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KINETIC STUDY OF OH REACTIONS WITH *N*-OCTANE AND *N*-DECANE USING RELATIVE RATE COMBINING WITH DISCHARGE FAST FLOW AND MASS SPECTROMETER TECHNIQUE

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Acquiring rate constants for gas phase reactions involving hydroxyl radicals (OH) is essential in modeling combustion chemistry and atmospheric chemistry[1,2]. There are several laboratory techniques used to measure rate constants for reactions[3], among them are: (1) fast-flow discharge system for absolute rate constant determination, normally under pseudo first order conditions[4,5] and (2) relative rate technique in which the ratio of the rate constant for the reactions of OH with a target and a reference compound is measured[6-12]. These techniques are widely applied to atmospheric chemistry studies and while these techniques produce useful kinetic data, they are each subject to some limitations because of unwanted secondary reactions. Some VOCs with low vapor pressure appear to be “sticky” and hence to be adsorbed onto the flow reactor wall. It becomes increasingly challenging to obtain accurate kinetic data under these circumstances due to large uncertainty in assessing the concentration of the excess reactant in the flow reactor and loss of the OH radicals.

To maximize the advantages and minimize the disadvantages of these two methods, we are developing a technique that combines the discharge fast flow system with the relative rate method, namely the RR/DF/MS technique, to carry out kinetic measurement for gas phase reactions involving OH radicals. The RR/DF/MS technique has recently been used in the study of rates of reactions of atomic fluorine methane and fluorinated methane compounds[13,14]. However, the RR/DF/MS has not previously been described in detail. Also to the best of our knowledge, the RR/DF/MS technique has not been employed to

study the reaction of OH radicals with VOCs. Present work focuses on developing the RR/DF/MS technique for OH kinetic study and on its application to kinetic parameter measurements for OH reactions with *n*-octane, cyclohexane and *n*-decane. These organic compounds are important air pollutants released from anthropogenic activities, and their reaction with atmospheric OH initiate the degradation of these compounds, which leads to formation of photochemical smog. Acquiring kinetic data for these reactions is key to understanding the impact of volatile organic compounds on the air quality.

EXPERIMENTAL

The RR/DF/MS experimental apparatus used for the kinetic study of gaseous phase reactions involving OH radicals has been described in detail previously[11,12].

The OH radicals were produced in the double sliding injector by reacting water vapor with fluorine atoms generated upstream of the double sliding injector by microwave discharge of 5% F_2 balanced in helium,

F_2 + microwave discharge $\rightarrow$ 2F (1)

F + H_2O $\rightarrow$ HF + OH k_2(298 K) = 1.4 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} [15] (2)

Kinetic analysis formulation

Assuming that the target compound and the reference compound reacted only with OH radicals,

OH + A (target compound) $\rightarrow$ products (I)

OH + B (reference compound) $\rightarrow$ products (II)

We can apply the rate law to reactions I and II,

$$-\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{I}}[\mathrm{OH}][\mathrm{A}] \qquad \text{(III)}$$

$$-\frac{d[\mathrm{B}]}{dt} = k_{\mathrm{II}}[\mathrm{OH}][\mathrm{B}] \qquad \text{(IV)}$$

Then,

$$-\frac{\partial}{\partial[\mathrm{OH}]}\left(\frac{\partial(\ln[\mathrm{A}])}{\partial t}\right) = -\frac{\partial^2(\ln[\mathrm{A}])}{\partial t\partial[\mathrm{OH}]} = k_{\mathrm{I}} \qquad \text{(V)}$$

and

$$-\frac{\partial}{\partial[\mathrm{OH}]}\left(\frac{\partial(\ln[\mathrm{B}])}{\partial t}\right) = -\frac{\partial^2(\ln[\mathrm{B}])}{\partial t\partial[\mathrm{OH}]} = k_{\mathrm{II}} \qquad \text{(VI)}$$

Integrating over time and [OH] we have

$$\ln\frac{[\mathrm{A}]_{t,[\mathrm{OH}]}}{[\mathrm{A}]_{t,0}} = \frac{k_{\mathrm{I}}}{k_{\mathrm{II}}}\ln\frac{[\mathrm{B}]_{t,[\mathrm{OH}]}}{[\mathrm{B}]_{t,0}} \qquad \text{(VII)}$$

where $[A]_{t,0}$, $[B]_{t,0}$, $[A]_{t,[OH]}$ and $[B]_{t,[OH]}$ represented the concentration of reactants A and B in the absence and presence of OH radical at time $t = t$, and k_I and k_{II} were the rate constants for reactions I and II, respectively[3]. Plotting $\ln([[A]_{t,[OH]}/[A]_{t,0})$ vs.

$\ln([B]_{t,[OH]}/[B]_{t,0})$ should yield a straight line with slope k_I/k_{II} and zero intercept. When k_{II} is known from independent studies, k_I can then be calculated by multiplying k_{II} with the slope.

RESULTS AND DISCUSSION

As a calibration of the RR/DF/MS technique we first examined the reactions of OH with *n*-octane and cyclohexane using 1,4-dioxane as reference compound,

$$C_8H_{18}(n\text{-octane}) + OH \rightarrow H_2O + C_8H_{17} \quad (3)$$

$$C_4H_8O_2(1,4\text{-dioxane}) + OH \rightarrow H_2O + C_4H_7O_2 \quad (4)$$

and

$$c\text{-}C_6H_{12}(\text{cyclohexane}) + OH \rightarrow H_2O + c\text{-}C_6H_{11} \quad (5)$$

$$C_4H_8O_2(1,4\text{-dioxane}) + OH \rightarrow H_2O + C_4H_7O_2 \quad (4)$$

Figure 1 shows typical kinetic data acquired for reactions 3 and 5 using the RR/DF/MS technique, which can be described by equation VII. A linear regression for each of group of data in Figure 2 produced a rate constant ratio of k_3/k_4 = 0.800 ± 0.028 and k_5/k_4 = 0.626 ± 0.018, respectively. This leads to a value of $k_{3(298K)}$ = (8.88 ± 0.31)x10^{-12} cm^3 $molecule^{-1}$ s^{-1} and $k_{5(298K)}$ = (6.95 ± 0.20)x10^{-12} cm^3 $molecule^{-1}$ s^{-1} for reactions 3 and 5, respectively. Within experimental uncertainty they were in very good agreement with the recommended values of $k_{3(298K)}$ = 8.71 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and $k_{5(298K)}$ = 7.21 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for reactions 3 and 5, respectively[2].

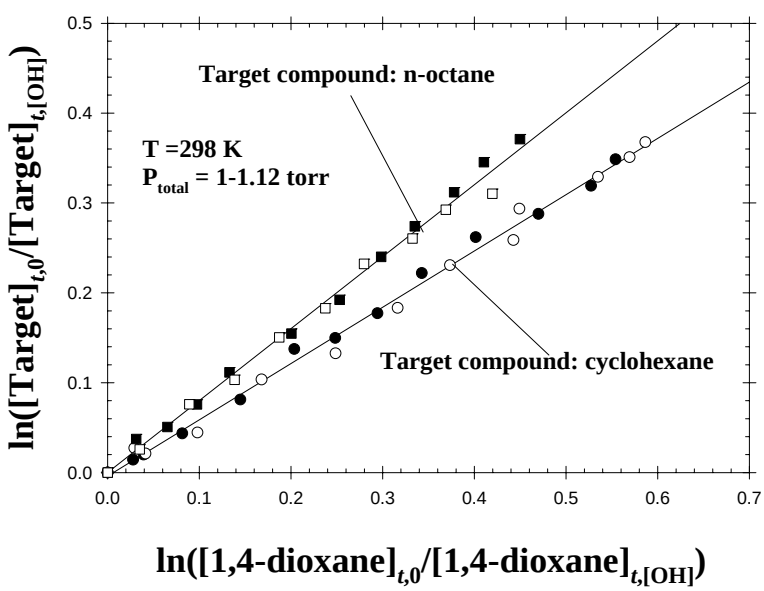

Figure 1. Kinetic data acquired with RR/DR/MS technique at a fixed reation time of 20 ms (open square and circle) and 40 ms (filled square and circle) for reactions of OH with *n*-octane and cyclohexane using 1,4-dioxane as a reference compound.

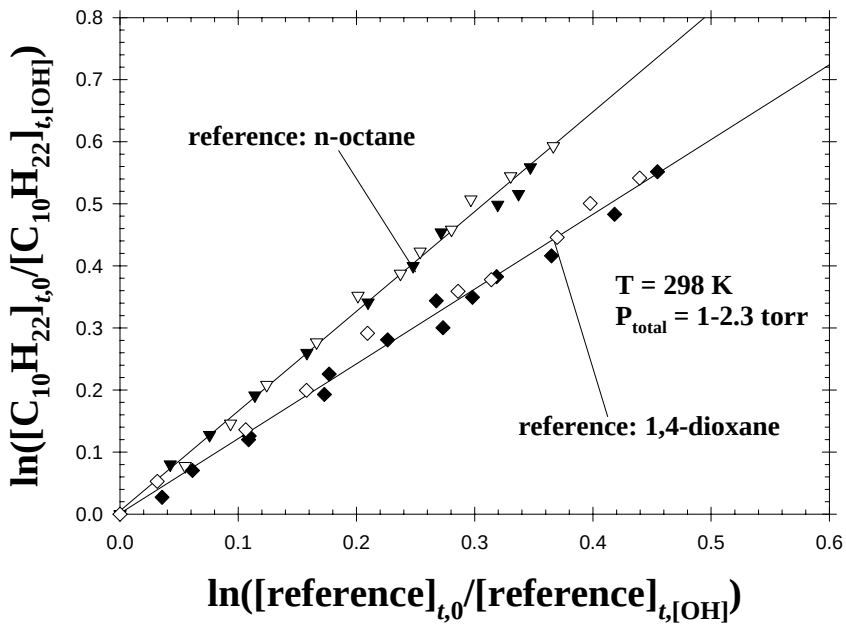

Figure 2. Kinetic data acquired with RR/DF/MS technique at a fixed reaction time of 20 ms (open triangle and diamond) and 40 ms (filled triangle and diamond) for reaction of OH with *n*-decane using *n*-octane and 1,4-dioxane as reference compounds.

The reaction of OH radicals with *n*-decane was then investigated in the present study using the RR/DF/MS technique with both *n*-octane and 1,4-dioxane as reference compounds,

$$C_{10}H_{22}(n\text{-decane}) + OH \rightarrow H_2O + C_{10}H_{21} \quad (6)$$

$$C_8H_{18}(n\text{-octane}) + OH \rightarrow H_2O + C_8H_{17} \quad (3)$$

and

$$C_{10}H_{22}(n\text{-decane}) + OH \rightarrow H_2O + C_{10}H_{21} \quad (6)$$

$$C_4H_8O_2(1,4\text{-dioxane}) + OH \rightarrow H_2O + C_4H_7O_2 \quad (4)$$

Figure 2 shows the plot of $\ln([n\text{-decane}]_{t,0}/[\text{n-decane}]_{t,[OH]})$ against $\ln([\text{reference}]_{t,0}/[\text{reference}]_{t,[OH]})$ at 298 K. Least-squares analysis of the kinetic data in Figure 3 produced a rate constant ratio of $k_6/k_3 = 1.603 \pm 0.052$ and $k_6/k_4 = 1.204 \pm 0.050$, respectively. Note that the rate constant ratio using *n*-octane as reference compound in the present work was about 12% higher than that reported by Aschmann *et al.*[9] and Behnke *et al.*[10]. This small discrepancy might reflect the difference between relative rate measurements performed under static and fast flow conditions. In our measurement the reaction time was confined to less than 50 ms, which was much shorter than that used in the chamber kinetic studies and the measurement in our flow reactor eliminated any interference due to secondary reactions after 50 ms. The rate constant for the reaction of OH with *n*-decane was determined to be $k_6 = (1.38 \pm 0.08) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The kinetic results obtained for reactions 3, 5 and 12 using the

RR/DF/MS technique will be compared with values measured using different techniques.

CONCLUSION

A technique combining the discharge fast-flow system with mass spectrometer and relative rate method (RR/DF/MS) has been developed to measure rate constants for the reactions of hydroxyl radical with *n*-octane and cyclohexane using 1,4-dioxane as a reference compound and for the reaction of hydroxyl radical with *n*-decane employing *n*-octane and 1,4-dioxane as reference compounds. Kinetic results obtained using the RR/DF/MS technique were in very good agreement with previous measurements for reactions 3, 4 and 6. This indicates that the RR/DF/MS technique is a reliable tool for kinetic measurement of gaseous phase reaction involving OH radicals.

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