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# Kinetics of Reactions of CCN Radical with Alcohols

Zhi-qiang Zhu, Min Ji, Shao-hua Zhang, Lin-sen Pei, Yang Chen*

*Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China*

The reaction kinetics of cyanomethylidyne radical, $CCN(\widetilde{X}^2\Pi)$, with a series of primary alcohols were studied at about 1.33 kPa total pressure and room temperature using pulsed laser photolysis/laser-induced fluorescence (LP/LIF) technique. The CCN radical was produced via laser photolysis of $CCl_3CN$ with the fourth harmonic output of a Nd: YAG laser (266 nm). The relative concentration of the $CCN(\widetilde{X}^2\Pi)$ radical was monitored by LIF in the (0, 0) band of the $CCN(\widetilde{A}^2\Delta \leftarrow \widetilde{X}^2\Pi)$ transition at 470.9 nm. Under pseudo-first-order conditions, the reaction rate constants of $CCN(\widetilde{X}^2\Pi)$ with a series of primary alcohol molecules ($n$-$C_nH_{2n+1}OH$, $n$=1-6) were determined by measuring the time evolution of the relative concentration of $CCN(\widetilde{X}^2\Pi_i)$. The measured rate constants increased monotonously with the number of carbon atoms in the alcohols, and the values for reactions of $CCN(\widetilde{X}^2\Pi)$ with alcohols were larger than those for reactions of $CCN(\widetilde{X}^2\Pi)$ with alkanes ($C_1-C_5$). Based on the bond dissociation energies and linear free energy correlations, it was believed that the reactions of $CCN(\widetilde{X}^2\Pi)$ with alcohols proceeded via a hydrogen abstraction mechanism that was analogous to $CCN(\widetilde{X}^2\Pi)$ with alkanes. The experimental results indicated that the H atoms on the C−H bonds were activated at the presence of the OH group in alcohol molecules and the hydrogen abstraction from the C−H bonds in the alcohol molecules was the dominant reaction pathway. The relation between the rate constants and the long-distance attractive potentials between the CCN radical and the alcohol molecules was discussed.

**Key words:** Kinetics, Cyanomethylidyne radical, Alcohols

## I. INTRODUCTION

The cyanomethylidyne (CCN) radical is an important and fascinating species in astrophysics and in spectroscopy research. A large number of nitrogen-containing carbon chain species such to be CN and CCCN have been observed in stellar envelopes [1-4], while the trace of CCN is still out of sight to date [5,6]. The CCN radical is thought as the source of the series of $C_nN$, $HC_nN$ [7-9] and $N\equiv C-(C\equiv C)_n-C\equiv N$ [10], and it maybe help us to understand the interesting fact of the abundance of long C-chains while the scarcity of rings through the *ab initio* calculations show the former usually more energetic than the later [9]. Moreover, CCN is believed to be involved in combustion processes in fuel-rich natural gas flames [11], and it may play a role in high temperature combustion and coal gasification processes when nitrogen is present [12]. CCN is a typical linear triatomic molecule with prominent Renner-Teller effect [13,14] which is the coupling between the bending vibration and electronic orbital angular moment. In fact, the Renner-Teller coupling in the ground state is quite large ($\varepsilon$=0.42) [15].

There are a great deal of spectroscopic work on the CCN radical since the first spectroscopic study of CCN was reported in 1965 by Merer and Travis [16], who performed flash photolysis of diazoacetonitrile, $HC(CN)N_2$, to generate the radical and observed absorption spectra of the $\widetilde{A}^2\Delta \leftarrow \widetilde{X}^2\Pi$, $\widetilde{B}^2\Sigma^- \leftarrow \widetilde{X}^2\Pi$ and $\widetilde{C}^2\Sigma^+ \leftarrow \widetilde{X}^2\Pi$ band systems in the 350-470 nm region. Many of the subsequent studies focused the $\widetilde{A}^2\Delta \leftarrow \widetilde{X}^2\Pi$ system [17-22] and the ground electronic state [6,23-26]. For instance, Kakimoto *et al.* studied laser-induced fluorescence (LIF) spectra of the $\widetilde{A}^2\Delta(000) \leftarrow \widetilde{X}^2\Pi(000)$ band using a cw dye laser with Doppler-limited resolution [17]. Hakuta and Uehara used an $Ar^+$ laser to pump the CCN radical into the $\widetilde{A}^2\Delta$ state and observed the resulting LIF [18]. Ohshima and co-worker observed the lowest $J$=3/2-1/2 rotational transition of the CCN radical in its $\widetilde{X}^2\Pi$ state by using a Fabry-Perot-type Fourier-transform microwave spectrometer combined with a pulsed discharge nozzle [26]. In contrast to the abundance of the spectroscopic data, the study of the reaction kinetics of CCN is limited. In order to understand fully the importance of the CCN radical in the drastically different environments, the rates of reactions of CCN with a wide range of compounds must be characterized.

In 2003, we reported the rate constants of the reactions of $CCN(\widetilde{X}^2\Pi)$ with alkanes and deduced that the reactions proceeded via hydrogen abstraction [28]. In this work, we have investigated the reactions of $CCN(\widetilde{X}^2\Pi)$ with a series of primary alcohols, and report the bimolecular reaction rate constants for reactions of the $CCN(\widetilde{X}^2\Pi)$ radical with primary alcohols

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*Author to whom correspondence should be addressed. E-mail: yangchen@ustc.edu.cn, Tel: +86-551-3606619, Fax: +86-551-3607084

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$(C_1-C_6)$ in the presence of excess Ar buffer gas at about 1.33 kPa total pressure and room temperature using the pulsed laser photolysis/laser induced fluorescence (LP/LIF) technique. The probable mechanism for these reactions is discussed, based on the bond dissociation energy (BDE) correlations and linear free energy correlations.

## II. EXPERIMENTS

The pulsed laser photolysis/laser-induce fluorescence (LP/LIF) experimental investigations were carried in a stainless steel cell by using steady-flow method, which has been described previously [27-29]. Only a brief summary of the main features is given here. The mixture of trichloroacetonitrile ($Cl_3CCN$), Ar (the buffer gas), and reactant primary alcohols flowed slowly through the reaction cell. The mixing ratios of $Cl_3CCN$ and primary alcohols such as one typical ratio 1:5 in these experiments which ensured pseudo-first-order conditions. Flows of all reagents and argon were controlled by calibrated mass flow controllers (D08-3D/ZM, Beijing), and the total pressure of the cell during the experiments was kept at 1.33 kPa. The CCN radical was produced via photolysis of $Cl_3CCN$ with the fourth harmonic output of a Nd:YAG laser (New wave) at 266 nm. Typical photolysis pulse energy and time jitter of the photolysis laser were 8 mJ and 2 ns, respectively. The third harmonic output (at 355 nm) of a second Nd:YAG laser (Spectra Physics, GCR-170) was used for pumping a dye laser (Sirah, with C480 dye). The repetition rate of all the lasers involved in the experiments was 10 Hz. The output of the dye laser, as the probe radiation, was about 2.5 mJ/pulse at 470.9 nm, which corresponded to the rotational band head of the (0-0) vibration band of the CCN ($\tilde{A}^2\Delta \leftarrow \widetilde{X}^2\Pi$) transition. In order to minimize the scattered light, the laser beam was confined to about 0.2 mm in diameter through a series of light baffles.

The fluorescence was collected by a lens system and focused onto a photomultiplier (PMT, R928, Hamamastu). The signal from PMT without amplifying was recorded by a digital storage oscilloscope (TDS380, Tektronix) or a transient digitizer and then averaged over 256 laser pulses with a computer data acquisition system. A digital delay generator (Stanford DG535) was used to vary the delay time between the photolysis laser and the probe dye laser pulses. And the delay time varied from zero to several hundred microseconds in these experiments.

Material: $Cl_3CCN$(Aldrich, 99%), methanol (Shanghai, ≥99.5%), ethanol (Shanghai, ≥99.5%), *n*-propanol (Shanghai, ≥99.0%), *n*-butanol (Shanghai, ≥99.5%), *n*-pentanol (Shanghai, ≥99.5%), *n*-hexanol (Shanghai, ≥99.0%). All specimens were degassed by repeated freeze-pump-thaw cycles with liquid nitrogen. Ar (Nanjing gas 99.999%) was used directly from a cylinder without further purification.

## III. RESULTS

LIF signal of the CCN radical (produced by the multiphoton photolysis of $Cl_3CCN$ at 266 nm) were observed in the range between 460 and 475 nm with about 200 ns lifetime. This LIF signal could be assigned to the $\tilde{A}^2\Delta \leftarrow \widetilde{X}^2\Pi$ transition of the CCN radical based on the previous spectroscopic data [17,18]. The 0-0 band of the CCN($\tilde{A}^2\Delta \leftarrow \widetilde{X}^2\Pi$) transition at 470.9 nm was selected to detect the relative concentration of the CCN ($\widetilde{X}^2\Pi$) radical based on the simple relation of the LIF signal and the concentration. The pseudo-first-order conditions were always ensured during all experiments. In a typical experiment, the CCN($\widetilde{X}^2\Pi$) radical concentration was about $5\times10^{11}$ molecule/cm$^3$, estimated from the incident light intensity, the absorption cross-section, and the pressure of $Cl_3CCN$. The partial pressure of the primary alcohols varied from 0.16 Pa to 0.73 Pa ($5.5\times10^{13}$-$2.5\times10^{14}$ molecule/cm$^3$) for *n*-hexanol or $4.5\times10^{14}$-$4.0\times10^{15}$ molecule/cm$^3$ for ethanol. Obviously, for any reactant primary alcohol, its concentration was much lager than that of the CCN radical. Thus under the pseudo-first-order conditions, the kinetic equation can be simply written as below:

$$[CCN] = A\exp(-k_1 t) \tag{1}$$
$$k_1 = k[\text{reactant}] + k_0 \tag{2}$$

here, $k_1$ is the pseudo-first-order decay rate, and $t$ is the delay time between the photolysis laser and the dye laser pulses, $k$ is the desired removal rate constant for the reaction of CCN($\widetilde{X}^2\Pi$) with reactant $R$, which was primary alcohol, and $k_0$ is the loss rate constant of CCN($\widetilde{X}^2\Pi$) in the absence of the added reactant due to self-reaction, reaction with the precursor molecules, and diffusion of the detected species out of the probed volume.

Figure 1 shows a plot of the typical integrated LIF signal amplitude of CCN as a function of the delay time. As shown in Fig.1, the CCN kinetic signals were found to be well approximated by single exponential decays over the range $t$=5-100 $\mu$s, which were found to be reasonably fit to pseudo-first-order kinetics, even at low reactant concentrations. This suggests that vibrational relaxation effects are insignificant in these experiments. Either CCN was produced vibrationally cold, or vibrational relaxation was accomplished within 5 $\mu$s, and thus the initial vibrational excited CCN($\widetilde{X}^2\Pi$) would not affect the experiment results.

The $k_1$ values are then obtained at various reactant concentrations and fitted by the linear equation (see Fig.2). Typical plots of $k_1$ versus [R], are shown in Fig.3 for R=$CH_3OH$, $C_2H_5OH$, $C_3H_7OH$. The slope of these plots represents the bimolecular rate constant $k$. The rate constants of reactions of CCN($\widetilde{X}^2\Pi$) with the selected normal alcohols ($C_1-C_6$) at 298 K are summarized in Table I. To the best of our knowledge, there
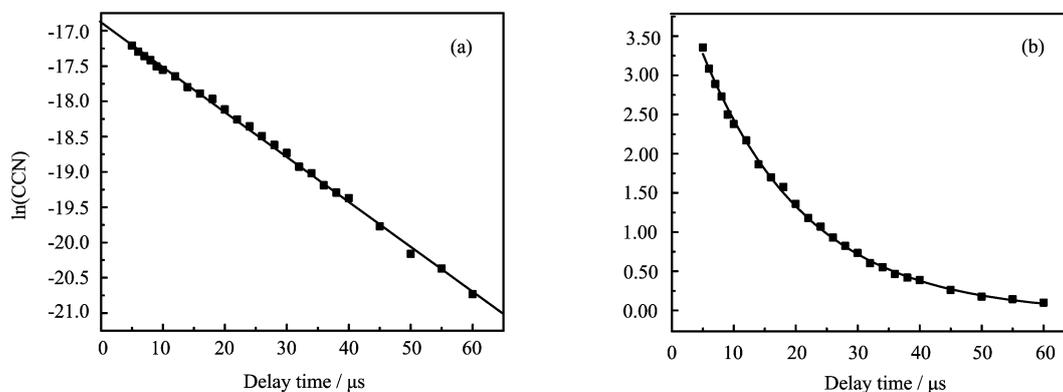
FIG. 1 (a) Typical plots of $CCN(\widetilde{X}^2\Pi)$ intensity versus the delay time between the photolysis laser (266 nm) and probe laser (470.9 nm) at 1.33 kPa total pressure and 298 K. The solid line is the result of weighted linear least-square fits to the data. (b) The raw data.

TABLE I Rate constant $k(cm^3/molecule\ s)$ for the reaction of $O(^3P)$, OH and $CCN(\widetilde{X}^2\Pi_i)$ with alcohols or alkanes measured at room temperature

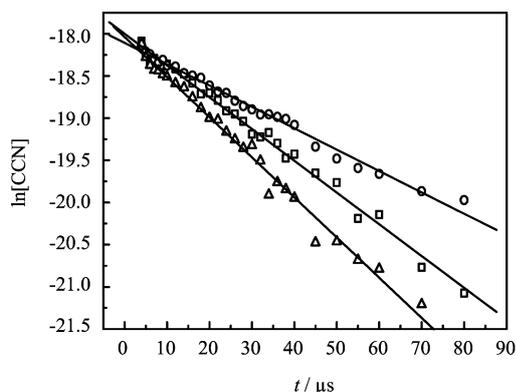| Compound | $k(CCN)\times10^{-11}$ | $k(O(^3P))\times10^{-15}$ [31,37] | $k(OH)\times10^{-13}$ [31,39,40] | Compound | $k(CCN)\times10^{-11}$ [28] |
|---|---|---|---|---|---|
| $CH_3OH$ | 0.229 | 7.79 [36] | 9.44 | $CH_4$ | $5.834\times10^{-3}$ |
| $C_2H_5OH$ | 2.423 | 55.7 | 32.7 | $C_2H_6$ | 0.29 |
| $C_2H_5CH_2OH$ | 3.738 | | 55.3 | $n$-$C_3H_8$ | 0.92 |
| $n$-$C_3H_7CH_2OH$ | 6.219 | 123 | 85.7 | $n$-$C_4H_{10}$ | 4.16 |
| $n$-$C_4H_9CH_2OH$ | 12.640 | | | $n$-$C_5H_{12}$ | 6.884 |
| $n$-$C_5H_{11}CH_2OH$ | 13.971 | | 158 | $n$-$C_6H_{14}$ | 11.504 |



FIG. 2 Plots of $CCN(\widetilde{X}^2\Pi)$ intensity versus the delay time at different concentration of alcohol. The solid lines are the results of weighted linear least-squares fits to the data. $C_2H_5OH$: ($\circ$) 0.453; ($\square$) 1.36; ($\triangle$) 2.26 ($10^{15}$molecule/cm$^3$).



FIG. 3 Plots of pseudo-first-order decay constant $k_1$ $vs.$ the concentration of alcohols in presence of excess Ar buffer gas at 1.33 kPa total pressure and 298 K. The solid lines are the results of weighted linear least-squares fits to the data.

were no literature data of the CCN reactions with alcohols for comparison.

## IV. DISCUSSION

It is well known that chemical reaction is a complicated process. To understand every reaction detail and the rate of each step is essential. Though we
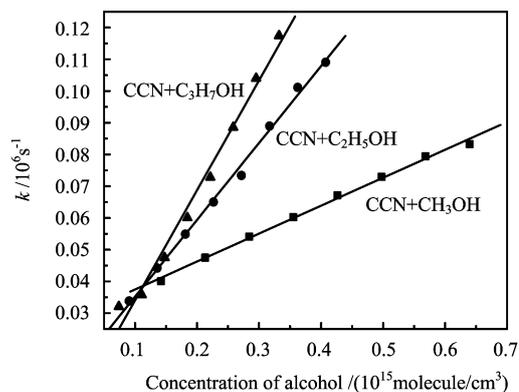
could not know the precise mechanism of the reaction of $CCN(\widetilde{X}^2\Pi)$ with alcohols by only analyzing qualitatively the overall rate constants, we may still achieve some reasonable conclusions.

In the previous work [28], we have studied the rate constants for the reactions of $CCN(\widetilde{X}^2\Pi)$ with alkanes and concluded that the reactions proceeded via the H-atom abstraction mechanism. To compare the results,

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the rate constants at room temperature for the reactions of CCN($\widetilde{X}^2\Pi$) with alcohols and alkanes are listed in Table I and shown in Fig.4, respectively. As shown in Fig.4, the CCN($\widetilde{X}^2\Pi$) removal rate constants for alcohols are uniformly larger than those for the corresponding alkanes, and both of these two sequences increase monotonically with the C-atoms number contained in the alcohol and alkane molecules. Based on the above experimental results and the similarity in the configurations of alkanes and alcohols, we deduce that the reactions of CCN($\widetilde{X}^2\Pi$) with alcohols probably proceed also via the same mechanism, H-atom abstraction. The following analysis of the linear free energy (LFE) correlation with other reactions known to proceed via hydrogen abstraction [30] and the bond dissociation energy (BDE) correlation seems to support this view.
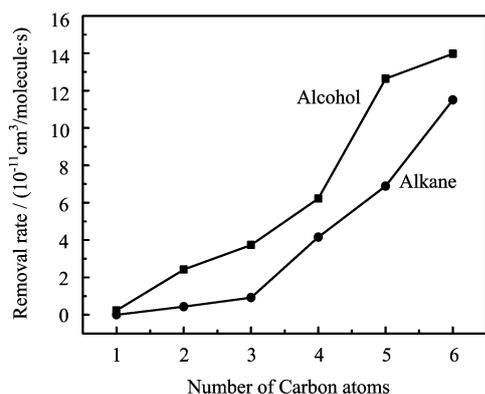


FIG. 4 the dependence of the experimental rate constants for removal of CCN($\widetilde{X}^2\Pi$) by alcohols and alkanes on the number of C atoms in alcohol and alkane molecules.

## A. LFE correlation

In general, electrophilic species such as CN, OH and CCN are known to react with small hydrocarbons via two major pathways, addition and abstraction. The additional reactions correlate with ionization potential (IP), while the abstraction reactions correlate with free energy [30-32]. Moreover, when they react with a series of homolog compounds, there are similar mechanistic pathways, parallel intermediates (IM) and transition state (TS) structures refer to the reactions [30]. Levine's group has explored the relationships between the structural and physical properties of these molecules and their reactivity. In their view [30], if reactive species, such as O($^3$P) and OH etc, are known to react with a series of organic compounds such as alkanes and alcohols by abstraction, there may exist linear relationships between their overall rate constants as the function of some physical properties of the homolog compounds, where the physical property is the number of C-atom or the CH$_2$ group of the linear C-chain alkane or alcohol molecule. Conversely, if there exist linear

relationships between the overall rate constants, it is reasonable to consider that the reactions have similar reaction mechnisms.

The available rate constants are listed in Table I which shows the reactions of CCN($\widetilde{X}^2\Pi$) with alcohols are analogous to O($^3$P) and OH reaction mechanisms. Plots of $\ln k$(O($^3$P)) and $\ln k$(OH) versus $\ln k$(CCN($\widetilde{X}^2\Pi$)) are linear (see Fig.5) as expected for reactions proceeding via the same mechanism, H abstraction. This comparison suggests that the CCN ($\widetilde{X}^2\Pi$)+alcohols are the H-abstraction reactions. From the reference [30], the LFE correlation is a significantly qualitative method, which appears to have more qualitative than quantitative usefulness in estimating rate constants.
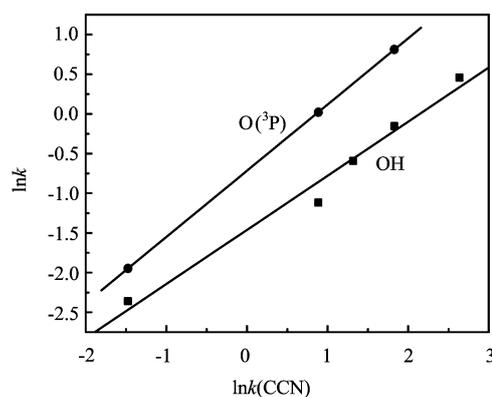


FIG. 5 Linear free energy correlation of the rate constants for CCN($\widetilde{X}^2\Pi_i$), OH and O($^3$P) react with the small alcohols. The O($^3$P) and OH reactions are known to proceed via hydrogen abstraction. Lines are least-squares best fit.

## B. BDE correlation

Intuitively, for H-atom abstraction reaction, the rate constants depend greatly on two conditions: the number of C−H bond of the alkane or alcohol molecule and the bond dissociation energy (BDE) of the C−H bond at room temperature. For some alkane or alcohol with the same number of C-atom, the remarkable difference in the rate constants between CCN($\widetilde{X}^2\Pi$) with alkanes and CCN($\widetilde{X}^2\Pi$) with alcohols indicates the C−H bond energy in the alcohols is smaller than that in the corresponding alkanes due to the presence of the OH substituent group. Due to the large electronegativity of O atom, the C−H bonds near the O-atom are activated and the bond energy decrease distinctly. For example, in the methanol molecule, the bond dissociation energy of the C−H bonds is $401.9\pm0.6$ kJ/mol [33], which is smaller than the bond dissociation energy of the C−H bonds in the methane ($439.3\pm0.1$ kJ/mol). And the bond dissociation energy of the secondary hydrogen in the alcohol molecules ($401.4\pm1.5$ kJ/mol) is smaller

than that in the alkane molecules (413±2.0 kJ/mol) [33,34]. The hydrogen abstraction from the C−H bonds in the alcohol molecule is easier than that in the alkanes. In fact, the average rate constants of the CCN radical abstraction of the secondary hydrogen in alcohols and alkanes can be estimated to be $2.22 \times 10^{-11}$ and $1.65 \times 10^{-11}$ cm$^3$/(molecule s), respectively, by linear fitting in Fig.4. For the same reason, the bond dissociation energy of the O−H bond in the alcohol molecule is larger than the one of the other C−H bonds; the value is 438±3.0 kJ/mol, which is near the 439.3±0.1 kJ/mol of the C−H bond in methane [35,36]. In our previous work [28], we have studied that the rate of the reaction of CCN($\widetilde{X}^2\Pi$) with methane is very small ($<6\times10^{-14}$cm$^3$/(molecule s)). So the hydrogen abstraction from the O−H bond of the alcohol can be neglected. These agree with the experimental results.

## C. Comparison with the results calculated using the orbiting theory

In general, for the H-abstraction reaction, the pre-exponential factor $A$ in Arrhenius equation is small [41]. While the fact that the rate constants of CCN with alcohols increase rapidly with the number of H-atoms in the alcohols shows that these reactions have big $A$ factor. And the big $A$ factor may come from the long-distance potential involving CCN radical and alcohol molecule. Now, we discuss the relation between the reaction rate constant and the long-distance potential by using orbiting theory [27,41,42].

According to this theory, the effective potential in the collision process could be expressed using the most favorable orientation method as

$$V = \frac{Eb^2}{r^2} - \frac{C_3}{r^3} - \frac{C_4}{r^4} - \frac{C_6}{r^6} \tag{3}$$

or the averaged orientation method as

$$V = \frac{Eb^2}{r^2} - \frac{C_6'}{r^6} - \frac{C_8}{r^8} \tag{4}$$

The $C_n$ coefficients may be expressed in terms of the dipole ($\mu$) and quadrupole moments ($Q$), polarizability ($\alpha$) and ionization potential ($I.P.$) [42,43] of the CCN and its collision partner (alcohols). In a collision at a given kinetic energy $E$, there exists an impact parameter $b_0$ where the maximum of the effective potential is just equal to kinetic energy $E$ and only for $b<b_0$, the collision pair should be effectual for the reaction. So the effectual cross section for the given kinetic energy $E$ can be expressed as

$$\sigma_{\text{eff}}' = \pi b_0{}^2(E) \tag{5}$$

Then the thermally averaged collision cross section at a given temperature $T$ can be expressed as
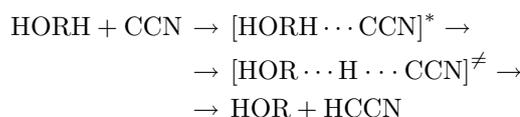
$$\sigma_{\text{eff}} = \left(\frac{1}{k_BT}\right)^2 \int_0^\infty \sigma_{\text{eff}}'(E)E \exp\left(-\frac{E}{k_BT}\right)\mathrm{d}E \tag{6}$$

where $k_B$ is Boltzmann constant. And the reaction rate will be written as

$$k = \sigma_{\text{eff}}\,\bar{V} \tag{7}$$

where $\bar{V}=(8k_BT/\pi\mu)^{1/2}$ is the averaged relative kinetic velocity.

The results of the calculations at 298 K using orbiting theory, the parameters used in the calculations and the experimentally measured cross sections $\sigma_{\text{exp}}$ (calculated by Eq.(7)) are summarized in Table II and illustrated in Fig.6. In the calculation, we used the second method, the averaged orientation method (Eq.(4)), and only gave the calculated cross section $\sigma_{\text{avg}}$. Figure 6 shows that there exists a preferable linear relationship between the calculated cross sections and the experimental cross sections. It suggests that the long-distance attractive potential in the collision pair plays an important role in the reaction initial stages and there may exist a large transition state (TS) whose scale is analogous to the complex. So the following deduce is reasonable:

$$\text{HORH} + \text{CCN} \rightarrow [\text{HORH}\cdots\text{CCN}]^* \rightarrow$$
$$\rightarrow [\text{HOR}\cdots\text{H}\cdots\text{CCN}]^{\neq} \rightarrow$$
$$\rightarrow \text{HOR} + \text{HCCN}$$

Moreover the reaction probability factor $P=\sigma_{\text{exp}}/\sigma_{\text{cal}}$ as expected increases with the number of C-atom in alcohol molecule. It also shows that the above conclusion is more available for the lager C-atom number of alcohols.
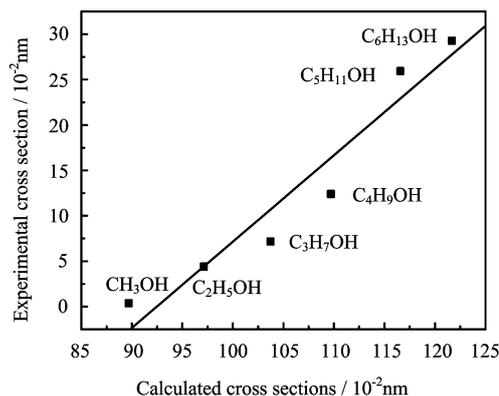


FIG. 6 Plot of the experimental measured cross section $\sigma_{\text{exp}}$ vs. the calculated cross section $\sigma_{\text{avg}}$. The experimental measured cross section calculated using Eq.(7). Line is least-squares best fit.

Obviously, the above discussion can only be viewed as guidance to the mechanism of the reactions. The simple one-dimensional collision calculation is an approximate version of the actual dynamics of the reactions, which is suggested that the model is more qualitatively applicable than quantitatively.

TABLE II Summary of the measured reaction cross sections $\sigma_{\exp}$, the calculated cross sections $\sigma_{\mathrm{avg}}$, and the parameters used in the calculations at room temperature

| Reactant | $\mu^{\mathrm{a}}$/Debye | $\alpha^{\mathrm{b}}$/Å$^3$ | $Q^{\mathrm{c}}$/$10^{-26}$esu cm$^2$ | $I.P.^{\mathrm{a}}$/eV | $\sigma_{\exp}{}^{\mathrm{d}}$/$10^{-2}$nm$^2$ | $\sigma_{\mathrm{avg}}{}^{\mathrm{e}}$/$10^{-2}$nm$^2$ | $P$ |
|---|---|---|---|---|---|---|---|
| CH$_3$OH | 1.70 | 3.27 | 0.50 | 10.85 | 0.38 | 89.70 | 0.004 |
| C$_2$H$_5$OH | 1.69 | 5.12 | 1.65 | 10.49 | 4.40 | 97.13 | 0.045 |
| C$_3$H$_7$OH | 1.68 | 6.93 | 2.40 | 10.10 | 7.18 | 103.72 | 0.069 |
| C$_4$H$_9$OH | 1.66 | 8.78 | 3.00 | 10.04 | 12.41 | 109.70 | 0.113 |
| C$_5$H$_{11}$OH | 1.75$^{\mathrm{c}}$ | 10.63 | 6.78 | 9.74$^{\mathrm{c}}$ | 25.93 | 116.57 | 0.222 |
| C$_6$H$_{13}$OH | 1.69$^{\mathrm{h}}$ | 12.54 | 7.35$^{\mathrm{h}}$ | 9.91$^{\mathrm{h}}$ | 29.27 | 121.68 | 0.241 |
| CCN | 0.60$^{\mathrm{f}}$ | 2.33$^{\mathrm{g}}$ | 4.13$^{\mathrm{h}}$ | 12.40$^{\mathrm{h}}$ | | | |

[a] Ref.[44].

[b] Calculated using the Lorentz-Lorenz equation $\left(\dfrac{n^2-1}{n^2+2}\right)\dfrac{M}{d} = \dfrac{4}{3}\pi N_A \alpha$, where $M$ is molecular weight, $d$ is density of the specimen (in units g/mL), $N_A$ is Avogadro constant, and $n$ is refractive index, the $n$ data following Ref.[44].

[c] Calculated using MP2/6-311++G(d,p) method.

[d] Experimental data.

[e] Calculated using the averaged orientation method.

[f] Ref.[45,46].

[g] Estimated following Ref.[47].

[h] Calculated using B3LYP/6-311++G(d,p) method.

## V. CONCLUSION

For the first time, the CCN radical rate constants for gas phase reactions with normal alcohols have been measured at room temperature from the decay of the CCN radical using the LP-LIF technique. The reaction rate constants increase with carbon chain length and are uniformly larger than that of the corresponding alkanes. By comparing with the corresponding reactions of CCN with alkanes, and O ($^3$P) and OH with alcohols, along with the qualitative analysis of LFE correlation and BDE correlation, we deduce that the H-atom abstraction is a plausible mechanism in the CCN reactions with alcohols. The OH group in the alcohols, with the strong electronegativity of O atom, plays the important role that activates locally the C−H bonds of the nearby C-atoms (by lowering the C−H bond energies) and thus increases the rate constants over the corresponding alkanes. The H-atom on the O−H bond rarely affect the reactions of CCN with alcohols. The calculation by using Orbiting theory shows that the long-distance attractive potential could play an important role in the reaction initial stages and may affect the reaction rate.

## VI. ACKNOWLEDGMENTS

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