) at 298 K	(1.25 ± 0.04) × 10^4
$\Delta H_{II}^{\ddagger}$ (kJ/mol)	36.7 ± 1.3
$\Delta S_{II}^{\ddagger}$ (J/(mol K))	−43.2 ± 4.6

The two-term rate equation obtained here is quite common in the noncomplementary redox chemistry of iodide ion.[12−16] Equation 2 seems to be consistent with the following mechanism:

$$ClO_2 + I^- \rightleftharpoons ClO_2I^- \qquad K_a\text{, fast pre-equilibrium} \qquad (6)$$

$$ClO_2I^- \rightarrow ClO_2^- + I^{\bullet} \qquad k_1 \qquad (7)$$

$$I^{\bullet} + I^- = I_2^- \qquad \text{fast} \qquad (8)$$

$$ClO_2I^- + I^- \rightarrow ClO_2^- + I_2^- \qquad k_2 \qquad (9)$$

$$ClO_2 + I_2^- = ClO_2^- + I_2 \qquad \text{fast} \qquad (10)$$

$$I_2 + I^- = I_3^- \qquad \text{fast} \qquad (11)$$

In this mechanism ClO$_2$I$^-$ is either an outer-sphere complex or a weakly bonded species characterized by stability constant K_a. Provided that I$^{\bullet}$ and I$_2^-$ are at steady state, standard derivation yields $k_I = 2k_1K_a$ and $k_{II} = 2k_2K_a$. In principle reaction 7 is reversible. However, reaction 8 is close to diffusion controlled,[17] and under the applied conditions the reverse step of reaction 7 is negligible compared to the fast formation of I$_2^-$.

On the basis of a somewhat limited data set Stanbury and co-workers[15] showed excellent LFER for the k_I path. The correlation remains valid when additional data are included (Figure 3). The data for the ClO$_2$−I$^-$ reaction is also in

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agreement with previous results. The correlation was observed regardless of the charge and type of the oxidants. The only exceptions are the data for the reactions of PuO_2^{2+} and NpO_2^{2+} (open circles in Figure 3). In these cases the deviation is supposedly due to the nonadiabaticity of the electron-transfer reaction.[15] The rest of the data indicates that probably the same mechanism is operative in all reactions which have the same, close to diffusion-controlled reverse rate constant. Earlier it was suggested that these reactions proceed via an outer-sphere mechanism.[15,16] On this basis, the Marcus theory[18] was tested by using the following equations:

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{12}$$

$$\log f = \frac{(\log K_{12})^2}{4 \log k_{11}k_{22}/Z^2} \tag{13}$$

In eq 13, k_{12} ($= k_1K_a$) and K_{12} are the rate constant and equilibrium constant for the cross reaction:

$$ClO_2 + I^- = ClO_2^- + I^\bullet \tag{14}$$

Parameters k_{11}, k_{22}, and Z ($\sim 10^{11}$ M^{-1} s^{-1}) are the self-exchange rate constants and the collision frequency, respectively. It should be noted that one of the reactants is neutral in both redox couples; therefore, work terms do not complicate the calculation of the rate constant.

Due to the protolytic equilibrium[10] between chlorite ion and chlorous acid ($pK_a = 1.72$) the redox potential for the ClO_2/ClO_2^- couple is pH dependent.[19] However, in slightly acidic to neutral (pH > 4.0) solutions the dominant species is ClO_2^- and the redox potential[20] is invariably $E° = 0.936$ V. The self-exchange rate constant for the same couple was reported recently,[21] $k_{11} = (2.6-6.7) \times 10^4$ M^{-1} s^{-1} (average: 3.3×10^4 M^{-1} s^{-1}).

The parameters for the $I^\bullet/I^-$ couple are more controversial. On the basis of theoretical calculations, Woodruff and Margerum[22] estimated that $E° = +1.42$ V. According to Stanbury and co-workers[15] this value would be consistent with a larger than diffusion-controlled rate constant for the reverse step of reaction 14. Their estimate for $E°$ is +1.33 V. For the self-exchange rate constant two markedly different values were published. Adedinsewo and Adegite have reported[14] $k_{22} = 7 \times 10^7$ M^{-1} s^{-1}. However, on the basis of that paper, it is not clear if this value is given for the $I^\bullet/I^-$ or the $I^\bullet/I_2^-$ couple. The considerably smaller than expected diffusion-controlled rate constant was attributed to solvent reorganization in the activation process. Stanbury and co-workers concluded 1.4×10^9 M^{-1} s^{-1} as a lower limit for the same rate constant.[15] This value seems to be more reasonable for redox couples involving a radical species. The results presented here lend further support to the conclusions of Stanbury and co-workers. When their data was used, a satisfactory agreement was found between the experimental and calculated rate constants for the cross reaction, $k_{12}^{exp} = 926$ M^{-1} s^{-1} and $k_{12}^{calc} = 679$ M^{-1} s^{-1}. With other literature parameters, much larger deviations were obtained between these values.

In the case of related reactions of iodide ion, earlier attempts for the interpretation of the third-order term in eq 2 were based on the Marcus theory. Without specifying the actual redox couples, Adedinsewo and Adegite suggested that the values of f and k_{11} (eqs 12 and 13) are the same for both the second- and third-order terms.[14] According to their suggestion, k_I and k_{II} can be related to each other on the basis of thermodynamic considerations, and the k_{II}/k_I ratio should be around 300 M^{-1}. For most of the available data the actual k_{II}/k_I ratio is within 1 order of magnitude of the expected value. Clearly, our results for the ClO_2-I^- system do not comply with the expectations ($k_{II}/k_I \sim 7$ M^{-1}).

Table 2. Test of the Marcus Cross Relation for the Third-Order Path[a,b]

oxidant[c]	ϵ_{22} (V)	k_{22} (M^{-1} s^{-1})	k_{12}^{meas} (M^{-1} s^{-1})	k_{12}^{calc} (M^{-1} s^{-1})
$IrBr_6^{2-}$	0.843	2.0×10^8	4.3×10^3	7.6×10^3
V(III)	−0.255	1.0×10^{-2}	1.8×10^{-14}	5.1×10^{-14}
$Os(phen)_3^{3+}$	0.840	3.1×10^8	1.7×10^4	8.8×10^3
$Os(bpy)_3^{3+}$	0.837	1.8×10^8	9.2×10^3	6.3×10^3
$Fe(5,6\text{-}(CH_3)_2\text{-phen})_3^{3+}$	0.97	3.3×10^8	1.6×10^6	1.5×10^5
$Fe(4,7\text{-}(CH_3)_2\text{-phen})_3^{3+}$	0.87	3.3×10^8	1.3×10^6	1.8×10^4
$Fe(3,4,7,8\text{-}(CH_3)_4\text{-phen})_3^{3+}$	0.81	3.3×10^8	5.4×10^4	4.6×10^3
$Fe(4,4'\text{-}(CH_3)_2\text{-bpy})_3^{3+}$	0.88	3.3×10^8	2.6×10^4	2.2×10^4
ClO_2	0.934[d]	3.3×10^4 [e]	6.5×10^3 [f]	7.3×10^2

[a] For the $2I^-/I_2^-$ couple: $\epsilon_{11} = 1.04$ V, $k_{11} = 1.15 \times 10^3$ M^{-1} s^{-1} from ref 15. [b] ϵ_{22}, k_{22}, and k_{12} values were taken as cited in refs 13, 14, and 15. [c] phen, 1,10−phenanthroline; bpy, 2,2′-bipyridine. [d] From ref 20. [e] From ref 21. [f] This work.

The main problem with the considerations of Adedinsewo and Adegite is that the Marcus theory cannot be directly applied for the overall third-order term. This problem was discussed by Stanbury and co-workers in detail.[15] The theory implies a bimolecular electron exchange process (k_{11}) between $2I^-$ and I_2^-, which was interpreted by postulating the highly hypothetical I^-,I^- species.[15,23] With this self-exchange process the Marcus theory predicted the rate constants for a few selected reactions reasonably well.[15] In other cases, including the ClO_2-I^- reaction, the agreement is less satisfactory (Table 2).[24] In order to justify the proposed self-exchange process the Franck−Condon barrier was estimated for the $I_2^-/I^-,I^-$ redox couple on the basis of various models.[23] Still, a quantitative interpretation of the reorganizational energies and an exact description of the self-exchange process could not be given.

The third-order term requires the formation of a transition species with a composition of $ClO_2I_2^{2-}$. By analogy with the other path, eq 9 can be rewritten in the following form:

$$ClO_2I^- + I^- \rightleftharpoons ClO_2I_2^{2-} \qquad K_{a2}\text{, fast pre-equilibrium} \tag{9a}$$

$$ClO_2I_2^{2-} \rightarrow \{ClO_2I^{2-} + I^\bullet\} \rightarrow ClO_2^- + I^- + I^\bullet \qquad k_{2b} \tag{9b$_1$}$$

or

$$ClO_2I_2^{2-} \rightarrow ClO_2^- + I_2^- \qquad k_{2b} \tag{9b$_2$}$$

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(24) In ref 15, k_{11} was defined for a third-order process which led to incompatible dimensions in eqs 12 and 13. The problem was corrected in ref 23 by introducing the ion-pair formation constant, K_{IP}, for the I^-,I^- species. While the new interpretation of the self-exchange reaction between I_2^- and I^-,I^- resolves the problem of incompatibility, it does not significantly modify the value of the calculated rate constants for the cross reactions.

Table 3. Activation Parameters for the Oxidation of Iodide Ion

oxidant	$\Delta H_I^\ddagger$ (kJ/mol)	$\Delta S_I^\ddagger$ (J/(mol K))	$\Delta G_I^{\ddagger\ 298}$ (kJ/mol)	$\Delta H_{II}^\ddagger$ (kJ/mol)	$\Delta S_{II}^\ddagger$ (J/(mol K))	$\Delta G_{II}^{\ddagger\ 298}$ (kJ/mol)	$\Delta H_{II}^\ddagger - \Delta H_I^\ddagger$ (kJ/mol)	$\Delta G_{II}^\ddagger - \Delta G_I^\ddagger$ (kJ/mol)
$Os(bpy)_3^{3+}$ [a]	72.9	−31.0	82.1	38.1	−41.9	50.6	−34.8	−31.5
$Os(phen)_3^{3+}$ [a]	57.4	−16.7	62.4	31.4	−54.4	47.6	−26.0	−14.8
$IrBr_6^{2-}$ [b]	33.1	−100.5	63.1	17.7	−110.5	50.6	−15.4	−12.5
ClO_2 [c]	35.4	−63.5	54.3	36.7	−43.2	49.6	1.3	−4.7

[a] Reference 13. [b] Reference 15. [c] This work.

This approach assumes that (i) the fast formation of a second outer-sphere complex precedes the actual redox step and (ii) the rate-determining step is the electron-transfer process within the complex. Thus, the experimentally determined rate constant can be given as follows: $k_{II} = 2k_{2b}K_aK_{a2}$. As indicated, the immediate products of the redox step are not well defined in this case. Therefore, successful application of the Marcus theory, which requires the exact knowledge of the self-exchange electron-transfer steps, seems to be extremely difficult. In earlier studies with $Os(phen)_3^{3+}$ and $Os(bpy)_3^{3+}$ as oxidants,[13] it was suggested that the $\Delta H_{II}^\ddagger - \Delta H_I^\ddagger$ difference is roughly equal to the enthalpy of formation of the I_2^- radical ($\Delta H° = -23.4$ kJ/mol[25]). This led to a conclusion that the actual electron-transfer step is associated with the same $I^- - I^\bullet$ bond formation as the formation of I_2^-. According to these considerations I_2^- would form directly from the outer-sphere complex in reaction 9b₂. As shown in Table 3, in other systems the agreement between $\Delta H_{II}^\ddagger - \Delta H_I^\ddagger$ and ΔH° is not so convincing. The observed deviations may indicate either that the reactions proceed via a different path or that other factors also have significance in the activation process.

Mechanistic details of the third-order path can be evaluated by comparing k_I and k_{II}. The ratio of these rate constants is given as follows: $k_{II}/k_I = (2k_{2b}K_aK_{a2})/(2k_1K_a) = (k_{2b}/k_1)K_{a2}$. The value of K_a in this expression can be estimated on the basis of the Fuoss equation.[26] According to literature data, the stability constant of the outer-sphere complex between a charged and a neutral species is around 0.3 M^{-1} in the absence of specific interactions.[27] The estimation of K_{a2} is less straightforward; however, on the basis of electrostatic and statistical considerations, it is probably even smaller than K_a. Accordingly, by using the data from Table 1, $k_{2b}/k_1 > 7.0$. This indicates that the electron transfer within the precursor complex is more favorable in the third-order process than in the second-order path. We can reach the same conclusion on the basis of the activation parameters. The experimentally determined free activation energies and their difference can be expressed as follows:

$$\Delta G_I^\ddagger = \Delta G_1^\ddagger + \Delta G_a + \ln 2$$

$$\Delta G_{II}^\ddagger = \Delta G_{2b}^\ddagger + \Delta G_a + \Delta G_{2a} + \ln 2$$

$$\Delta G_{II}^\ddagger - \Delta G_I^\ddagger = \Delta G_{2b}^\ddagger - \Delta G_1^\ddagger + \Delta G_{2a}$$

On the basis of these equations, and provided that $K_{2a} < 1.0$ ($\Delta G_{2a} > 0$) $\Delta G_{2b}^\ddagger - \Delta G_1^\ddagger < -4.7$ kJ/mol (Table 3), i.e., the energy barrier of the electron transfer is smaller through the k_{II} path. Only limited information is available for the activation parameters of related reactions of I^- (Table 3). For the $IrBr_6^{2-}-I^-$ system, $\Delta G_{II}^\ddagger - \Delta G_I^\ddagger$ is more negative than observed here. Because of the similar charges of the reactants, K_{2a} is also expected to be much smaller than for the ClO_2-I^- reaction. Thus, the results indicate an even more significant difference between the energy barriers of the two pathways than in the ClO_2-I^- reaction. For the reactions of the osmium complexes $\Delta G_{2a} < 0$ cannot be excluded. However, in order to predict a more favorable second-order than third-order path, an unrealistically small value needs to be considered for ΔG_{2a}. In other words K_{2a} should be larger than 390 M^{-1} ($Os(phen)_3^{3+}$) or 3.3×10^5 M^{-1} ($Os(bpy)_3^{3+}$).

It seems, regardless of the charge product of the reactants, that the same mechanism is operative in all systems. In general, a longer distance and weaker interactions are expected between the redox centers in the third-order transition state as compared to the second-order path. Still, the electron-transfer step within the activated complex is always faster in the third-order process. This finding, in spite of the very qualitative nature of the considerations presented here, lend some support to the assumption that the third-order process also occurs via an outer-sphere mechanism.

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Supporting Information Available: Table listing measured and calculated rate constants for the oxidation of iodide ion by chlorine dioxide and various temperatures (1 page). Ordering information is given on any current masthead page.

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