Kinetics of the reactions of vinyl radicals with molecular oxygen and chlorine at temperatures 200–362 K

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Received 13th March 2003, Accepted 9th May 2003 First published as an Advance Article on the web 21st May 2003

Published on 21 May 2003. Downloaded by University of Western Ontario on 27/10/2014 13:31:40.

The kinetics of the $C_2H_3 + O_2$ and $C_2H_3 + Cl_2$ reactions have been studied in direct measurements at temperatures between 200–362 K using a tubular flow reactor coupled to a photoionization mass spectrometer (PIMS). The vinyl radicals were homogeneously generated by the pulsed laser photolysis of methyl vinyl ketone at 193 nm. The subsequent decays of the radical concentrations were monitored in time-resolved measurements to obtain the reaction rate coefficients under pseudo-first-order conditions. Reaction products identified were HCO and H₂CO for the oxygen reaction and C₂H₃Cl for the chlorine reaction, respectively. The rate coefficients of both reactions were independent of the bath gases (He or N₂) and pressures within the experimental range, 0.13-0.53 kPa, and can be expressed by the Arrhenius equations $k(C_2H_3 + O_2) = (4.62 \pm 0.40) \times 10^{-12}$ exp $(1.41 \pm 0.18$ kJ mol⁻¹/*RT*) cm³ molecule⁻¹ s⁻¹ and $k(C_2H_3 + Cl_2) = (4.64 \pm 0.59) \times 10^{-12}$ exp $(3.12 \pm 0.27$ kJ mol⁻¹/*RT*) cm³ molecule⁻¹ s⁻¹ good agreement with previous direct measurements.

Introduction

Unsaturated hydrocarbon free radicals such as alkenyl and alkynyl radicals are known to play an important role in hydrocarbon combustion processes, particularly in soot formation.^{1–3} Vinyl radicals, the simplest alkenyl radicals, have an important role in PAH's (polycyclic aromatic hydrocarbons) formation in acetylene-rich environments.^{1–3} For example, benzene can be formed in a reaction sequence consisting of H-atom addition to C_2H_2 (forming the vinyl radical) followed by successive C_2H_2 addition and back-formation of H, making the catalytic cycle.^{1,2} On the other hand, under oxygen-rich conditions vinyl radical concentrations are effectively suppressed by the rapid reaction between vinyl radicals and molecular oxygen.

$$C_2H_3 + O_2 \rightarrow HCO + H_2CO$$

\$\to\$ other products (1)

Thus the reaction (1) retards soot formation and is consequently an important reaction in combustion processes.¹ Both experimental^{4–10} and theoretical^{11–14} studies of this reaction have previously been conducted at ambient and higher temperatures.

Chlorination reactions of unsaturated hydrocarbons involve two-step free radical chain reactions started by a H atom abstraction of Cl atom reaction (2a) or a Cl atom addition to a double or triple bond reaction (2b) and followed by the reaction of the formed radical reaction (3 or 4).^{15,16}

$$Cl + RH \rightarrow HCl + R^{\bullet}$$
 (2a)

$$Cl + RH \rightarrow HRCl^{\bullet}$$
 (2b)

$$\mathbf{R}^{\bullet} + \mathbf{Cl}_2 \to \mathbf{R}\mathbf{Cl} + \mathbf{Cl} \tag{3}$$

$$HRCl^{\bullet} + Cl_2 \rightarrow HRCl_2 + Cl \tag{4}$$

These reaction steps appear to be exothermic and have little or no activation energy.^{15–23} Together they constitute an efficient cyclic process for the production of chlorine-containing hydro-

DOI: 10.1039/b302894a

carbons. Much is known about the reactions of chlorine atoms with saturated hydrocarbons, step (2a),¹⁷ but the reactions of saturated hydrocarbon free radicals with molecular chlorine, step (3),^{17–20} are less known. A few rate coefficient measurements exist for the reactions of chlorine atoms with unsaturated hydrocarbons, when both steps (2a) and (2b) are available.^{15,16,21,22} To our knowledge only one experimental kinetic study exists on reactions of unsaturated hydrocarbon free radicals with molecular chlorine, step (3), measured over a limited temperature range above ambient temperature.²³

Both reactions studied here have been investigated in direct measurements previously at ambient or higher temperatures, so that comparison under these conditions can be used as test cases for our new experimental setup, which is described below. There are no previous data available at temperatures below $25 \,^{\circ}$ C. Here we present the direct measurements for the reactions of vinyl radicals with molecular oxygen and chlorine over the atmospheric temperature range from $-70 \,^{\circ}$ C to $90 \,^{\circ}$ C.

Experimental

The vinyl radicals were generated by pulsed ArF (193 nm) excimer laser (ELI-76E) photolysis of methyl vinyl ketone^{7,8} along the tubular flow reactor to produce radicals homogeneously in the reaction mixture. The nascent radicals were rapidly thermalized by the buffer gas (either He or N₂).²⁴

$$CH_3C(O)C_2H_3 + h\nu(193 \text{ nm}) \rightarrow C_2H_3 + CH_3 + CO$$
 (5)

The quantum yield for the reaction channel (5) is close to unity.²⁵ The decay of the radicals or formation of products were subsequently monitored in time-resolved experiments using photoionization mass spectrometry (PIMS) in the presence of the molecular reactant (Cl_2 or O_2). Gas mixture was continuously sampled from a pinhole in the wall of the reactor and a beam formed was photoionized before it entered the mass spectrometer for the mass selection and detection of ions.

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The production of the radicals was synchronized with data collection using a commercial computer program for instrumentation (Labview 5.1). The fundamental idea was to isolate the radical reaction of interest from the other possible gas phase reactions of this radical in the gas mixture, *i.e.* conduct experiments under pseudo-first-order conditions, when the molecular reactant was always in large excess in comparison to the small initial radical concentration. The flowing gas mixture in the reactor contained the radical precursor (below 0.02%), the reactant (0–0.15%) and the carrier gas in large excess (>99.8%). Output intensities of the photolysing laser were measured to be between 20–70 mJ pulse⁻¹ (Gentec ED-200) and were attenuated by proper filters. The apparatus is shown schematically in Fig. 1.

The gas handling system for the reactant, the precursor, and the carrier gas was mainly made of Pyrex-glass. The concentrations of the reactants were calculated from the pressure change in a known volume, the total pressure, the temperature of the reaction mixture and the total flow rate. The total and partial pressures of gases were measured using a high precision, capacitance pressure gauge (CCM Instruments). The pressure within the reactor tube was measured at about 55 cm upstream from the sampling point. The pressure was then corrected for the pressure decrease along the flow direction to the middle of the reaction zone.²⁶ The correctness of calculated pressures was tested in separate measurements. Two reactor tubes with different sizes were used. They were made of seamless stainless steel (grade 316L, AISI) tubes with 6 and 17 mm inner diameters (id) and a conical pinhole (0.3 mm diameter) was made through the wall of each reactor. The inner surfaces of the reactors were coated with halocarbon wax.²⁷ Refrigerated bath with circulator for the external loop (Heto-Holten CBN 28-90/HMT 4000) was coupled to the reactor mantle to control the reactor temperature. Methanol was employed as a heat transfer fluid below ambient temperature and distilled water above it. Temperature inside the reactor was also measured by a K-type thermocouple located in the center of the reactor and at two centimeters downstream from the sampling point. Axial temperature profiles



Fig. 1 Schematic drawing of the laser photolysis–laminar flow reactor coupled to the photoionization mass spectrometer (PIMS). P is a pressure gauge. Pressures inside the chambers containing the flow tube and PIMS were typically 10^{-5} and 10^{-6} torr, respectively.

inside the reactors were measured in separate measurements using a sliding thermocouple under the same conditions (temperatures, pressures and flow rates) as in the real measurements. Temperatures were uniform within ± 2 K. The minimum length of the uniformly cooled (heated) zone was 30-40 cm, depending on the flow velocity, gas pressure and temperature. The flow rates were typically about $4-5 \text{ ms}^{-1}$ inside the reactor, which means that the gas mixture passes the uniformly cooled (heated) zone in about 80 ms. Our experimental temperature range was limited by the temperature controlling apparatus. The sample flow through the pinhole from the reactor to the vacuum chambers was measured as a function of the buffer gas (He or N_2) pressure and temperature. Under the experimental conditions used, the sample flow was observed to be about 3 and 20% of the total flow for 17 and 6 mm id tubes, respectively.

The gas mixture emerging from the sampling hole was formed into a beam by a conical skimmer before it entered the second vacuum chamber containing the PIMS. The beam passed the ion source before it entered the quadrupole mass spectrometer (Extrel, C-50/150-QC/19 mm rods). A portion of the gas was photoionized by an intense resonance lamp and ions formed were mass-selected before they were detected by an off-axis electron multiplier. The temporal ion signal from the electron multiplier was amplified (EG&G Ortec 9302) and recorded with a multichannel scaler (EG&G Ortec MCS plus) for different concentrations of the reactants (Cl₂ and O₂) from a short time before each laser pulse to 20-80 ms following the pulse. Typically data from 3000 to 10000 repetitions of the experiment were accumulated at about 5 Hz frequency before the vinyl radical ion signal profiles were fit to an exponential function $([C_2H_3]_t = \exp(-k't)[C_2H_3]_0)$.

The flow-type resonance radiation $lamps^{28}$ used were combined with proper salt windows to transmit the emission light of interest and to cut off the higher energy radiation. The lamps were powered by a microwave generator (Opthos MPG-4) using an Evenson cavity.²⁹ The atomic resonance lamps used to selectively photoionize the reactants and products for the mass spectrometer were the argon lamp (11.6 and 11.8 eV) with LiF-windows and the hydrogen lamp (10.2 eV) with MgF₂-windows. The energy of the photons for the selected lamp was higher than the ionization energy of the radical or closed-shell molecule of interest, yet it was lower than the energy required to initiate any significant fragmentation process producing radical ions from the precursor or destroying the radical or closed-shell molecule measured. The argon lamp was used to detect H₂CO and hydrogen lamp to detect C2H3, CH3COC2H3, HCO and C2H3Cl. The radical precursor, $CH_3C(O)C_2H_3$ (Aldrich, purity >99%), was degassed before use; oxygen (Aga purity of 99.998%), chlorine (Messer-Griesheim purity of 99.8%), helium (Messer-Griesheim purity of 99.9996%), and nitrogen (Aga purity of 99.9999%) were each employed as supplied.

Results

In a typical set of experiments to measure the rate coefficients of the reactions $C_2H_3 + X_2$ ($X_2 = O_2$ or Cl_2), the vinyl radical ion signal profiles were monitored first in the absence of the molecular reactant to observe the "wall reaction", k_6 :

$$C_2H_3 \rightarrow heterogeneous loss$$
 (6)

The first order decay rate of reaction (6) consists of all first order processes occurring in the reaction mixture and on the reactor wall without the added molecular reactant.

The rate of reaction (6) was measured by reducing precursor concentration or laser intensity until the rate measured for this process no longer depended on these parameters and an exponential fit to the temporal ion signal showed no deviation from the first order decay. The initial vinyl radical concentrations were then below 10^{11} molecules cm⁻³, which was estimated by using the measured decomposition fraction of the precursor in the laser photolysis. When these conditions were achieved, it was presumed that all radical-radical processes were suppressed (*i.e.* that they had negligible rates compared to the first order processes occurring in the system). Experiments were also performed with high precursor concentration but with low laser intensity to detect the possible radical-precursor interactions. However, these changes had only a minor effect on k_6 (and no effect on $k(X_2)$), thus it can be concluded that the most important first order process was the heterogeneous reaction on the reactor wall.

The first order decay rate (k') of the vinyl radical signal was then measured as a function of the added molecular reactant concentration. The molecular reactant was always in great excess over the vinyl radical concentration, resulting in pseudo-first-order reaction kinetics. Since the only significant reactions consuming the vinyl radicals during these experiments were reaction (1) (or reaction (3)) and reaction (6), the bimolecular reaction rate coefficient $k(X_2)$ could be obtained from the slope of the line fitted through these decay rates k'when plotted vs. [X2]. Note that under these experimental conditions $k' = k(X_2) \times [X_2] + k_6$. The formation profiles of the products were also measured. Plots of the first order C₂H₃ decay rate k' vs. $[O_2]$ and $[Cl_2]$ are shown in Figs. 2 and 3 with typical examples of the vinyl radical decay and the formation profiles of the products, respectively. For the gas phase reaction with only one reaction channel and product yield one, $k'_{\text{rise}} = k'_{\text{decay}} - k_6$. Decay rates (k' values) with X₂ present in

C₂H₃

60 70

нсо

H,CO

т З 60 70

10 20 40 time / ms

Ó

[O₂] / 10¹³ cm⁻³

т 2

-10 0 10 20 40 time / ms



1



Fig. 3 Plot of the first order C₂H₃ decay rate k' vs. [Cl₂] at T = 202 K and P = 0.13 kPa in a 17 mm id reactor tube. Inserts show the typical ion signal profiles for the C₂H₃ decay and the C₂H₃Cl formation under the conditions of the solid circle in the plot: [Cl₂] = 3.9×10^{12} molecule cm⁻³, $k'_{decay} = 151 \pm 2 \text{ s}^{-1}$, (k'_{rise} (C₂H₃Cl) = $123 \pm 3 \text{ s}^{-1}$) and $k_6 = 30 \text{ s}^{-1}$. Uncertainties are 1σ .

reaction mixture at the highest X_2 concentrations used were typically about 10 times larger than k_6 (*i.e.* k' extending up to about 500 s⁻¹).

Although the dependence of the decay constant k' on the reactant concentration was always linear at each temperature and pressure over wide range of reactant concentration (when 17 mm id tube was used), further experiments were still performed to find out the possible presence of a second order C_2H_3 heterogeneous wall-loss process.

$$C_2H_3 + [X_2]_{surface} \rightarrow heterogeneous loss$$
 (7)

Some experiments were performed with the smaller, 6 mm id reactor tube to significantly vary the surface to volume ratio²⁶ (almost with a factor of three). If reaction (7) occurred to any significant extent, one would expect a higher bimolecular reaction rate coefficient $k(X_2)$ for the 6 mm id tube than for the 17 mm id tube. However, this was not observed. Only the first order reaction rate k_6 , "the wall reaction", was higher for the 6 mm than for the 17 mm id tube and this increase ($k_6(6$ mm)/ $k_6(17$ mm)) was approximately equal to the increased surface to volume ratio. This is in accordance with previously noted conclusion that the most important first order process in the absence of the reactant was the first order heterogeneous reaction on the reactor wall. Therefore, we conclude that the second order C₂H₃ heterogeneous wall-loss process could not have any significant effect on our results.

Decomposition of O_2 and Cl_2 molecules due to photolysis at 193 nm could not be measured with our current setup. Using the available data for the absorption cross sections of O_2^{30} and Cl_2 ,³¹ their decompositions at 193 nm under experimental conditions can be estimated to be less than 0.0003% for O_2 and 0.03% for Cl_2 , respectively. Even with the highest chlorine

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300

200

100

50

0

Ò

k'/s⁻¹

Table 1 Conditions and results of the experiments used to measurethe rate coefficients of the reaction $C_2H_3 + X_2 \rightarrow \text{products} (X_2 = O_2, Cl_2)^a$

T/K	P^{b}/kPa	$\frac{10^{-12}}{cm^{-3}}$ [X ₂]/	$rac{k_{ m w}{}^c}{ m s}^{-1}$	$\frac{10^{-12}k^d}{\mathrm{cm}^{-3}\mathrm{s}^{-1}}$
$X_2 = C$	$O_2, C_2H_3 + O_2 - O_2$	\rightarrow HCO + H ₂ CO		
200	0.53	4.3-24.0	28	10.3 ± 0.4
203	0.13	1.7-9.4	32	10.8 ± 0.3
220	0.13	4.5-30.0	27	9.9 ± 0.1
220	0.25	8.1-34.4	75^e	10.1 ± 0.1
244	0.13	2.3-15.1	32	9.5 ± 0.2
267	0.13	4.0-27.3	40	9.1 ± 0.2
267 ^f	0.13	4.3-24.6	31	8.9 ± 0.2
298	0.13	3.9-14.7	28	8.2 ± 0.4
298	0.26	8.1-48.3	67^e	8.1 ± 0.2
336	0.15	2.6-28.2	25	7.7 ± 0.1
362	0.13	4.2-28.3	33	7.5 ± 0.2
362	0.53	4.9-33.3	30	7.0 ± 0.2
$k(C_2H_3)$	$(+O_2) = (4.62)$	$\pm 0.40) \times 10^{-12} >$	$exp(1.41 \pm$	$0.18 \text{ kJ mol}^{-1}/RT$
cm ³ mo	plecule ⁻¹ s ⁻¹			, ,

$X_2=Cl_2,C_2H_3+Cl_2\mathop{\rightarrow} C_2H_3Cl+Cl$							
202	0.13 ^g	1.1–5.8	29	31.3 ± 0.4			
202	0.13	1.0-6.1	30	30.5 ± 0.5			
220	0.13	1.5-9.0	27	24.7 ± 0.3			
221	0.25	2.9-16.2	80^e	24.4 ± 0.6			
241	0.13	2.0 - 18.0	32	20.7 ± 0.6			
267	0.13	1.9-11.5	23	20.1 ± 0.6			
298	0.17	1.7 - 11.8	25	16.2 ± 0.3			
298	0.27	3.3-24.2	61 ^e	16.0 ± 0.6			
336	0.13	2.9-22.7	27	13.6 ± 0.3			
362	0.13	2.2-16.7	27	13.6 ± 0.3			
362	0.53	3.6-16.3	23	13.3 ± 0.5			
$k(C_2H_3)$	(4.6)	$54 \pm 0.59) \times 10^{-12}$	$^2 \times \exp(3.12)$	± 0.27 kJ mol ⁻¹			
RT) cn	n ³ molecule ⁻¹	s^{-1}					

^{*a*} Range of precursor concentrations used: $(0.8-6) \times 10^{12}$ molecule cm⁻³. ^{*b*} Helium used as a buffer gas unless otherwise noted. ^{*c*} Reactor tube diameter 17 mm unless otherwise noted. ^{*d*} Uncertainties shown are 1σ ; estimated overall uncertainty $\pm 20\%$. ^{*e*} Reactor tube diameter 6 mm. ^{*f*} Flow velocity reduced to half of normal. ^{*g*} Nitrogen used as a buffer gas.

concentrations used $(2.4 \times 10^{13} \text{ molecule cm}^{-3})$, the amount of chlorine atoms produced was about 1×10^9 molecule cm $^{-3}$ in the photolysis. Taking into account that our initial radical concentrations were typically between $(5-10) \times 10^{10}$ molecule cm $^{-3}$, it is unlikely that such a small atom concentration can have any significant effect on our results.

The measured bimolecular reaction rate coefficients for the vinyl radical reactions with molecular oxygen and chlorine (also fitted to an Arrhenius expression $k = A \exp(-E_a/RT)$) are shown in Table 1 with their statistical uncertainties (1σ) and the experimental conditions. These values for the bimolecular reaction rate coefficients, obtained from the direct measurements of the vinyl radical reactions with molecular reactants, are compared with prior direct measurements in Fig. 4, where the corresponding Arrhenius expressions are also plotted.

Discussion

The bimolecular reaction rate coefficient obtained for the vinyl radical reaction with molecular oxygen at 298 K is between those of Knyazev and Slagle⁸ and Fahr and Laufer⁷ (see Fig. 4). The values of the other previous, direct measurements^{4–6} also agree well with these values at 298 K, $10.6 \pm 2.1 \times 10^{-12}$



Fig. 4 Semilogarithmic plot of the measured bimolecular rate coefficients *versus* 1000/T and comparison with selected previous data.^{7,8,23} Corresponding Arrhenius expressions are also plotted.

(Park *et al.*),⁴ $10.1 \pm 3.7 \times 10^{-12}$ (Slagle *et al.*)⁵ and $10 \pm 4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Krueger and Weitz).⁵ Estimated overall uncertainties in our rate constants are about $\pm 20\%$. They arise mainly from the uncertainties in determing reactant concentrations and from the uncertainties in decay rates. The temperature dependence of the reaction rate coefficients is also in good agreement with that of Knyazev and Slagle.⁸ The current values for the bimolecular reaction rate coefficients for the vinyl radical reaction with molecular chlorine also agree well with prior results of Timonen and Gutman.¹⁸ However, small systematic offsets seem to exist for both reactions. The origin of these small differences, which are comparable to the sizes of the uncertainties, could not be pointed out.

The only reaction products identified for the vinyl radical reaction with molecular oxygen were HCO and H₂CO. These products have also been observed experimentally by Gutman and co-workers.^{4,5} They confirmed that the main reaction channel is $C_2H_3 + O_2 \rightarrow HCO + H_2CO$, $(\Delta H^\circ = -366 \text{ kJ} \text{mol}^{-1} \text{ }^{14})$ at low pressures and at ambient temperature and above. Although the H₂CO⁺ ion signal rise for the stable product (H₂CO) shown in Fig. 2 is noisy, it reflects the decay of the vinyl radical within 2σ uncertainties when vinyl radical heterogenous loss is taken into account (Note that $k'_{\text{rise}}(\text{H}_2\text{CO}) = k'_{\text{decay}}(\text{C}_2\text{H}_3) - k_6$, if each reacting vinyl radical, which is not lost in the heterogenous reaction, produces one H₂CO molecule). The ion signal profile of the HCO⁺ was fitted to an analytical expression that was derived from the following kinetic mechanism for this system:

$$C_2H_3 + O_2 \rightarrow HCO + H_2CO \tag{1}$$

$$HCO + O_2 \rightarrow HO_2 + CO$$
 (8)

$$HCO \rightarrow heterogeneous loss$$
 (9)

Under the experimental conditions used in inserts of Fig. 2, the ion signal intensity of HCO⁺ is given by $I_t(\text{HCO}^+) = I^0(\text{HCO}^+) \times k_f/(k_d - k_f) \times (\exp(-k_f t) - \exp(-k_d t))$, where the formation and disappearance rates of HCO are $k_f = 113 - 30 = 83 \text{ s}^{-1}$ and $k_d = k_8 \times [\text{O}_2] + k_9 = 82 + 30 = 112 \text{ s}^{-1}$ (k_8 and k_9 estimated using values from ref. 32, where experiments were performed under similar conditions). $I^0(\text{HCO}^+)$ is a scaling constant. The resulting fit together with the

formation kinetics of H_2CO support the observations of Gutman and co-workers^{4,5} that the main products for the vinyl radical reaction with molecular oxygen at low pressures are HCO and H_2CO .

For the vinyl radical reaction with molecular chlorine the only reaction product identified was C₂H₃Cl, which ion signal rise in Fig. 3 properly reflects the decay of the vinyl radical within 1 σ uncertainty, when the vinyl radical heterogenous loss is taken into account as above. This confirms the previously proposed¹⁸ main reaction channel, C₂H₃ + Cl₂ \rightarrow C₂H₃Cl + Cl, $(\Delta H^{\circ} = -158 \text{ kJ mol}^{-120})$.

The rate coefficients of both reactions increase slightly with decreasing temperature in our temperature range. Thus the results show that the same trend, which was previously observed above ambient temperature, still continues at lower temperatures for both reactions studied. For the vinyl radical reaction with molecular oxygen this is in accordance with exist-ing theoretical studies,^{11,12,14} where it is suggested that the reaction proceed via the initial formation of a transient energised complex on a potential energy surface with no barrier between reactants and complex. It is also expected that this energised complex is in equilibrium with the reactants $(C_2H_3 + O_2)$ due to its unimolecular dissociation. It is this faster dissociation of the energised complex back to the reactants at higher temperatures, which is believed to be the origin of the observed negative temperature dependence of this reaction.^{12,14} Similar mechanism can probably be used to explain observed, slightly more pronounced negative temperature dependence of the vinyl radical reaction with molecular chlorine. However, more studies on reactions of radicals with molecular chlorine are needed before the hypotesis can be confirmed

We conclude that the described new experimental apparatus can be used to study chemical kinetics at lower temperatures and is especially applicable to the atmospheric temperature range.

Acknowledgements

We are greatly thankful to our laboratory technicians, especially to Mr Markku Rasilainen, for the help in construction work of our apparatus. Acknowledgments for the financial support in the construction of the apparatus and research work to: Research Council for Biosciences and Environment of Academy of Finland and Maj and Torr Nessling Foundation. A.J.E. also thanks the Jenny and Antti Wihuri Foundation and Kone Foundation for their research grants.

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