ROTATIONALLY RESOLVED RATE CONSTANT MEASUREMENTS FOR REMOVAL OF CH($A^2\Delta$ and $B^2\Sigma^-$) BY KETENE

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Rate constants for total removal of CH($A^2\Delta$) and CH($B^2\Sigma^-$) in collisions with ketene were measured. For the $A^2\Delta$ state, rate constants increased with vibrational quantum number; measured values were $(4.5 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $(8.0 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for $v' = 0$ and $v' = 2$ respectively. For $v' = 0$, rotational levels with quantum numbers from $N' = 4$ to $N' = 16$ were removed with similar rates within experimental errors; collisional disappearance of levels with higher rotational quantum numbers was faster for a factor of about 1.4. Calculations of cross sections for ketene and other fast colliders, assuming a multipole model, obtained a qualitative correlation with experimental values. CH($B^2\Sigma^-$) was more efficiently removed than CH($A^2\Delta$, $v' = 0$); for the lowest rotational levels a rate constant of $(5.8 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ was measured and a moderate increase with rotational quantum number was observed.

KEY WORDS: Methylidene, Quenching, Excited States.

INTRODUCTION

The collisional removal of CH($A^2\Delta$) at room temperature^{1–7} and at the higher temperatures characteristic of combustion flames^{8–12} have been studied in some extent. Despite the amount of data reported, the mechanisms involved in the quenching processes are not completely understood. Studies of the cross-section dependence on temperature and rotational quantum number indicate that the quenching mechanism differs from that established for other hydrides^{3,6,13} where collisional deactivation seems to be controlled, by long-range multipole attractive forces; some exceptions could be the quenching of CH($A^2\Delta$) by highly efficient collision partners as acetone,¹⁴ ammonia³ and chloromethanes.⁷

The quenching properties of other electronic states of CH have also been the subject of a number of studies. The $a^4\Sigma^-$ electronic state of CH in collisions with H_2 and hydrocarbons shows rate constants 100–1000 times smaller than those obtained for CH(X^2II);¹⁵ this is in agreement with calculations predicting that the H-atom

abstraction reaction of $\text{CH}(\text{a}^4\Sigma^-)$ has an activation barrier. It has been noted that on the basis of spin and orbital symmetry conservation rules, some similarity can be established between the collisional quenching of CH and CH_2 ; $\text{CH}(\text{a}^4\Sigma^-)$ parallels the kinetic behaviour of $\text{CH}_2(\text{X}^3\text{B}_1)$ in which a barrier for abstraction reactions has been found; $\text{CH}(\text{X}^2\Pi)$ undergoes insertion and addition reactions in resemblance with the a^1A_1 state of CH_2 . Removal rate constants of $\text{CH}(\text{X}^2\Pi)$ by several diatomic and polyatomic molecules are faster than for $\text{CH}(\text{A}^2\Delta)^2$ although some exceptions have been found.⁷ For the higher lying $\text{CH}(\text{B}^2\Sigma^-)$ more limited information is available;^{8,10,16} quenching studies carried in atmospheric and low pressure hydrocarbon flames^{8,10} show that the $\text{B}^2\Sigma^-$ state is quenched more rapidly than the $\text{A}^2\Delta$ state;¹⁰ however, recent measurements for several quenchers indicate that enhancement of quenching rates in going from the $\text{A}^2\Delta$ to the $\text{B}^2\Sigma^-$ states, does not always take place.¹⁶

In a recent work we have found that multiphoton dissociation of ketene with an ArF laser leads to formation of CH in several electronically excited states and we have observed that ketene is a very efficient quencher of the $\text{A}^2\Delta$ and $\text{B}^2\Sigma^-$ states of CH. In order to accumulate data which could provide information about the quenching mechanisms of the CH radical in collisions with fast quenchers, we have studied the removal by ketene of several vibrational and rotational energy levels of the electronic $\text{A}^2\Delta$ and $\text{B}^2\Sigma^-$ states of CH.

EXPERIMENTAL

CH in the $\text{A}^2\Delta$, and $\text{B}^2\Sigma^-$ electronic states were produced following multiple photon dissociation of gas samples of ketene at room temperature, with an ArF excimer laser. Fluorescence from excited CH photofragments was observed at right angles with respect to the photodissociation laser. The fluorescence was focused onto the entrance slit of a 0.5 m Jarrell-Ash monochromator and viewed by a photomultiplier EMI 9816QB. Time resolved fluorescence was recorded by a 40 MHz digital oscilloscope Tektronix 2430A (risetime of 12 ns and vertical resolution of 8 bits). Typically, 32 decay traces were averaged before being transferred to a personal microcomputer to be stored and analyzed.

Samples of ketene were synthesized by pyrolysis of acetic anhydric vapour at 500°C and then degassed and purified by trap-to-trap distillation. Mass-spectrometric analysis of samples indicated no more than 1% impurities.

Pressures were measured by a capacitive manometer MKS Baratron, type 227A (pressure range up to 1 Torr).

RESULTS

Quenching of $\text{CH}(\text{A}^2\Delta)$

a) Quenching of $\text{CH}(\text{A}^2\Delta, v' = 0$ and $v' = 1$)

Rate constants for removal of the $v' = 0$ and $v' = 1$ levels of $\text{CH}(\text{A}^2\Delta)$ were measured. Time resolved emission from the overlapping Q-branches of the $\text{CH}(\text{A}^2\Delta, v' = 0 \rightarrow$

$X^2\Pi$, $v'' = 0$) and $CH(A^2\Delta$, $v' = 1 \rightarrow X^2\Pi$, $v'' = 1$) bands at $\lambda = 430.7 \pm 1$ nm was recorded. We estimate that contribution to the total emission from $v' = 1$ is smaller than 50% within the above bandwidth.

Decay traces at pressures of ketene in the range from 40 to 200 mTorr were fitted to single exponentials. A typical decay trace and semilogarithmic plot are shown in Figure 1. Linear Stern-Volmer plots obtained representing reciprocal decay lifetimes versus ketene pressure are shown in Figure 2. The rate constant for total quenching of $CH(A^2\Delta)$ by ketene obtained from the slope of the Stern-Volmer linear graph is listed in Table 1.

Table 1 Lifetimes extrapolated at zero pressure and removal rate constants for collisions with ketene, measured for several rotational levels of $CH(A^2\Delta)$ and $CH(B^2\Sigma^-)$.

Vibronic state	Rotational line P , Q , $R(N')$	$k_M/10^{-10}$ cm^3 $molec^{-1}$ s^{-1}	Lifetime/ns
$A^2\Delta$, $v' = 0$, 1	Q-branch	4.5 ± 0.5	590 ± 40
$A^2\Delta$, $v' = 0$	R(4)	4.4 ± 0.5	575 ± 50
	R(5)	4.9 ± 0.5	615 ± 45
	R(6)	4.3 ± 0.4	590 ± 45
	R(7)	4.0 ± 0.6	545 ± 60
	R(8)	4.4 ± 0.4	535 ± 50
	R(9)	4.2 ± 0.5	590 ± 70
	R(13)	4.6 ± 0.4	535 ± 45
	R(16)	4.8 ± 0.4	545 ± 45
	R(19)	5.5 ± 0.4	590 ± 45
	R(22)	6.5 ± 0.4	600 ± 40
$A^2\Delta$, $v' = 2$	Q-branch	8.0 ± 1	300 ± 40
$B^2\Sigma^-$, $v' = 0$	P(1,2,5-7)	5.8 ± 0.3	340 ± 30
	P(11-13)	7.3 ± 0.3	415 ± 30

b) Quenching of $CH(A^2\Delta$, $v' = 2$)

Deactivation of $CH(A^2\Delta$, $v' = 2$) was studied by recording the time resolved fluorescence at $\lambda = 432.5 \pm 0.2$ nm at different ketene pressures in the range from 30 to 150 mTorr; the isolated spectral region corresponds to the Q-branch of the $CH(A^2\Delta$, $v' = 2 \rightarrow X^2\Pi$, $v'' = 2$) transition without rotational resolution. Fluorescence traces were analyzed finding that they followed monoexponential decays in the whole range of ketene pressures investigated. Stern-Volmer analysis of decay data lead to the linear representation shown in Figure 2; the rate constant for total removal by ketene and collision-free lifetime are listed in Table 1. To our knowledge no measurements of the radiative lifetime for the $v' = 2$ level of $CH(A^2\Delta)$ have been reported in the literature; similar values than those measured for $v' = 0$ and for rotational levels with $N' < 11$ of $v' = 1$ would be expected;^{17,18} however the collision-free lifetime measured in the present work is shorter, which would be in agreement with previous indications of weak predissociation of this level.¹⁷

Figure 1 Quenching of $\text{CH}(\text{A}^2\Delta, v' = 0,1)$ by 125 mTorr of ketene. Typical decay trace, semilogarithmic plot and residuals.

c) Dependence on rotational quantum number

Removal rates of several rotational levels of $\text{CH}(\text{A}^2\Delta, v' = 0)$ by pressures of ketene in the range from 20 to 200 mTorr were measured. Isolation of a particular $\text{R}(\text{N}')$ line of the $\text{CH}(\text{A}^2\Delta, v' = 0 \rightarrow \text{X}^2\Pi, v'' = 0)$ transition was achieved by setting the appropriated spectral resolution in the monochromator. Decay traces corresponding to rotational levels with $\text{N}' > 15$ were analyzed between the maximum signal intensity and the point where the signal reaches 5% of the initial maximum value. In the whole range of ketene pressures investigated decays could be fitted to single exponentials. Time resolved fluorescence from lower rotational levels showed also

Figure 2 Rates for removal of $CH(A^2\Delta)$ versus ketene pressure obtained from analysis of fluorescence decays: a) from levels with vibrational quantum number $v' = 0$ and $v' = 1$, b) from levels with $v' = 2$.

good monoexponential decays for traces recorded at pressures of ketene below 80 mTorr. At higher ketene pressures, small deviations from the monoexponential behaviour at times longer than 600 ns could be observed; the latter could indicate that at high pressures of ketene, relaxation of levels with high rotational quantum number can result in some population of the lower rotational levels, similarly to the behaviour observed in a number of systems.^{14,19-21} In order to separate this small long-living contribution, traces obtained at ketene pressure over 80 mTorr were analyzed from the point of maximum fluorescence intensity up to 15% of the maximum value; the analyses showed that in this region a single-exponential decay dominates the time resolved fluorescence.

Stern-Volmer plots of removal rates versus ketene pressure, measured for rotational levels $N' = 6$, $N' = 19$ and $N' = 22$ are shown in Figure 3. In Table 1 the rate constants for several rotational levels are listed together with the lifetimes obtained from the zero pressure intercept of the linear Stern-Volmer plots. Rate constants show, within experimental error, no dependence on rotational quantum number up to rotational levels with $N' < 19$, increasing moderately at $N' = 22$. The collision-free lifetimes obtained for different rotational quantum numbers differ from each other no more than 15% which is within experimental error; the average value is 572 ± 50 ns, close to that reported in the literature.^{3,5,13,17}

Quenching of $CH(B^2\Sigma^-)$.

Decay rates for quenching of the $CH(B^2\Sigma^-, v' = 0 \rightarrow X^2II, v'' = 0)$ fluorescence in the presence of 15–200 mTorr of ketene were measured. For rotational levels with low

Figure 3 Rates for removal of several rotational levels of $\text{CH}(\text{A}^2\Delta, V' = 0)$ versus ketene pressure, obtained from analysis of rotationally resolved fluorescence decays: a) from levels with rotational quantum number $N' = 6$, b) $N' = 19$, c) $N' = 22$.

quantum numbers pressure-dependent time-resolved emissions at $\lambda = 390 \pm 0.5$ nm were recorded; within this bandwidth the observed fluorescence corresponds to emission from rotational levels $N' = 5-7$ with a smaller contribution from $N' = 1,2$.

Measurements of the total disappearance rate constants of levels with higher rotational quantum numbers were also performed; in this case the experiments were carried at $\lambda = 398.5 \pm 1.2$ nm; within this wavelength interval, only rotational levels with $N' = 11-13$ contribute to the emission. Pressure-dependent decay lifetimes were obtained fitting single exponentials to the recorded traces. Stern-Volmer analysis of traces obtained for low rotational levels gave a very good fitting to a straight line; the slope was about 25% smaller than that obtained for rotational levels with $N' = 11-13$. Both linear plots are shown in Figure 4. Zero-pressure intercepts for low rotational levels lead to a value slightly slower than for higher N' ; this is in accordance with previous measurements indicating that the radiative lifetimes for the $\text{B}^2\Sigma^-$ state have a slight dependence on rotational quantum number.¹⁷ Total removal rate constants and collision free lifetimes are listed in Table 1.

DISCUSSION

For a particular rotational level of $\text{CH}(\text{A}^2\Delta, v' = 0)$, the rate constants listed in Table 1 represent the contribution of electronic quenching (reactive or inelastic) and rotational energy transfer. In atmospheric flames, rotational energy transfer has been shown to be several times faster than electronic quenching.⁸ In collisions with ketene, an estimation of the relative importance of rotational relaxation can be obtained by

Figure 4 Removal rates of several rotational levels of $\text{CH}(\text{B}^2\Sigma^-, v' = 0)$ obtained from analysis of fluorescence decays: a) from levels with rotational quantum number $N' = 5-7$; b) from levels with $N' = 11-13$.

analyzing the relative intensities of resolved rotational lines belonging to the R-branch of the $\text{CH}(\text{A}^2\Delta, v' = 0 \rightarrow \text{X}^2\text{II}, v' = 0)$ emission spectra, recorded at different pressures of ketene. The analysis showed that $\text{CH}(\text{A}^2\Delta, v' = 0)$ is formed with rotational populations which cannot be described in terms of a single Boltzmann type distribution;^{23,24} however we found that collisions with ketene in the pressure range from 40 to 250 mTorr produced only moderately small changes in the rotational distribution; the latter is also in agreement with the time resolved experiments reported above, in which only small deviations from monoexponential decays were obtained. From the spectral observations mentioned above, the contribution of rotational relaxation to the total disappearance of each level can be roughly estimated as less than 15% of the total rate constant. Therefore we conclude that, although some rotational relaxation takes place, the main contribution to the removal of the $\text{A}^2\Delta$ state by ketene arises from electronic quenching. The rate constants measured in this work for quenching of several N' levels of $\text{CH}(\text{A}^2\Delta, v' = 0)$ in collisions with ketene, are of the same magnitude to those reported for colliders such as CS_2 and large hydrocarbons⁷ and faster than those observed for NH_3 ,^{3,6} acetone¹⁴ and the lowest alkane series.^{2-4,6} For the fastest quenchers, such as NH_3 , it has been said that long range attractive forces are probably involved in the collisional relaxation mechanism. The same mechanism seems to take place in the collisional quenching by acetone; for the latter, measurements carried for rotational levels up to $N' = 7$ show that increasing rotational quantum number leads to decreasing rate constants¹⁴. Removal of $\text{CH}(\text{A}^2\Delta, v' = 0)$ by ketene is not enhanced with rotational quantum number up to $N' < 16$. However it has been pointed that when highly efficient polar quenchers are involved, this behaviour would also be compatible with a relaxation

mechanism dominated by the attractive part of the potential.¹³ For several fast quenchers of CH(A²Δ), with high dipole moments, we have calculated thermally averaged cross sections at 300 K assuming a multipole model²² and using the orientationally averaged expressions for the multipole forces.⁶ Calculated and experimental cross sections are given in Table 2. For ketene and ammonia a qualitative correlation is obtained; for the chloromethanes, although they are slower quenchers, the calculated cross sections are somewhat faster than those calculated for ketene and ammonia. Different reaction probabilities for each quencher, following complex formation, could account for the deviations; if this were the case, the lower probabilities observed for the chloromethanes would suggest that addition to the unsaturated bonds of ketene is more efficient than reactivity towards carbon-halogen bonds.

Table 2 Cross-sections for collisional removal of CH(A²Δ): experimental* and thermally averaged values calculated assuming a multipole model. Parameters used in the calculation.

Quencher	μ/D	$Q/10^{-26}$ esu cm ³	α/A^3	IP/eV	σ_{exp}/A^2	σ_Q/A^2
CH ₂ CO	1.42 ^a	-0.7 ^b	4.12 ^{c**}	9.41 ^d	57	93
NH ₃	1.47 ^a	-1 ^e	2.26 ^c	10.19 ^d	37	78
CHCl ₃	1.01 ^a	3.5 ^f	8.23 ^c	11.42 ^d	27	101
CH ₂ Cl ₂	1.6 ^a	4.1 ^f	6.48 ^c	11.35 ^d	13	102
CH(A ² Δ)	0.88 ^g	2.287 ^h	2.2 ^f	8.25 ^f		

^a Taken from reference 25

^b Taken from reference 26

^c Taken from reference 27

^d Taken from reference 28

^e Taken from reference 22

^f Taken from reference 7

^g Taken from reference 29

^h Value given for CH(X²II) in reference 30

* Obtained from the experimental rate constants by the expression $\sigma_{\text{exp}} = k_M/(8 kT/\pi\mu)$ at 300 K

** Estimated from bond polarizabilities

Comparison between rate constants obtained for CH(A²Δ, $v' = 0$) and CH(A²Δ, $v' = 2$) shows a significant increase of total deactivation rate by ketene with vibrational energy. Vibrational energy transfer in electronically excited states of other hydrides has been shown to be competitive with that for electronic quenching;¹³ however for CH(A²Δ) in atmospheric pressure flames, rate for vibrational energy transfer from $v' = 1$ to $v' = 0$ is only a small fraction of the electronic relaxation⁸ For $v' = 2$, measurements of the ratio between vibrational energy transfer and electronic relaxation have not been reported in the literature; the higher efficiency of removal rate constant observed with increasing vibrational energy of CH(A²Δ) could reflect the contribution of vibrational relaxation; on the other hand, collisional energy transfer to the rotational manifold of $v' = 0$ and $v' = 1$ of CH(B²Σ⁻), lying on the same energy region, could significantly enhance the deactivation rate for the $v' = 2$ level of A²Δ.

Regarding the various terms contributing to the total removal rate constants measured for the B²Σ⁻ state, similar considerations to those discussed above could apply. We have found that rotational populations obtained at pressures of ketene

between 80 and 500 mTorr can be fitted to hot Boltzmann distributions with temperatures which do not differ in more than 6% over the whole range of ketene pressures investigated²⁴. This seems to indicate that the main contribution to removal of $\text{CH}(\text{B}^2\Sigma^-)$ by ketene arises from electronic quenching. The total disappearance rate constant measured for the $\text{B}^2\Sigma^-$ state in the low N' levels is of the same magnitude as that obtained for the high rotational levels of $\text{A}^2\Delta$; at higher N' the rate is about 25% faster. In atmospheric pressure flames of methane, oxygen and nitrogen, dependence of rate constants on rotational quantum number was also observed although its degree was found to vary with the collisional environment of the flame.¹¹ Comparison with recent data obtained for a wide number of quenchers,¹⁶ shows that removal rate by ketene is of the same magnitude as that measured for hydrocarbons; for both, ketene and hydrocarbons, quenching of the $\text{B}^2\Sigma^-$ state is faster than for the $\text{A}^2\Delta$ state. This increase of rate constant is only moderate in the case of ketene compared to the hydrocarbons where quenching of the $\text{B}^2\Sigma^-$ state is more than twice as efficient as for the $\text{A}^2\Delta$ state.^{11,16} The enhancement of $\text{B}^2\Sigma^-$ state quenching rates observed with the hydrocarbons has been tentatively explained by the participation of an efficient $\text{B}^2\Sigma^- \rightarrow \text{A}^2\Delta$ energy transfer in which the energy mismatch would be disposed as vibrational excitation of the C–H stretching vibration in the hydrocarbons, rendering the process near resonant.¹⁶ The smaller enhancement of rate constant in going from the $\text{A}^2\Delta$ to the $\text{B}^2\Sigma^-$ states observed by ketene where less number of the appropriated vibrational modes are present, could fit within the above picture. In flames, electronic energy transfer from $\text{CH}(\text{B}^2\Sigma^-, v' = 0)$ to $\text{CH}(\text{A}^2\Delta, v' = 1)$ has been observed.¹⁰ Under our experimental conditions, characterized by the broad rotational distribution in which both states are formed and by the low ratio between total populations of $\text{B}^2\Sigma^-$ to $\text{A}^2\Delta$, an increase of the $\text{A}^2\Delta$ state populations due to energy transfer from $\text{B}^2\Sigma^-$ would be difficult to observe.

Some final conclusions could be tentatively drawn: removal rate constants measured in the present work for the $\text{A}^2\Delta$ state are close to those obtained if collisional complex formation is assumed; the rates measured with ketene are faster than those reported for large alkanes which is in agreement with previous results indicating that addition to the π -bonded systems of the unsaturated molecule enhances the quenching efficiency;² further work would be needed to identify the reactive channels contributing to the total removal of excited CH by ketene. More systematic work with a large number of quenchers would also be required in order to assess the influence of vibrational and electronic energy content on the removal rates; in collisions with ketene, rates tend to increase with increasing energy which would be consistent with the higher number of collisionally coupled relaxation channels available at higher energies.

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