

Rate Constants of the Reactions of OH Radicals with Cyclopropane and Cyclobutane

S. DÓBÉ, T. TURÁNYI, A. A. IOGANSEN,* and T. BÉRCES

Central Research Institute for Chemistry, Hungarian Academy of Sciences,
Pusztaszeri u. 59-67, H-1025 Budapest, Hungary

Abstract

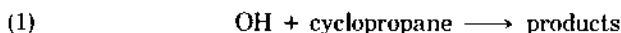
The kinetics of the reactions of hydroxy radicals with cyclopropane and cyclobutane has been investigated in the temperature range of 298–492 K with laser flash photolysis-resonance fluorescence technique. The temperature dependence of the rate constants is given by $k_1 = (1.17 \pm 0.15) \times 10^{-16} T^{2.2} \exp[-(1037 \pm 87) \text{ kcal mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = (5.06 \pm 0.57) \times 10^{-16} T^{2.2} \exp[-(228 \pm 78) \text{ kcal mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reactions $\text{OH} + \text{cyclopropane} \rightarrow \text{products}$ (1) and $\text{OH} + \text{cyclobutane} \rightarrow \text{products}$ (2), respectively. Kinetic data available for OH + cycloalkane reactions were analyzed in terms of structure-reactivity correlations involving kinetic and energetic parameters.

Introduction

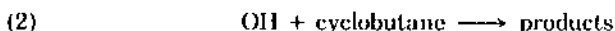
Hydrogen atom abstractions from hydrocarbons by hydroxy radicals play an important role in atmospheric chemistry and in combustion. This is the reason that a large number of rate constants have been determined for the reactions of OH radicals and alkanes both by relative and by direct experimental techniques (see ref. [1]). Some of these data have been used as reference values in relative rate studies (e.g., data for reactions $\text{OH} + \text{C}_6\text{H}_6$ and $\text{OH} + n\text{-C}_6\text{H}_{14}$), while others contributed to the exploration of structure-reactivity correlations [2–4].

In contrast to the OH + alkane reactions, only few previous rate measurements were made for OH + cycloalkane. Beside the room temperature direct kinetic studies of OH + cycloalkane reactions [5–9], rate constants as a function of temperature were obtained by Droege and Tully [10] from laser flash photolysis/laser induced fluorescence measurements for OH + cyclopentane and OH + cyclohexane. However, only room temperature rate constants are available for OH + cyclopropane [5,11], OH + cyclobutane [12], and OH + higher cycloalkanes [5,13].

In this article we report on absolute rate constants for reactions



and



in the temperature range of 298–492 K.

* Permanent address: Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Moscow 117977, U.S.S.R.

were determined at different temperatures. As can be seen from the representative results shown in Figure 1 and Figure 2, good straight lines were obtained when these pseudo first order rate constants were plotted against cycloalkane concentration. The second order rate constants were then extracted from the slopes of such plots. The kinetic data are summarized in Table I.

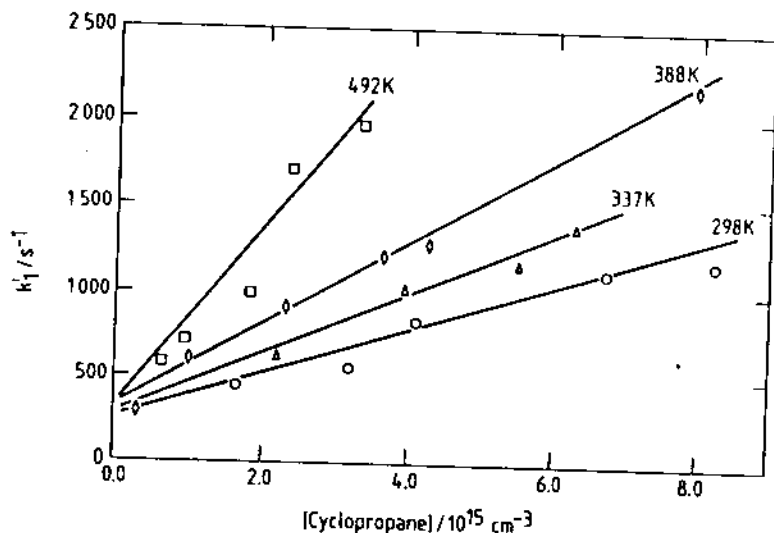


Figure 1. Plots of pseudo first order rate constants for reaction (1) against cyclopropane concentrations.

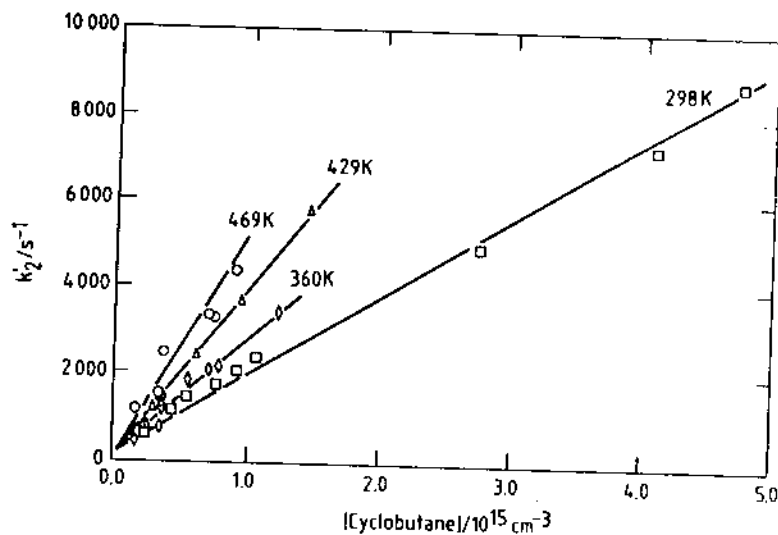


Figure 2. Plots of pseudo first order rate constants for reactions (2) against cyclobutane concentrations.

Experimental

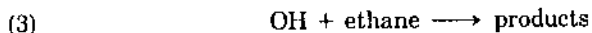
Kinetic measurements were carried out by using the laser flash photolysis/resonance fluorescence technique. Some details of the technique were given in ref. [14]. The basic parts of the apparatus were: (i) A gas handling system which provided a steady flow of a gas mixture through the reactor with a flow rate high enough to replace completely the reactor filling between two flashes and (ii) A reaction cell which was made of stainless steel and had a black anodized interior. Reactor was thermostated by using 4 heating cartridges and temperature measurements were made with a retractable Cromel-Alumel thermocouple; (iii) A Lambda Physik LPX 105 excimer laser with argon fluoride gas filling was used as the 193 nm light source in the photolytic generation of the hydroxy radicals from nitric acid and (iv) The detection system, where OH radicals were monitored by resonance fluorescence perpendicular to the photolysis line. Excitation light was obtained by microwave discharge in water vapor diluted with Ar. Induced fluorescence was focused through a 310 nm interference filter onto a photomultiplier tube (EMI, 9781 B); (v) Multiplier signal was fed into a digital storage oscilloscope (HITACHI, VC-6041 (Z) model) and finally, the digitalized information was processed by a microcomputer. The [OH] decay profile was obtained by averaging 256 signals.

The gas mixture which entered the reactor contained HNO_3 vapor, varying concentrations of the cycloalkane and Ar buffer gas enough to make up the overall pressure to 80–85 torr. Typical initial hydroxy radical concentration was $[\text{OH}]_0 = 1 \times 10^{12} \text{ cm}^{-3}$ and pseudo first order conditions were fulfilled in all experiments, i.e., $[\text{OH}]_0 \ll [\text{cycloalkane}]$. Quantitative data were extracted from the [OH] decay profile after about 1/3 of [OH]₀ was consumed. In this region, first order kinetics was strictly obeyed.

Nitric acid gas was prepared from concentrated HNO_3 (63% purity, Carlo Erba) with concentrated H_2SO_4 in 1:2 ratio; purification was made by bulb-to-bulb distillation in vacuum. Cyclopropane ($\geq 99\%$, J.T. Baker Chem. Co.) was purified by preparative GC to yield a sample of $\geq 99.99\%$ *c*- C_3H_6 with 0.01% propylene impurity. Cyclobutane was synthesized from 1,4-dibromobutane with Li-amalgam as described in the literature [15]. After GC purification, the *c*- C_4H_8 content was $\geq 99.96\%$ Ar (99.996%, Linde) and C_2H_6 (99.97%, Matheson) were used without further purification.

Results

The experimental technique used in this work has been tested by determining the room temperature rate constant of reaction



for which reliable kinetic data can be found in the literature. The average of six determinations gave $k_3 = (2.74 \pm 0.40) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in good agreement with $2.68 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the value which is the recommendation for k_3 given in Atkinson's recent review [1].

By monitoring the OH resonance fluorescence as a function of reaction time, pseudo first order rate constants k_1 ($\equiv k_1[\text{c-C}_3\text{H}_6]$) and k_2 ($\equiv k_2[\text{c-C}_4\text{H}_8]$)

TABLE I. Bimolecular rate constants for reactions of OH with cyclopropane and cyclobutane.*

T/K	$k_i/10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
	k_1	k_2
298 ± 3	1.11 ± 0.24	17.5 ± 1.2
325 ± 1	1.33 ± 0.08	
327 ± 1		22.2 ± 2.0
337 ± 1	1.52 ± 0.22	
360 ± 2		23.6 ± 1.4
362 ± 1	1.91 ± 0.42	
388 ± 1	2.36 ± 0.16	
392 ± 2		28.9 ± 3.0
429 ± 2		34.9 ± 2.8
467 ± 2	3.65 ± 0.58	
469 ± 3		39.8 ± 4.0
476 ± 3	4.12 ± 0.34	
492 ± 3	4.62 ± 0.62	

* Quoted errors are 2σ values.

Arrhenius representations of the rate parameters are presented in Figure 3. Although the temperature dependences of the rate constants are reasonably well described by the simple Arrhenius equation (broken lines), however, some curvature is obvious in the $\log k$ vs. $1/T$ plots. Therefore we

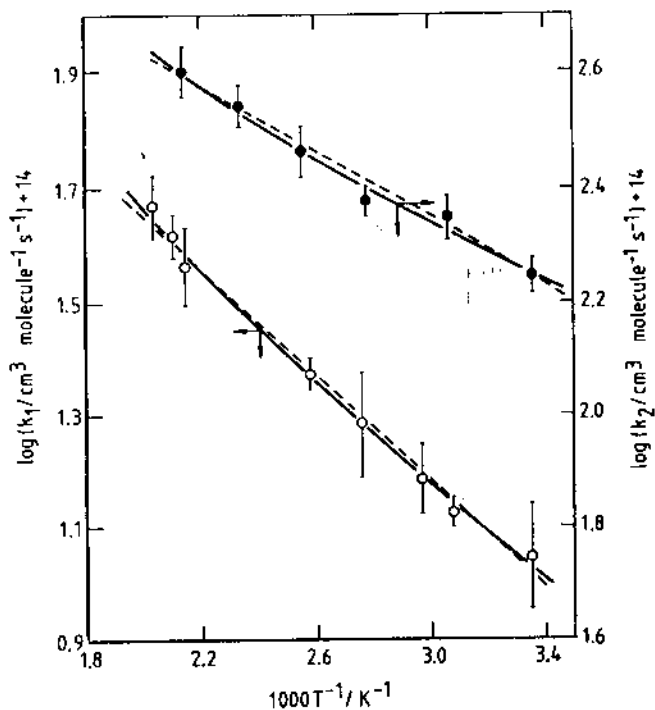


Figure 3. Arrhenius representation of kinetic data for reaction (1), O, and reaction (2), ●. The error bars represent $\pm 2\sigma$ errors. ---, Arrhenius equation; —, eq. (4).

chose to describe our experimental results by the expression

$$(4) \quad k = BT^n \exp(-H/RT)$$

with the exponent n fixed at the value of $3/2$ (see full lines). The use of this function is supported also by the results of Droege and Tully [10] on the reactions $\text{OH} + \text{cyclopentane}$ and $\text{OH} + \text{cyclohexane}$ for which eq. (4) with n values close to 1.5 has been found to be consistent with their experimental data. Nonlinear least squares fits of the B and H parameters in eq. (4) to the experimental results gave the following rate constant expressions (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ units):

$$(5) \quad k_1 = (1.17 \pm 0.15) \times 10^{-16} T^{3/2} \exp[-(1037 \pm 87) \text{ kcal mol}^{-1}/RT]$$

and

$$(6) \quad k_2 = (5.06 \pm 0.57) \times 10^{-16} T^{3/2} \exp[-(228 \pm 78) \text{ kcal mol}^{-1}/RT]$$

where the quoted errors are 2σ values. Equations (5) and (6) were used to obtain the solid lines indicated in Figure 3.

Discussion

The room temperature rate constants and the parameters of eq. (4) for OH reactions with cyclopropane and cyclobutane together with those for reactions with higher cycloalkanes are summarized in Table II. Our room temperature rate constants are about 30% higher than the literature values, which are for the reactions of cyclopropane 0.80 [11] and 0.62 [5] and of cyclobutane 12.0 [12] (all in $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units).

A two orders of magnitude increase in reactivity can be observed with increasing ring size. The specific reactivities of the CH_2 groups towards OH radical attack, expressed as $k_{\text{in}}/(\text{No. of ring } \text{CH}_2\text{-groups})$, are in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units: 0.37 (0.23) for $c\text{-C}_3\text{H}_6$, 4.4 (3.0) for $c\text{-C}_4\text{H}_8$, 10.0 (10.8) for $c\text{-C}_5\text{H}_{10}$, 11.9 (13.5) for $c\text{-C}_6\text{H}_{12}$, and 16.9 (13.5) for $c\text{-C}_7\text{H}_{14}$, where the numbers before and within the brackets are experimental and estimated [16] values, respectively. Reactivity of a CH_2 group in the strained cyclopropane and cyclobutane molecules is seen to be considerably smaller than in the five-, six- and seven-membered ring compounds. The effect of ring strain is accounted for explicitly in Atkinson's estimation method [16] by introducing "ring factors," however, significant deviation of the estimates from the

TABLE II. Kinetic data for $\text{OH} + \text{cycloalkane} \rightarrow \text{products}$ reactions.^{a,b}

Reaction	Ref.	$k_1(298 \text{ K})/10^{-13}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$B_1/10^{-16}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	H_1 cal mol^{-1}
$\text{OH} + \Delta$	this work	1.11 ± 0.24	1.17 ± 0.15	1037 ± 87
$\text{OH} + \square$	this work	17.5 ± 1.2	5.06 ± 0.57	228 ± 78
$\text{OH} + \bigcirc$	[9]	50.2 ± 2.2	7.02 ± 0.25	-205 ± 26
$\text{OH} + \bigcirc$	[9]	71.4 ± 3.1	8.97 ± 0.08	-272 ± 6
$\text{OH} + \text{---}$	[12]	118 ± 20		

^a Parameters are given in accordance with eq. (4) using $n = 1.5$ value.

^b Quoted errors are 2σ values.

measured rate constants is still apparent from the examination of the results given above. Differences between measured rate constants and values predicted from the structure-reactivity relationship had been observed also for reactions of OH radicals with cyclic ethers [17].

In Figure 4, experimental and estimated bimolecular rate constants are plotted vs. the number of CH₂-groups (i.e., the ring size). The striking feature of this plot is the large difference between the experimental rate constants for reactions of the smaller cycloalkanes with OH and the reactivities of the corresponding open chain alkanes. Since the plot of alkane reactivities is shown only for comparison, the experimental results are indicated in the figure by a fitted line given by the dashed line.

The increase in reactivity from *c*-C₃H₆ to *c*-C₆H₁₂ is caused mainly by the change of the energetic parameter H from about 1 kcal mol⁻¹ to a small negative value. In spite of this, no good correlation is found if log(*k*_{bi}/No. of CH₂-groups) or H is plotted against the ring strain energy.

A linear correlation was found to exist for several classes of organic compounds between the logarithm of the rate constant per C—H bond and the corresponding bond dissociation energy [5]. The correlation is based on the assumption that the differences in reactivity reflect differences in activation energies. Since we find that in case of OH + cycloalkane reactions the B constant per C—H bond depends on ring size, here we prefer to establish a correlation between the H parameters for hydrogen atom abstraction from cycloalkanes by OH and the appropriate C—H bond dissociation energies.

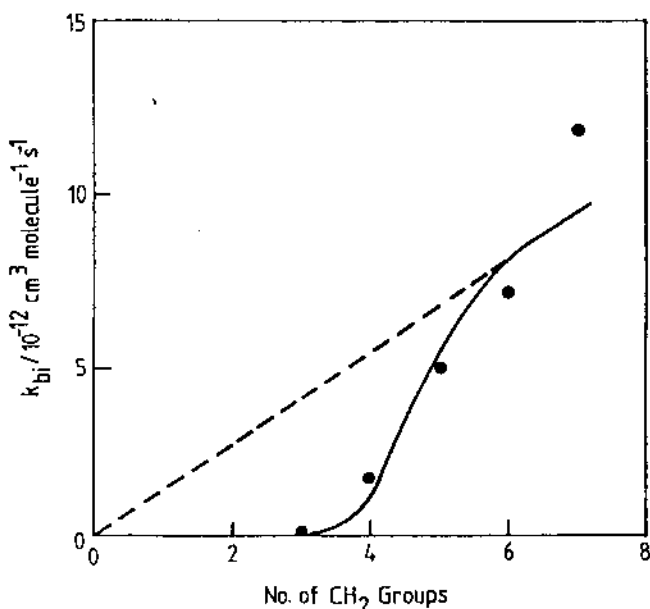


Figure 4. Bimolecular rate constants for OH + cycloalkane reactions as a function of the number of CH₂-groups in the reactant. Solid points: experimental values; solid line: estimations obtained with Atkinson's method [15]; and dashed line: estimations corresponding to the CH₂ reactivity in open chain alkanes [17].

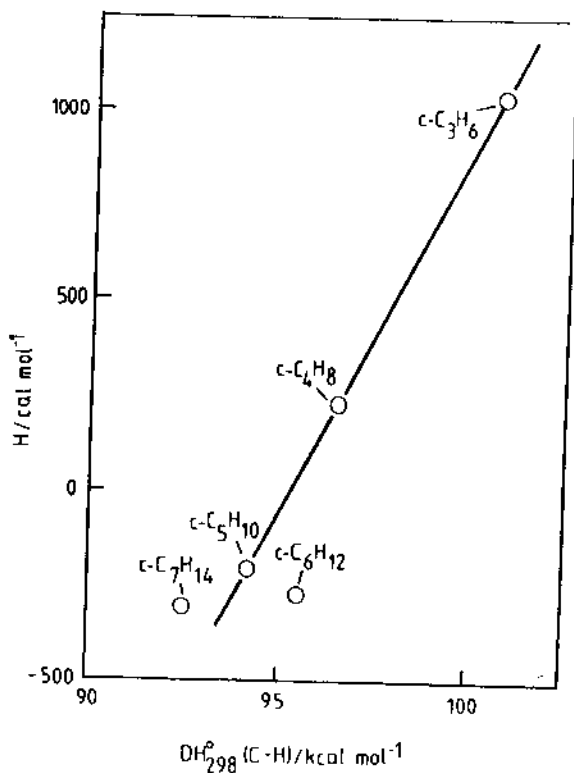


Figure 5. Plot of H parameter vs. C—H bond dissociation energies. $DH_{298}^0(\text{C}-\text{H})$ values are from ref. [18] except for $c\text{-C}_5\text{H}_{10}$ [19].

The plot of H vs. $DH_{298}^0(\text{C}-\text{H})$, presented in Figure 5, shows a good linear correlation for the OH + cycloalkane reactions. The deviations observed for the cyclohexane and cycloheptane reactions are of the order of the experimental errors. In case of cyclohexane, the error arises probably from the dissociation energy, while in case of cycloheptane an estimated H value is plotted which is obtained from the room temperature rate constant [13] with an estimated B parameter ($10.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). For the bond dissociation energy in cyclopropane, we used the older value from ref. [20]. The more recent recommendation [19] disagrees with the linear correlation deduced with the rest of cycloalkanes.

Our attempts to correlate the H parameters for hydrogen atom abstractions to the strain energies and C—H bond dissociation energies, respectively, in the cycloalkanes, indicate that it is the bond strength which governs the reactivities and the ring strain energies influence the reaction rates only by effecting the dissociation energies. This is in agreement with previous conclusions extracted from the study of the room temperature rate constants for reactions of mono- [5], bi-, and tricycloalkanes [21] with OH radicals.

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