

Kinetic studies on the collisional quenching of $\text{CCl}_2(\tilde{A}^1\text{B}_1$ and $\tilde{a}^3\text{B}_1)$ by ketones

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Abstract

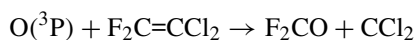
CCl_2 free radicals were produced by a pulsed dc discharge of CCl_4 (in Ar). The ground electronic state $\text{CCl}_2(X)$ radical was electronically excited to the $\tilde{A}^1\text{B}_1(040)$ vibronic state with a Nd:YAG laser pumped dye laser at 541.52 nm. Experimental quenching data of excited $\text{CCl}_2(\tilde{A}^1\text{B}_1$ and $\tilde{a}^3\text{B}_1)$ by ketone molecules were obtained by observing time-resolved total fluorescence signal of the excited CCl_2 radical, which showed a superposition of two exponential decay components under the presence of quencher. The quenching rate constants K_A of $\text{CCl}_2(A)$ state and K_a of $\text{CCl}_2(a)$ state were derived by analyzing the experimental data according to a proposed three-level-model involving $\tilde{X}^1\text{A}_1$, $\tilde{A}^1\text{B}_1$, and $\tilde{a}^3\text{B}_1$ states. On the whole, K_A and K_a increase with increasing the number of C–H bonds in ketone molecules. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Experimental data; Fluorescence signal; Ketone molecules

1. Introduction

In view of the extensive study of the role played by dichlorocarbene, CCl_2 , as an intermediate of some organic chemical reactions [1–6], direct spectroscopic observation and kinetic study of this species would be of considerable interest to both chemical physicist and chemist. Since a direct spectroscopic observation of CCl_2 was carried out in 1967 by Milligan and Jacox using a matrix-isolation technique [7], CCl_2 radical was produced through pyrolysis, photolysis, discharge and chemical reaction of some chlorinated hydrocarbon molecules which contain two or more chlorine atoms in the same carbon [8–25]. It is found that many industrial processes, such as plasma etching of semiconductor surface [26,27] and reprocessing of burnt nuclear fuel [28], relate to CCl_2 radicals.

Although much effort has gone into the study of the CCl_2 radical, almost all investigations were focused on spectroscopy and only a few studies have been performed on kinetics of CCl_2 radicals. In 1977 Huie et al. [13] produced CCl_2 radicals through the reaction



The radiative lifetimes and quenching rate constants by O_2 were measured at wavelengths 515, 484, 445 and 437 nm. In 1980 Tsee et al. [16] measured the reaction rate constants of the ground state CCl_2 radical with NO , O_2 , F_2 , CO , C_3H_8 , C_2H_4 , and Ar. The CCl_2 radical was generated through photolysis of a halogenated hydrocarbon and probed in a time-resolved manner via LIF using a tunable dye laser. In 1986 Ibuki et al. [19] measured the emission spectrum of excited CCl_2 , which were generated by the direct photodecomposition of CCl_4 and CBrCl_3 molecules using H Lyman- α , Ar I resonance lines and synchrotron radiation as light sources. They found that the fluorescence decay curve was a superposition of two lifetime components. In addition, the quenching rate constants of $\text{CCl}_2(\tilde{A}^1\text{B}_1)$ by CCl_4 and CBrCl_3 were measured. In 1989 Ibuki et al. [20] generated CCl_2 radicals by the photodecomposition of C_2Cl_6 using synchrotron radiation and obtained the kinetic results similar to those in [19]. In 1996 Wagner [29] produced $\text{CCl}_2(\tilde{X})$ radicals by the chemical reaction and measured the reaction rate constant of the ground state CCl_2 with Cl_2 . In 2000 Merelas et al. [25] measured the rate constants at room temperature for the collisional removal of CCl_2 , which was generated by IRMPD of $\text{CF}_2=\text{CCl}_2$, in its $\tilde{X}^1\text{A}_1(000)$ and $\tilde{A}^1\text{B}_1(070)$ states by simple alkenes, $\text{CF}_2=\text{CCl}_2$, He and Ar, etc.

Ketone molecules, which are the intermediate in the photooxidation reaction of some organic molecules with NO_x ,

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are involved in the process of the atmospheric chemical reaction [30]. Thus the quenching activity of ketone molecules seems to be worth pursuing.

In this work, CCl_2 radicals were produced by a pulsed dc discharge of CCl_4 (in Ar) and the time-resolved LIF signals from CCl_2 radicals were measured in order to study the quenching of the excited CCl_2 radicals by ketone molecules. The quenching rate constants K_A and K_a were acquired by analyzing the experimental data according to a proposed three-level-model.

2. Experimental

The dc discharge-LIF kinetic experimental set-up used in this work, which was described previously [31], involves a pulsed dc discharge, preparation of gases, a reactor, a laser source, signal detection, data processing, and time-sequence system. The schematic diagram is shown in Fig. 1.

The dc discharge system is comprised of a high-voltage power supply and a discharge cavity. The core part of the discharge cavity [32] is a polytetrafluoroethylene discharge head with 1 mm gas pathway, which screwed on the movable stainless steel tube. A pair of tungsten pins with a space of 0.5 mm was put into the head perpendicularly to the gas pathway. The pins were fixed onto the discharge head by two screw nails acting as both power terminal and rivet. The power source consists of a silicon-controlled rectifier and a pulsed high-voltage transformer with turn ratio of 1:100 and the primary voltage is adjustable. The pulsed dc discharge is initiated between the pair of tungsten needles. The discharge cavity is set at right angle to the laser beam. The distance

between the discharge pins and the laser beam is adjusted by moving the stainless steel tube and was 30 mm in this work.

The experiments were performed in a stainless steel reactor by using steady-flow technique. The reactor, preparation of gases and control of flow velocity were described in detail previously [31–35]. Some modifications were made in this work. The parent molecule CCl_4 and the quenching molecules were diluted in a large excess of Ar and stored in 10 liter reservoirs prior to experiments. Three gas mixtures were slowly flowing into the reaction vessel: f_1 , the flow of CCl_4 about 1% in Ar; f_2 , the flow of a quenching molecule mixed with Ar; and f_3 , the flow of pure Ar. In the reaction vessel the total pressure P_{total} was about 200 Pa and the partial pressure of CCl_4 , P_{CCl_4} , was about 0.5 Pa. In our experiments, P_{total} and P_{CCl_4} were kept constant. The gases in the vessel were renewed per 0.1 s in order to avoid the accumulation of the discharge-produced species and reaction products. The ground state CCl_2 radical was electronically excited to the $\tilde{A}^1\text{B}_1$ (040) state by laser radiation at 541.52 nm of the dye laser (Lumonics, HD500) pumped by a Nd:YAG laser (Spectra Physics, GCR-170, repetition rate of 10 Hz). The fluorescence signal transmitted through a cut-off filter ($\lambda \geq 565$ nm) was detected by a photomultiplier (GDB56, Beijing). The photomultiplier output was monitored by a digital storage oscilloscope (TDS380, Tektronix) or recorded by a transient digitizer, and then averaged with a computer data acquisition system. In our experiment the signal was averaged over 1000 laser shots. In order to avoid the mutual disturbing between the laser and discharge system, two photo-electronic isolators were connected between the multi-channel delay generator and the laser, and between

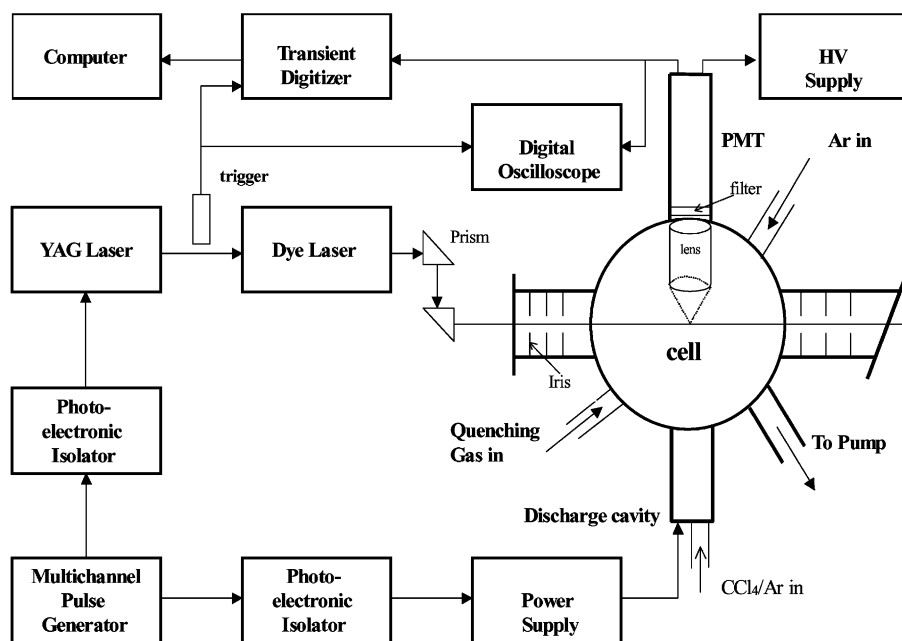


Fig. 1. Block diagram of the radical kinetic experimental apparatus.

the multi-channel delay generator and the discharge system, respectively.

Our supersonic jet apparatus is basically similar to that described in detail previously [24]. The sample gas seeded in Ar at stagnation pressure of 5 atm flowed through a pulsed nozzle (general valve) with 0.5 mm orifice diameter into an expansion chamber at a repetition rate of 10 Hz. The light source was same as aforementioned.

2.1. Materials

Ar (99.999%, Nanjing) was taken from cylinders without further purification. All ketones and CCl₄ in this work were analytical reagent grade, carefully degassed, further purified by freeze-pump-thaw cycles in a vacuum system, vaporized into reservoirs, and mixed with the bath gas Ar before use.

3. Results and discussion

3.1. Description of kinetic model

A typical time-resolved fluorescence signal of CCl₂ radical is shown in Fig. 2, in which the quenching process by CH₃COCH₂CH(CH₃)₂ exists.

The decay profile was fitted to

$$y = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \quad (1)$$

It can be seen that the decay profile may be satisfactorily analyzed as a superposition of two lifetime components. By contrast, we have measured the time-resolved LIF signal in supersonic free jet conditions, which is shown in Fig. 3. Because of the collision-free supersonic jet conditions, we can assume that the monoexponential decay curve corresponds to the radiative decay of \tilde{A} state. The superposition of two lifetime components is certainly caused by collisions.

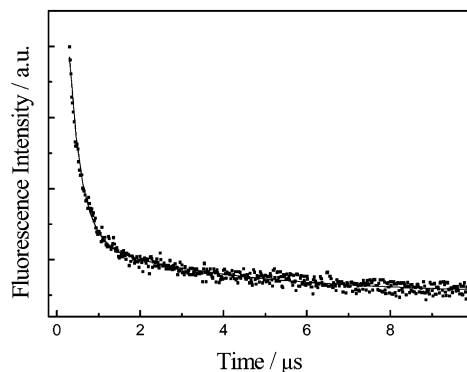


Fig. 2. A typical LIF decay profile of the electronically excited CCl₂ quenched by CH₃COCH₂CH(CH₃)₂: dots are the experiment data and solid line is the fitting result. Excitation wavelength is 541.52 nm. $A_1 = (1.804 \pm 0.121) \times 10^4$; $A_2 = (7.515 \pm 0.132) \times 10^2$; $k_1 = (4.812 \pm 0.061) \times 10^6 \text{ s}^{-1}$; $k_2 = (1.351 \pm 0.050) \times 10^5 \text{ s}^{-1}$.

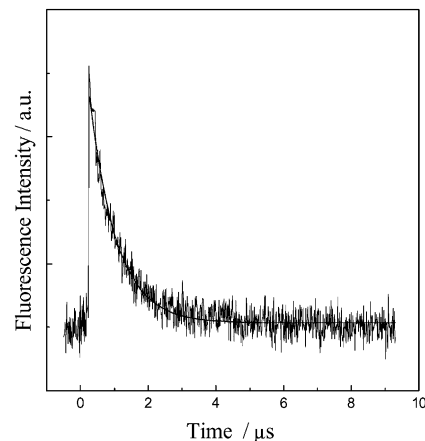
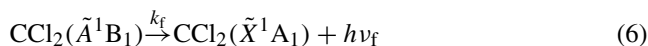
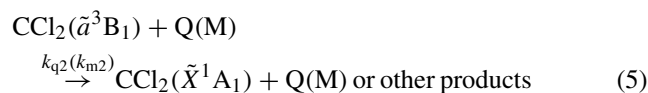
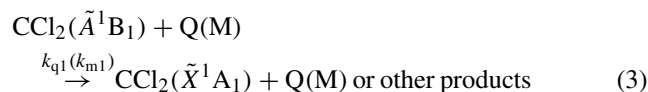
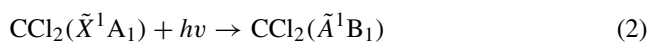


Fig. 3. Time-resolved LIF spectrum of jet-cooled CCl₂($\tilde{A}^1\text{B}_1$). Excitation wavelength is 541.52 nm.

Nguyen et al. [36] have calculated the energy levels of the CCl₂ radical and found that the state $\tilde{a}^3\text{B}_1$ lies between $\tilde{A}^1\text{B}_1$ and $\tilde{X}^1\text{A}_1$. Ibuki et al. [19] speculate that the collision-induced intersystem crossing between the $^1\text{B}_1$ and $^3\text{B}_1$ states plays an important role for the non-exponential behavior. That is, the vibrationally excited CCl₂($\tilde{A}^1\text{B}_1$) radicals produced in the primary excitation process are converted to vibrationally excited CCl₂ in the $^3\text{B}_1$ state through bimolecular collisions. Since the phosphorescence lifetime of the CCl₂($\tilde{a}^3\text{B}_1 \rightarrow \tilde{X}^1\text{A}_1$) transition is expected to be very long, the hot CCl₂($\tilde{a}^3\text{B}_1$) radical would be again quenched to the lower vibrational levels of the $\tilde{A}^1\text{B}_1$ state. Thus the following collisional kinetic mechanism is proposed [31].



where Q is the quencher and M denotes other molecules (including CCl₄, Ar and the discharge-produced species, etc.). The concentrations of M were kept constant in our experiment.

Since what we shall discuss afterwards is a fast pump process (the pulse width of dye laser is 5 ns) and laser intensity is not too high (3–5 mJ per pulse), we assumed the pump and dump would not influence the description of the

kinetic behavior after the laser irradiation [37]. It is assumed that the partial densities of $\text{CCl}_2(\tilde{A})$ and (\tilde{a}) levels after each laser pulse, are N_A^0 and $N_a^0 = 0$, respectively. The constant k_f represents the Einstein spontaneous emission coefficient from \tilde{A} to \tilde{X} while k_{q1} represents the sum of the rate constant of chemical reactions of the \tilde{A} state and the $\tilde{A}^1\text{B}_1 \rightarrow \tilde{X}^1\text{A}_1$ transition caused by collision with Q. Here k_{q2} involves the rate constant of chemical reactions and the physical quenching of $\tilde{a}^3\text{B}_1$. N_q and N_m are the concentration of quencher and M, respectively, while k_{mi} ($i = 1$ and 2) represents the collisional removal rate constant by M molecules, ξ_i and ξ_{mi} ($i = 1$ and 2) represent collisional transition rate constants between \tilde{A} and \tilde{a} state with quencher and M, respectively.

The kinetic equations for N_A and N_a can be expressed as:

$$\begin{aligned} \frac{dN_A}{dt} &= -k_f N_A - k_{q1} N_q N_A - \xi_1 N_q N_A - k_{m1} N_m N_A \\ &\quad - \xi_{m1} N_m N_A + \xi_2 N_q N_a + \xi_{m2} N_m N_a \\ &= -AN_A + BN_a \end{aligned} \quad (7)$$

where

$$A = k_f + k_{m1} N_m + \xi_{m1} N_m + k_{q1} N_q + \xi_1 N_q \quad (8)$$

$$B = \xi_2 N_q + \xi_{m2} N_m \quad (9)$$

$$\begin{aligned} \frac{dN_a}{dt} &= \xi_1 N_q N_A + \xi_{m1} N_m N_A - \xi_2 N_q N_a - \xi_{m2} N_m N_a \\ &\quad - k_{q2} N_q N_a - k_{m2} N_m N_a = CN_A - DN_a \end{aligned} \quad (10)$$

where

$$C = \xi_1 N_q + \xi_{m1} N_m \quad (11)$$

$$D = \xi_{m2} N_m + k_{m2} N_m + k_{q2} N_q + \xi_2 N_q \quad (12)$$

Thus, we can arrive at

$$\begin{aligned} N_A &= \frac{1}{\beta - \alpha} \{[(\beta - A)N_A^0 + BN_a^0]e^{-\alpha t} \\ &\quad + [(A - \alpha)N_A^0 - BN_a^0]e^{-\beta t}\} \end{aligned} \quad (13)$$

$$\begin{aligned} N_a &= \frac{1}{\beta - \alpha} \{[CN_A^0 + (A - \alpha)N_a^0]e^{-\alpha t} \\ &\quad - [CN_A^0 - (\beta - A)N_a^0]e^{-\beta t}\} \end{aligned} \quad (14)$$

where

$$\alpha + \beta = A + D, \quad \alpha\beta = AD - BC \quad (15)$$

Noting $N_a^0 = 0$, then

$$N_A = \frac{1}{\beta - \alpha} \{(\beta - A)N_A^0 e^{-\alpha t} + (A - \alpha)N_A^0 e^{-\beta t}\} \quad (16)$$

$$N_a = \frac{1}{\beta - \alpha} (CN_A^0 e^{-\alpha t} - CN_A^0 e^{-\beta t}) \quad (17)$$

Since the fluorescence emission of excited CCl_2 radicals is from \tilde{A} state, the detected fluorescence signal intensity is

proportional to N_A , i.e.

$$\begin{aligned} I &= \kappa k_f N_A \\ &= \frac{\kappa}{\beta - \alpha} N_A^0 k_f [(\beta - A)e^{-\alpha t} + (A - \alpha)e^{-\beta t}] \end{aligned} \quad (18)$$

where κ is the instrument coefficient.

Comparing Eq. (1) with (18):

$$\alpha = k_1, \quad \beta = k_2 \quad (19)$$

$$\begin{aligned} A_1 &= \frac{\kappa}{\beta - \alpha} N_A^0 k_f (\beta - A), \\ A_2 &= \frac{\kappa}{\beta - \alpha} N_A^0 k_f (A - \alpha) \end{aligned} \quad (20)$$

Thus

$$\frac{A_1}{A_2} = \frac{\beta - A}{A - \alpha} \quad (21)$$

$$A = \frac{A_1 \alpha + A_2 \beta}{A_1 + A_2} \quad (22)$$

$$D = \alpha + \beta - A \quad (23)$$

4. Conclusion

Before analyzing the time-resolved signal to derive the fluorescence decay rate constants, a small background that resulted from the scattered laser radiation in the reactor without discharge, was subtracted from the gross signal to get a net value. For example, the net time-resolved fluorescence signal of excited CCl_2 radicals quenched by $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$ and its fitting to two exponential decay curve are shown in Fig. 2. A_1 , A_2 , k_1 , and k_2 can be acquired by this fitting, while A and D can be calculated by (22) and (23). The Stern–Volmer plots of A and D versus $[\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2]$ based on Eqs. (8) and (12) are illustrated in Figs. 4 and 5. The slopes of the straight lines are the rate constants $K_A = k_{q1} + \xi_1$ and $K_a = k_{q2} + \xi_2$ of $\text{CCl}_2(\tilde{A})$ (040) and $\text{CCl}_2(\tilde{a}^3\text{B}_1)$ states quenched by $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$, respectively. The measured quenching rate constants of the excited CCl_2 radical by ketones

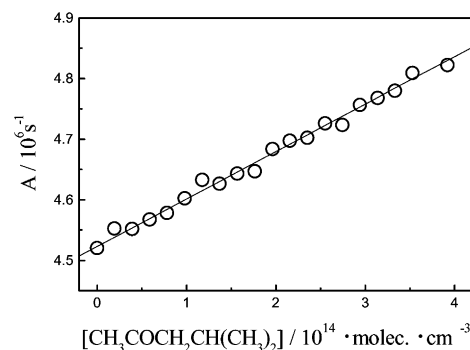


Fig. 4. Plot of A as a function of concentration of $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$.

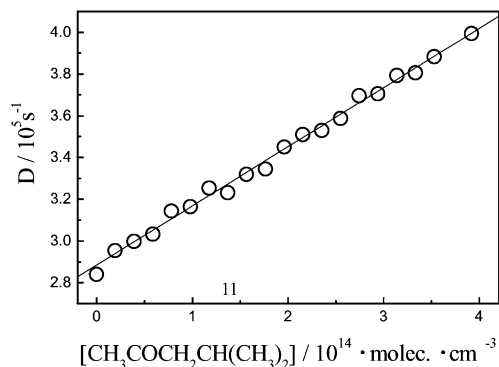


Fig. 5. Plot of D as a function of concentration of $\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$.

are listed in Table 1. The uncertainties of K_A and K_a are the standard deviations of the least-square fitting.

In order to compare the quenching activity of the alcohol with the ketone, the results for some alcohols are included in Table 1. We can see that the quenching rate constants of alcohol are faster than ketone compounds containing the same number of carbon atoms as in alcohol, indicating that the quenching activity of ketone molecules is less effective than alcohol molecules.

From Table 1, we can see that the rate constants, for the K_A and K_a , for removal of electronically excited CCl_2 increase steadily with increasing the number of C–H bonds in the ketones. The quenching of the electronically excited CCl_2 radical by ketones is a complicated process, including not only physical quenching but also chemical reactions. As far as the chemical reaction is concerned, if there is the same activity for $-\text{CH}_2-$ group in ketonic molecules, the more the number of carbon atoms, the faster the reaction rate constants. For large ketonic molecules, an increase of the number of $-\text{CH}_2-$ group may result in enhancement of reaction cross section. As to the physical quenching, the $E-V$ energy transfer process take places easily, because there

Table 1

Rate constants for collisional quenching of $\text{CCl}_2(\tilde{A}^1\text{B}_1)$ and $(\tilde{a}^3\text{B}_1)$ by ketone molecules (K_A , and K_a are in 10^{-10} cm^3 per molecule per s), $T = 293 \text{ K}$

Quencher	K_A	K_a	References
<i>n</i> -C ₃ H ₇ OH	8.73 ± 0.16	3.01 ± 0.28	[31]
<i>i</i> -C ₃ H ₇ OH	9.22 ± 0.13	2.92 ± 0.18	[31]
<i>n</i> -C ₄ H ₉ OH	9.73 ± 0.21	3.62 ± 0.22	[31]
<i>i</i> -C ₄ H ₉ OH	10.07 ± 0.18	3.71 ± 0.24	[31]
<i>t</i> -C ₄ H ₉ OH	9.63 ± 0.22	3.59 ± 0.21	[31]
<i>n</i> -C ₅ H ₁₁ OH	10.66 ± 0.20	3.98 ± 0.27	[31]
<i>i</i> -C ₅ H ₁₁ OH	10.85 ± 0.22	4.01 ± 0.26	[31]
<i>t</i> -C ₅ H ₁₁ OH	10.32 ± 0.23	3.87 ± 0.27	[31]
CH ₃ COCH ₃	4.87 ± 0.12	1.83 ± 0.09	This work
CH ₃ COCH ₂ CH ₃	5.93 ± 0.15	2.23 ± 0.12	This work
<i>c</i> -C ₅ H ₈ O	8.07 ± 0.17	2.71 ± 0.11	This work
<i>c</i> -C ₆ H ₁₀ O	8.83 ± 0.19	2.95 ± 0.12	This work
CH ₃ COCH ₂ CH(CH ₃) ₂	7.91 ± 0.14	2.69 ± 0.11	This work
CH ₃ COC(CH ₃) ₃	7.99 ± 0.13	2.84 ± 0.10	This work

are many vibrational modes in the molecule. The more the number of carbon atoms, the higher the density of the state, therefore the more the probability of energy transfer.

Acknowledgements

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