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RESEARCH REPORT

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OH(A²Σ⁺) QUENCHING BY ALKANES

Robert D. Stephens

Environmental Science Department

July 19, 1984



General Motors
Research Laboratories
Warren, Michigan 48090

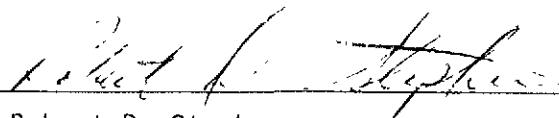
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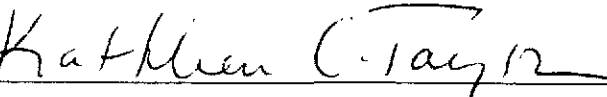
Title ● OH($A^2\Sigma^+$) Quenching By Alkanes

Date ● July 19, 1984

Reported by ●


Robert D. Stephens

Approved by ●


Kathleen C. Taylor, Head
Environmental Science Department



**General Motors Research Laboratories
Warren, Michigan 48090**

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PURPOSE

The purpose of this study was to derive the room temperature rate constants for the electronic quenching of $\text{OH}(A^2\Sigma^+)$ by a series of alkanes.

SUMMARY

This paper presents data used in the determination of the rate constants for the electronic quenching of $\text{OH}(A^2\Sigma^+)$ by a series of alkanes. The quenching measurements were obtained from discharge flow - resonance fluorescence investigations of $\text{OH}(X^2\Pi_1)$ reaction kinetics and are the first values reported for these species. An empirical relationship was found to exist between the measured rate constants for quenching of $\text{OH}(A^2\Sigma^+)$ by alkanes and the number of primary, secondary and tertiary hydrogens present in the alkane. The relative importance of each type of hydrogen to the quenching process follows the same ordering as the reactivity of hydrogens in reactions of alkanes with $\text{OH}(X^2\Pi_1)$.

INTRODUCTION

The importance of the hydroxyl radical in combustion and atmospheric chemical processes has made it the subject of study for many years. Extensive measurements of rate constants for both the $\text{OH}(X^2\Pi_1)$ reaction kinetics¹⁻⁷ and, to a lesser degree, $\text{OH}(A^2\Sigma^+)$ quenching kinetics⁶⁻¹⁰ have been reported. Quenching of $\text{OH}(A^2\Sigma^+)$ is thought to occur via energy transfer processes; however, chemical reactions have not been ruled out in most cases. Quenching processes are typically very efficient, occurring at rates near gas kinetic values. For this reason, quenching measurements have been useful in the quantification of OH concentration measurements made via laser induced fluorescence.^{11,12} A wider range of quenching measurements could also be useful in providing an improved understanding of quenching processes.

This paper presents measurements on the quenching of $\text{OH}(A^2\Sigma^+)$ by a series of alkanes made by the technique previously described.³ No previous literature values are available for the quenching of $\text{OH}(A^2\Sigma^+)$ by these species. The quenching kinetics are approximately three orders of magnitude faster than the corresponding $\text{OH}(X^2\Pi_1)$ reaction kinetics and occur at rates dependent upon the number of primary, secondary and tertiary hydrogens. The relative importance of each type of hydrogen to the quenching process follows the same ordering as the reactivity of hydrogens in reactions of alkanes with $\text{OH}(X^2\Pi_1)$.

EXPERIMENTAL

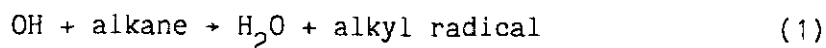
Since a detailed description of the experimental apparatus has been provided previously,³ a general review only will be provided here. The apparatus consists of a discharge-flow tube of 2.5 cm I.D. internally coated with halocarbon wax (Halocarbon Products Corp. series 15-00). The OH radicals were generated by the reaction of atomic hydrogen (produced by microwave dissociation of molecular

hydrogen) with an excess of nitrogen dioxide. This fast OH formation reaction occurred approximately 30 cm upstream of the first of eight injection ports equally spaced at 10 to 45 cm from a resonance fluorescence cell. Fluorescence was induced by a microwave resonance lamp containing approximately two torr (.266 kilopascals) of a mixture of 1% water in helium. The steady state OH fluorescence was monitored via a photomultiplier tube (EMI 9789QA) operated in the photon counting mode. Fluorescence was collected from a region approximately 0.5 cm in diameter through a series of lenses and apertures and an interference filter with peak transmittance at 3088 Å and full-width half-maximum transmittance at 3055 Å and 3172 Å.

The alkanes used in this study (99.5% purities except ethane at 99.0%) were analyzed by gas chromatography and gas chromatography-mass spectrometry and were found to meet the manufacturers specifications for purity. The helium (99.999%), hydrogen (92 ppm) in helium, nitrogen dioxide (274 ppm) in helium and alkanes were used without further purification.

All gas flows were controlled and measured via calibrated electronic mass flow controllers. The flow rates, pressure, temperature and photon count rates were collected and analyzed via computer. Statistical tests were applied to these measurements to verify that data collection occurred during stable experimental conditions. A series of eight measurements of each parameter was made at each reaction time and the data remeasured if the standard deviation in any measurement exceeded 3%.

This system was used to measure the ground state OH reaction kinetics at one torr (.133 kilopascals) for five reactions of the type:



as discussed elsewhere.⁴ The alkanes investigated were ethane, propane, n-butane, isobutane and 2,2-dimethylpropane. It is from these ground state OH reaction kinetics experiments that the values for the OH($A^2\Sigma^+$) quenching rate constants reported herein were derived.

The ground state OH reaction rates were obtained by measuring OH fluorescence intensity in the absence of the alkane reactant (I_F^0), then measuring the fluorescence intensity during the sequential addition of alkane through each of eight injection ports, and finally, after completion of reactant addition, remeasuring the fluorescence intensity in the absence of reactant. This last measurement of fluorescence intensity verifies that experimental parameters (e.g., resonance lamp intensity and OH concentration) have remained stable between the beginning and end of each experiment. These measurements provide information on relative OH concentration (fluorescence intensity) versus reaction time (determined by converting reaction distance to reaction time). Gas flow velocities used in all experiments were approximately 20 m s^{-1} .

The alkane gas flow rate was always less than 3% of total gas flow and did not, therefore, perturb the concentration of OH or other quenchers present in the experiments. All experiments were performed under pseudo-first-order conditions where $[\text{alkane}] \gg [\text{OH}] < 3 \times 10^{11} \text{ molecules cm}^{-3}$. A plot of \ln (fluorescence intensity) versus reaction time yields a slope which equals the observed pseudo-first-order decay rate, K_{OBS} , of OH, where $K_{\text{OBS}} = k_1[\text{alkane}] + k_w$. The k_w term represents the loss of OH at the flow tube wall. Figure (1) shows examples of data plotted in this fashion for several concentrations of dimethylpropane. An extrapolation of such data to zero reaction time provides a value for the OH fluorescence intensity (I_F) in the absence of removal of OH ($X^2\Pi_i$) by reaction with alkane but in the presence of added alkane, which also quenches fluorescence. These values of I_F were used in conjunction with the measured

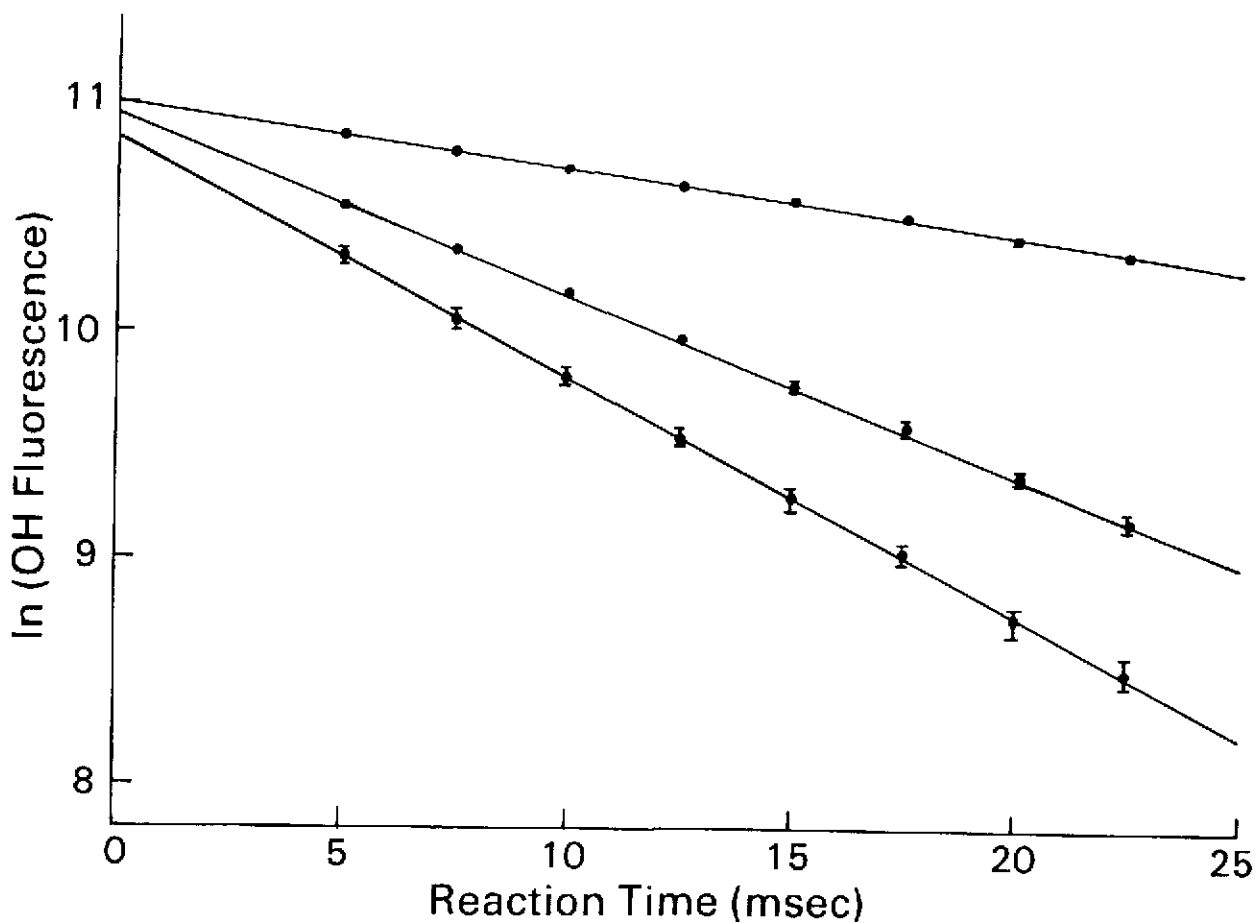
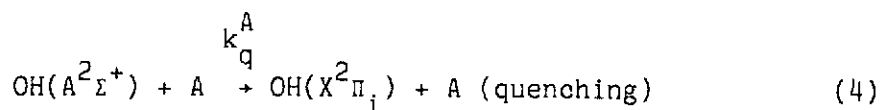
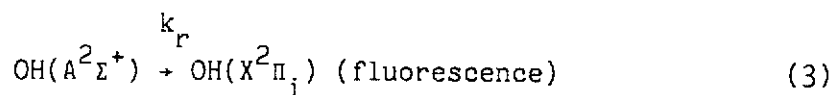
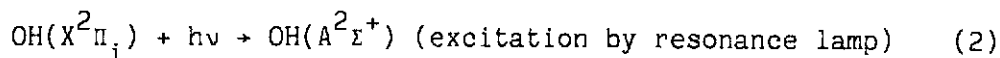


Fig. 1 Plots of the natural log of OH fluorescence signal vs reaction time at 296 K. The curves shown correspond to dimethylpropane concentrations of 4.54×10^{13} , 1.30×10^{14} and 1.90×10^{14} molec cm^{-3} , respectively from top to bottom. Statistical uncertainties shown are two standard deviations. Note that I_f (Y-Intercept) decreases with increasing reactant concentration.

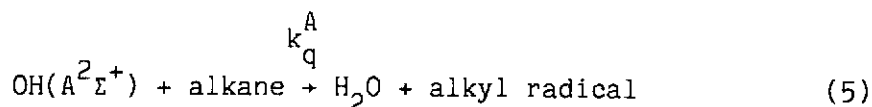
values of I_f^0 to calculate the quenching rate constants via a Stern-Volmer analysis.

RESULTS

The processes involved in the resonance fluorescence detection of OH are:



The term, k_r , is the rate constant for the radiative decay of $\text{OH}(A^2\Sigma^+)$ and k_q^A is the rate constant for $\text{OH}(A^2\Sigma^+)$ quenching by any species A. Although no evidence is available, it is possible that the $\text{OH}(A^2\Sigma^+)$ also chemically reacts with the quencher. For the alkanes this might occur analogously to reaction (1):



Under the experimental conditions employed, the primary species responsible for $\text{OH}(A^2\Sigma^+)$ quenching are helium, nitrogen dioxide and alkane. In the absence of alkane, the $\text{OH}(A^2\Sigma^+)$ fluorescence lifetime (τ_f^0) is:

$$\tau_f^0 = (k_r + k_q^{\text{He}} [\text{He}] + k_q^{\text{NO}_2} [\text{NO}_2])^{-1}$$

In the presence of alkane, the fluorescence lifetime (τ_f) is:

$$\tau_f = (k_r + k_q^{\text{He}} [\text{He}] + k_q^{\text{NO}_2} [\text{NO}_2] + k_q^{\text{A}} [\text{alkane}])^{-1}$$

At any given hydroxyl concentration, the ratio of OH fluorescence intensity in the absence of alkane to the fluorescence intensity in the presence of alkane is:

$$I_f^{\text{O}}/I_f = \tau_f^{\text{O}}/\tau_f = 1 + \tau_f^{\text{O}} k_q^{\text{A}} [\text{alkane}]$$

Using the radiative lifetime of $\text{OH}(\text{A}^2\Sigma^+)$ and the rate constants for quenching of $\text{OH}(\text{A}^2\Sigma^+)$ by nitrogen dioxide and helium as summarized by Schofield,⁸ the $\text{OH}(\text{A}^2\Sigma^+)$ fluorescence lifetime in the absence of alkane is essentially equal to the radiative lifetime of $\text{OH}(\text{A}^2\Sigma^+)$, i.e., approximately 0.76×10^{-6} s.⁸ Given the gas flow velocities employed in the experiments and the spatial resolution of fluorescence detection, the time resolution of fluorescence detection is long relative to processes (2) through (5), hence these processes are in steady state.

By plotting the ratio, I_f^{O}/I_f , versus concentration of alkane, a value for $\tau_f^{\text{O}} k_q^{\text{A}}$ is obtained as the slope. The values of k_q^{A} are, then, derived relative to the radiative lifetime of $\text{OH}(\text{A}^2\Sigma^+)$. Figure 2 shows the data plotted in this fashion. The values obtained in this study for I_f^{O}/I_f , alkane concentration and resultant $\tau_f^{\text{O}} k_q^{\text{A}}$'s are tabulated in Table I. Also listed is the value of the ratio of k_q to the approximate hard sphere collision rate constant. From Table I it can be seen that this ratio exceeds one for each alkane studied. The hard sphere collision rate constants were calculated using an $\text{OH}(\text{A}^2\Sigma^+)$ radius of 1.01×10^{-8} cm¹³ and the radius of the alkanes as calculated from gas viscosity values.¹⁴

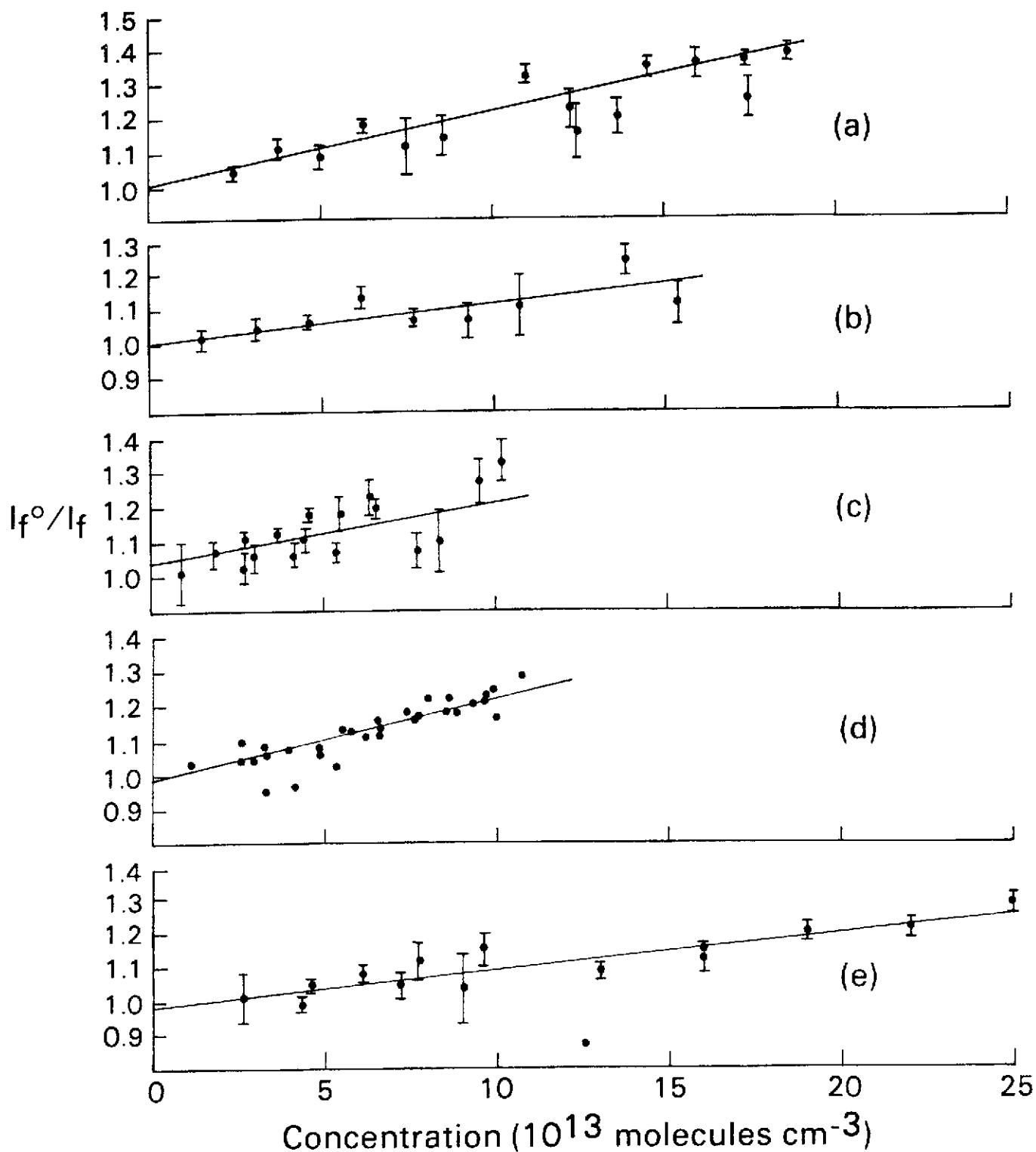


Fig. 2 Stern-Volmer plots, a) Ethane - note the different concentration scale for this plot only, b) Propane, c) Normal butane, d) Isobutane - error bars have been omitted for clarity, e) 2,2-dimethylpropane. Error bars in all plots are statistical uncertainties of $\pm 2 \sigma$.

Table I Summary of the reported quenching measurements showing the ratio I_f^0/I_f , alkane concentrations, the values obtained for τ_{fq}^{0kA} , and the ratio of the quenching rate constants obtained to the hard sphere collision rate constants. Uncertainties listed are two standard deviations. Concentration units listed are 10^{13} molecules cm^{-3} and units of τ_{fq}^{0kA} are $\text{cm}^3 \text{ molecule}^{-1}$.

Table I				
Compound	Conc.	I_f^0/I_f	τ_{fq}^{0kA}	k_q/k_{coll}
Ethane	12.3	1.05 ± .01		
	18.7	1.11 ± .03		
	24.9	1.09 ± .04		
	31.2	1.18 ± .02		
	37.3	1.12 ± .08		
	42.9	1.15 ± .03		
	55.2	1.33 ± .03		
	61.5	1.23 ± .06		
	62.3	1.16 ± .08		
	67.5	1.36 ± .04		
	67.7	1.27 ± .03		
	68.3	1.21 ± .05		
	72.4	1.35 ± .03		
	79.8	1.35 ± .04		
	86.9	1.36 ± .02		
	87.1	1.26 ± .06		
93.1	1.39 ± .03		4.15 ± .70 × 10 ⁻¹⁶	1.6 ± .3
Propane	1.55	1.01 ± .03		
	3.10	1.04 ± .03		
	4.64	1.06 ± .02		
	6.16	1.13 ± .03		
	7.70	1.07 ± .03		
	9.25	1.06 ± .05		
	10.8	1.11 ± .09		
	13.9	1.23 ± .05		
	15.4	1.11 ± .06		1.17 ± .72 × 10 ⁻¹⁵
Butane	0.91	1.01 ± .09		
	1.83	1.06 ± .04		
	2.74	1.11 ± .03		
	2.75	1.02 ± .04		
	2.98	1.05 ± .04		
	3.65	1.12 ± .02		
	4.18	1.06 ± .04		
	4.48	1.11 ± .04		
	4.57	1.18 ± .02		
	5.37	1.07 ± .03		
	5.49	1.18 ± .05		
	6.34	1.22 ± .05		
	6.56	1.09 ± .03		
	6.81	1.12 ± .09		
	7.75	1.07 ± .05		
	8.40	1.10 ± .09		
9.53	1.27 ± .06			
10.2	1.33 ± .06		1.77 ± 1.40 × 10 ⁻¹⁵	4.8 ± 3.8

Table I (cont'd)

Compound	Conc.	I_f^0/I_f	$\tau_{f,q}^0/k_q$	k_q/k_{coll}
Isobutane	1.09	1.03 ± .04		
	2.54	1.04 ± .03		
	2.54	1.09 ± .04		
	2.91	1.04 ± .04		
	3.29	1.09 ± .02		
	3.31	0.95 ± .09		
	3.31	1.06 ± .03		
	3.91	1.07 ± .03		
	4.09	0.97 ± .08		
	4.40	1.08 ± .03		
	4.83	1.06 ± .02		
	4.83	1.08 ± .03		
	5.41	1.03 ± .05		
	5.49	1.14 ± .04		
	5.50	1.13 ± .03		
	5.82	1.10 ± .04		
	6.21	1.11 ± .04		
	6.56	1.11 ± .03		
	6.57	1.16 ± .05		
	6.60	1.14 ± .03		
	7.40	1.18 ± .02		
	7.64	1.16 ± .07		
	7.71	1.17 ± .04		
	8.03	1.22 ± .08		
	8.59	1.18 ± .06		
	8.60	1.23 ± .04		
	8.78	1.18 ± .04		
	9.29	1.21 ± .03		
	9.71	1.22 ± .06		
	9.73	1.23 ± .05		
	9.87	1.25 ± .07		
	9.98	1.17 ± .04		
	10.7	1.29 ± .05	$2.35 \pm 0.42 \times 10^{-15}$	7.4 ± 1.3
2,2-Dimethylpropane	2.57	1.01 ± .07		
	4.29	0.99 ± .03		
	4.54	1.04 ± .02		
	6.04	1.07 ± .02		
	7.21	1.04 ± .04		
	7.72	1.11 ± .06		
	9.02	1.03 ± .10		
	10.6	1.14 ± .05		
	12.5	0.87 ± .59		
	13.0	1.08 ± .02		
	16.0	1.12 ± .04		
	16.0	1.14 ± .01		
	19.0	1.19 ± .02		
	22.0	1.20 ± .03		
	24.9	1.27 ± .03	$1.05 \pm 0.20 \times 10^{-15}$	$2.9 \pm .6$

DISCUSSION

Lin et al.¹⁵ developed a model which relates quenching cross sections to the attractive forces between an excited species (A*) and quencher (M). The intermolecular well depth between these species was approximated by

$\epsilon_{A^*M} \approx (\epsilon_{A^*A^*}\epsilon_{MM})^{1/2}$ resulting in the relationship

$$\ln \sigma_q^M = \ln C + \beta(\epsilon_{MM}/k)^{1/2}$$

where σ_q^M is the quenching cross section and $\beta = (\epsilon_{A^*A^*})^{1/2}/k T^2$. Fairchild et al.¹⁶ applied this relationship to the measurements of OH(A² Σ^+) quenching cross sections available in the literature and reported a "reasonable correlation" between the cross sections obtained at room temperature and $(\epsilon_{MM}/k)^{1/2}$. Although a correlation coefficient was not reported for the data employed in their analyses, we calculate a value for r of 0.81. With the inclusion of the data reported herein, the value of r is reduced to 0.77. The use of β and $\ln C$ obtained from the analysis by Fairchild et al. underestimated most cross sections obtained at elevated temperatures, however.

Experimental evidence on the fate of the A* M collision pair postulated upon for OH(A² Σ^+)¹⁶ is nonexistent. The possibility that reactive pathways exist has not been ruled out. Indeed, Zipf¹⁷ has evidence that OH(A² Σ^+) reacts with molecular nitrogen to form nitrous oxide. Many electronically excited atoms are also known to be quenched via chemical reactions. For example, O(¹D) is reactively quenched by many species.¹⁸ Its reactions are typically analogous to, but much faster than the reactions of O(³P) and OH(X² Π_1). These three species react with alkanes via hydrogen atom abstraction. Greiner has studied reactions of OH(X² Π_1) with alkanes and found that the reaction rate constants are dependent upon the number of primary, secondary and tertiary hydrogens in the

alkane.¹ Similarly, Anderson and Stephens⁴ found that their $\text{OH}(X^2\Pi_i) + \text{alkane}$ reaction rate constant measurements could be accurately estimated by the following equation:

$$\begin{aligned}
 k = & (1.30 \pm 0.61) \times 10^{-12} N_1 \exp[(-1001 \pm 138)/T] \\
 & + (1.21 \pm 0.28) \times 10^{-12} N_2 \exp[(-354 \pm 67)/T] \\
 & + (3.31 \pm 0.28) \times 10^{-12} N_3 \exp [(-281 \pm 25)/T] \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}
 \end{aligned}
 \tag{a}$$

In this equation N_1 , N_2 and N_3 are the number of primary, secondary and tertiary hydrogens, respectively.

In a fashion analogous to that used by Greiner¹ and Anderson and Stephens,⁴ the contributions to the quenching rate constants made by each hydrogen of each type was calculated. However, in these experiments the temperature dependence of quenching was not determined. Hence, the regression analysis took the form:

$$k_q^A = a N_1 + b N_2 + c N_3$$

Using the measured quenching rate constant, k_q^A for each alkane studied, along with the number of each type of hydrogen in that alkane, a value for each of the coefficients a , b and c was determined. The values of the coefficients a , b and c are the contributions to the quenching rate constant made by each hydrogen of each respective type, primary, secondary and tertiary. The values for a , b and c , when used with the values of N_1 , N_2 and N_3 yield an estimated quenching rate constant, k'_q for each alkane via the following relationship:

$$k'_q = 0.11 \times 10^{-9} N_1 + 0.42 \times 10^{-9} N_2 + 2.09 \times 10^{-9} N_3 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}
 \tag{b}$$

The values of the estimated quenching rate constants obtained from this equation are listed along with the measured values in Table II. Although the number of quenching rate constants measured in this study is limited to five, the correlation coefficient (r) between the estimated quenching rate constants (k'_q) and measured rate constants (k_q^A) exceeds 0.99. This empirical relationship, then accurately estimates the $\text{OH}(\text{A}^2\Sigma^+)$ quenching rate constants reported herein, and might be useful as a model for predicting rate constants for quenching of $\text{OH}(\text{A}^2\Sigma^+)$ by other alkanes.

Equations (a) and (b) demonstrate that the rate constants for both quenching of $\text{OH}(\text{A}^2\Sigma^+)$ and reactions of $\text{OH}(\text{X}^2\Pi_1)$ share a similar dependence upon the number of primary, secondary and tertiary hydrogens. Furthermore, the relative contribution of each type of hydrogen to the rate constants follows the same ordering:

$$3^\circ > 2^\circ > 1^\circ$$

For $\text{OH}(\text{X}^2\Pi_1)$, the contributions to the reaction rate constants by each hydrogen of each respective type (as reported by Anderson and Stephens⁴) follows the ratios 28.8 : 8.2 : 1, whereas for quenching of $\text{OH}(\text{A}^2\Sigma^+)$ the ratios are 19 : 3.8 : 1.

Although our measurements do not provide direct evidence, the dependence of the quenching rate constants upon the type and number of hydrogens present in an alkane is suggestive of reactive quenching of the type shown in reaction (5). These results do not conflict, however, with the explanation of the role of attractive forces in quenching processes. Indeed, a reasonable correlation exists ($r=0.75$) between $\ln \sigma_q^M$, as measured for the alkanes, and $(\epsilon_{MM}/k)^{1/2}$.

The measured quenching rate constants reported herein are the first available for these compounds. The values obtained are noteworthy due to their magnitude. Propane, n-butane, isobutane and dimethylpropane have values larger

Table II A summary of the measured (k_q^A) and estimated (k_q') quenching rate constants obtained in this study. Units are $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

Compound	k_q^A	k_q'
Ethane	$(5.46 \pm 0.92) \times 10^{-10}$	6.60×10^{-10}
Propane	$(1.54 \pm 0.95) \times 10^{-9}$	1.50×10^{-9}
Butane	$(2.33 \pm 1.84) \times 10^{-9}$	2.34×10^{-9}
Isobutane	$(3.09 \pm 0.55) \times 10^{-9}$	3.08×10^{-9}
2,2-Dimethylpropane	$(1.38 \pm 0.26) \times 10^{-9}$	1.32×10^{-9}

than any quenching rate constants previously reported for $\text{OH}(A^2\Sigma^+)$ despite the large values typical for quenching processes.

Although these measurements were not performed at temperatures directly applicable to combustion studies, the results indicate that quenching of $\text{OH}(A^2\Sigma^+)$ by hydrocarbons can possibly effect the accuracy of laser induced fluorescence measurements of OH concentrations in flame regions containing moderate hydrocarbon concentrations.

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