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The kinetics of hydroxyl radical reactions with cyclopropane and cyclobutane

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Abstract. A laser flash photolysis/resonance fluorescence investigation has been carried out to study the kinetics of the overall reactions OH + cyclopropane (1) and OH + cyclobutane (2) in the temperature range 298–490 K and at 298 K, respectively. The following kinetic parameters have been determined:

$k_1 = (3{\cdot}9 \pm 0{\cdot}6)10^{-12}\exp\{-(2{\cdot}2 \pm 0{\cdot}1)\text{kcal mol}^{-1}/RT\}\,\text{molecule}^{-1}\,\text{cm}^3\text{s}^{-1}$,

$k_2(298\,\text{K}) = (17{\cdot}5 \pm 1{\cdot}5)10^{-13}\,\text{molecule}^{-1}\,\text{cm}^3\text{s}^{-1}$.

Keywords. Reaction kinetics; OH radicals; cycloalkanes.

1. Introduction

The reactions of OH radicals play a very important role in combustions and the chemical processes of the atmosphere. It is now generally accepted that laser techniques provide one of the best ways of studying the kinetics of such elementary reactions. [For a detailed overview on OH radical reactions and the relevant experimental techniques see the review by Atkinson (1986).]

In this paper we present our first results of a laser flash photolysis reaction kinetics study on the overall reactions of hydroxyl radicals with cyclopropane and cyclobutane:

$$\text{OH} + \text{cyclopropane} \rightarrow \text{products}, \qquad (1)$$

$$\text{OH} + \text{cyclobutane} \rightarrow \text{products}. \qquad (2)$$

For these reactions only very few kinetic data are available in the literature.

2. Experimental

The experiments were performed by using the laser flash photolysis/resonance fluorescence technique. A schematic diagram of the experimental setup is shown in figure 1. The main parts of the apparatus are (1) the excimer laser (Lambda Physik LPX 100) used as the photolytic light source; (2) the heatable reactor; (3) the resonance fluorescence detection system, consisting of the OH lamp and the detecting electronics; and (4) the gas handling system. Hydroxyl radicals were produced by the 193 nm

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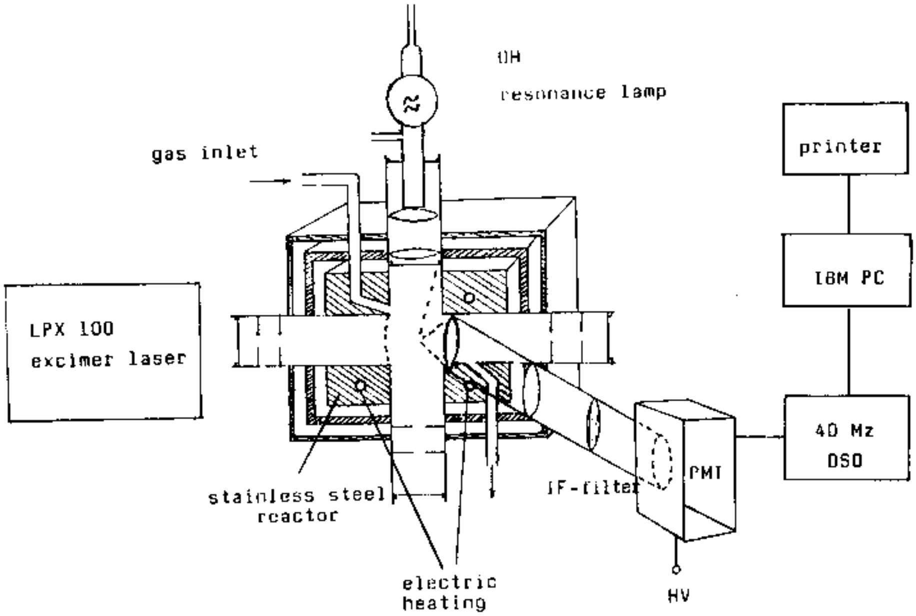

Figure 1. Schematic drawing of the laser flash photolysis/resonance fluorescence apparatus.

photolysis of HNO_3 provided by the excimer laser pulse. The initial OH radical concentrations were typically around $(1-2) \times 10^{12}$ molecule/cm^3. Following the laser flash, the OH concentration profiles were obtained by signal averaging with a 40 MHz digital storage oscilloscope (Hitachi VC-6041Z).

The purity of the reactants used in the experiments were as follows: cyclopropane (99·99%) and cyclobutane (99·86%). Argon (Linde, 99·996%) served as buffer gas.

3. Results and discussion

The reaction of OH radicals with cyclopropane has been studied in the temperature range 298–490 K and the cyclobutane reaction investigated at room temperature. In both series of experiments the overall pressure was typically 80–90 torr.

The reactions were carried out under pseudo first order conditions with [cycloalkane] ≫ [OH]. The bimolecular rate coefficients have been obtained by the usual first order scheme.

$$[\mathrm{OH}]_t = [\mathrm{OH}]_0 \exp(-k^I_{\mathrm{exp}} t),$$

$$k^I_{\mathrm{exp}} = k_i[\mathrm{cycloalkane}] + k_d.$$

Representative first order plots are shown in figures 2 and 3.

As a first step we have checked our experimental procedures for systematic errors by measuring the rate coefficients for the OH + ethane and OH + propane reactions at room temperature. The results are summarised in table 1 and are seen to agree satisfactorily with the recommendations of a recent review article (Atkinson 1986), therefore we conclude that no significant systematic errors are expected in the runs with cycloalkanes either.

In figure 4 the temperature dependence of the OH + cyclopropane reaction is shown

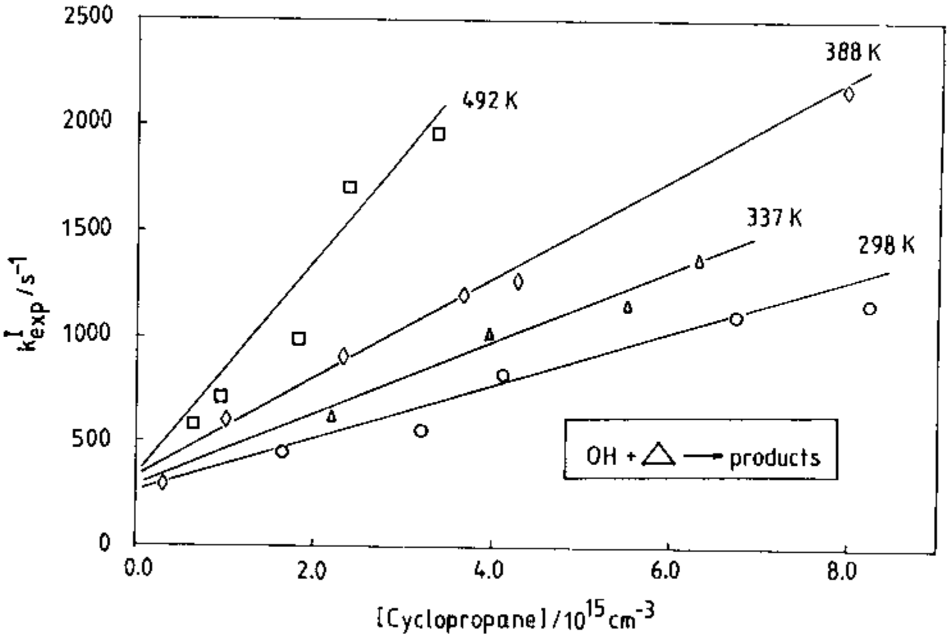

Figure 2. Representative pseudo first order plots of the OH + cyclopropane reactions.

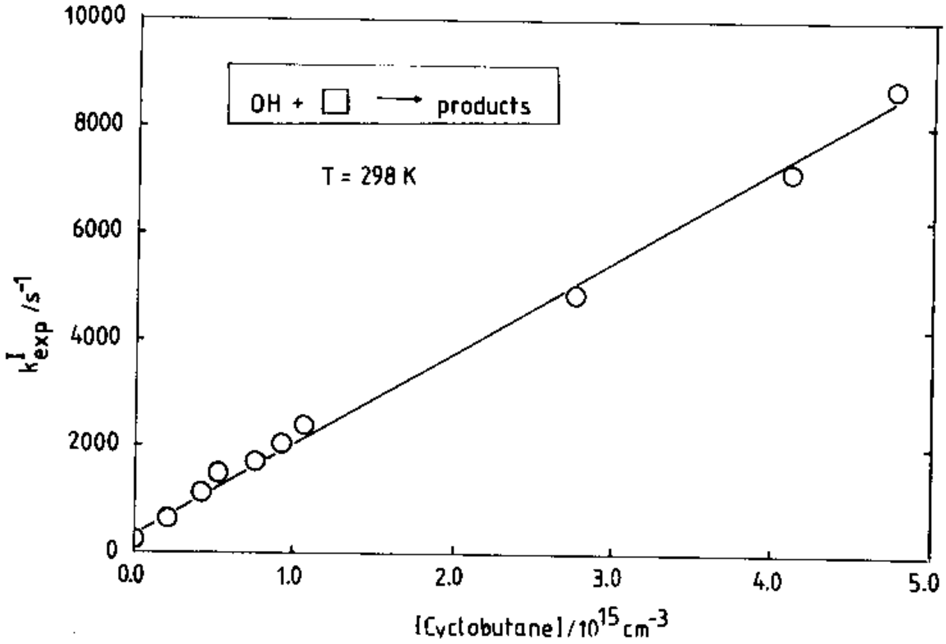

Figure 3. Pseudo first order plot of the OH + cyclobutane reaction.

in Arrhenius representation. We note here that the present investigation appears to provide the first rate coefficients above room temperature for reaction (1). The experimental data can be well described by the Arrhenius equation:

$$k_1 = (3{\cdot}9 \pm 0{\cdot}6)10^{-12} \exp\{-(2{\cdot}2 \pm 0{\cdot}1)\text{kcal mol}^{-1}/RT\} \text{ molecule}^{-1}\text{cm}^3\text{s}^{-1}.$$

Table 1. Summary and comparison of room temperature rate coefficients of OH radical reactions.

Reaction	$10^{13}k(298\,\mathrm{K})/\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ This work	$10^{13}k(298\,\mathrm{K})/\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ Literature value (references)
$OH + c\text{-}C_3H_6$	$1{\cdot}10 \pm 0{\cdot}14$	$0{\cdot}8 \pm 0{\cdot}2$ (Zetzsch 1980) $0{\cdot}62 \pm 0{\cdot}14$ (Jolly *et al* 1985)
$OH + c\text{-}C_4H_8$	$17{\cdot}5 \pm 1{\cdot}5$	$12{\cdot}0 \pm 3{\cdot}0$ (Gorse and Volman 1974)
$OH + c\text{-}C_5H_{10}$	—	$50{\cdot}6 \pm 2{\cdot}2$ (Droege and Tully 1987)
$OH + c\text{-}C_6H_{12}$	—	$72{\cdot}0 \pm 3{\cdot}1$ (Droege and Tully 1987)
$OH + C_2H_6$	$2{\cdot}74 \pm 0{\cdot}40$	$2{\cdot}74 \pm 0{\cdot}54$ (Atkinson 1986)
$OH + C_3H_8$	$1{\cdot}40 \pm 0{\cdot}30$	$1{\cdot}18 \pm 0{\cdot}35$ (Atkinson 1986)

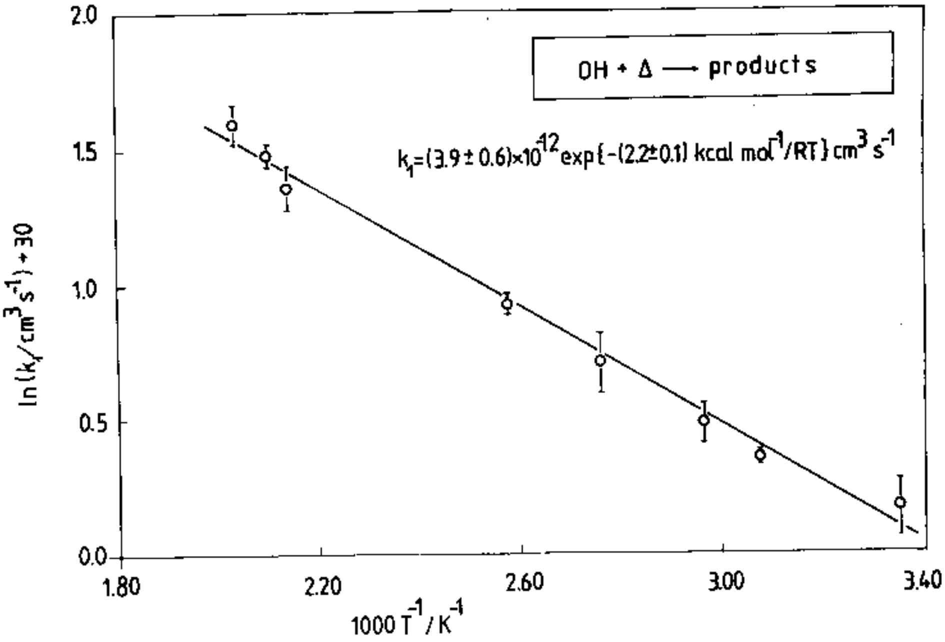

Figure 4. Arrhenius plot of the OH radical reaction with cyclopropane.

The kinetics of the overall reaction between OH radicals and cyclobutane has been investigated at room temperature, and the following rate coefficient has been determined:

$$k_2(298\,\mathrm{K}) = (17{\cdot}5 \pm 1{\cdot}5)\,10^{-13}\,\mathrm{molecule^{-1}\,cm^3\,s^{-1}}$$

In table 1 we have compared our room temperature rate coefficients with those available from the literature. It is seen that the values obtained in the present investigations are somewhat larger than those from the literature but overall the agreement is still reasonable.

The compilation of the kinetic data presented in table 1 clearly shows that the reactivity of the cycloalkanes in the reactions with OH radicals decreases with decreasing ring size, moreover, the highly strained cycloalkanes, cyclopropane and

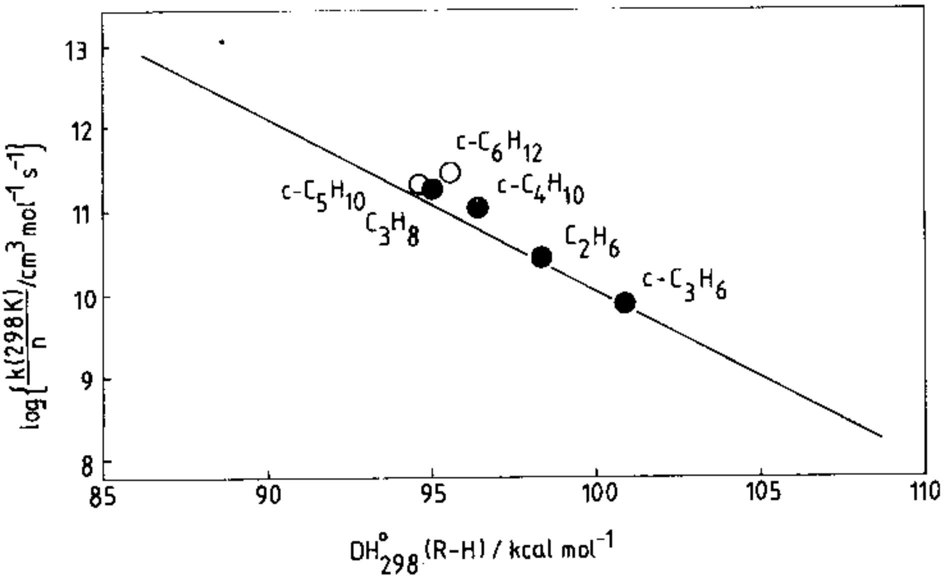

Figure 5. Correlation with bond dissociation energies (○, Droege and Tully (1987), ●, this work, the straight line is that given by Jolly *et al* (1985)).

cyclobutane react significantly slower than do their open chain counterparts. A trend of the order of reactivity per CH_2 group at room temperature can be given as follows:

$$k_{c-C_6H_{12}} > k_{c-C_5H_{10}} \simeq k_{n-\mathrm{alkane}} > k_{c-C_4H_8} > k_{c-C_3H_6}$$

The low reactivity of cyclopropane is caused by the relatively high activation energy of the reaction.

In order to search for quantitative relationships, the logarithm of the room temperature rate coefficients have been plotted against the C–H bond dissociation energies in figure 5 (the rate coefficients are divided by n, the number of equivalent C–H bond in the molecules). For comparison the straight line of Jolly *et al* (1985) is also shown which is based on a large data base of hydrogen abstraction reactions of OH radicals taken from the literature. A fairly good correlation can be seen in the figure between the rate coefficients and the BDE's, although the data points of the cycloalkanes appear to lie slightly, but systematically, above the straight line.

4. Conclusions

The hydrogen abstraction reactions of OH radicals with cyclopropane and cyclobutane are slow processes compared with other OH + hydrocarbon reactions. The present investigations provide kinetic parameters for the title reactions.

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