Evaluation of a Novel Multi-Pass Absorption Cell for Shock Tube Kinetic Studies

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The feasibility of using a novel multi-pass absorption technique in combination with a shock tube for sensitive monitoring of free radicals for high-temperature kinetic studies was evaluated. The method was applied to study several elementary reactions of hydroxyl (OH) and methyl (CH\textsubscript{3}) radicals.

The multi-pass cell consists of two dielectric mirrors comprising a stable cavity. Light from a traditional light source (such as Xe or Hg arc lamp, hollow cathode lamp, MW discharge resonance lamp, etc.) is used to monitor the transient absorption of the species inside the cell. The increase in the sensitivity is due to the multiple passes of the photons inside the cell, and is controlled by the mirrors reflectivity and the cell losses (such as on the cell windows) at the monitoring wavelength. No coherent effects are involved; the cell length variations on the wavelength scale do not lead to any intensity variations. The “gain” of the cell is related to the one pass loss with a simple relationship:

\[
\text{Gain} = (\text{One Pass Loss})^{-1}
\]

Increase in the sensitivity from 10 to 100 times is easily achieved using inexpensive dielectric mirrors and AR coated windows. This allows using lower initial concentration of free radicals and better isolating the elementary reactions of interest. The impact of the shock tube environment on the cell performance was evaluated. The gain reduction by the intra-cavity cell windows, the windows contamination and the AR coating deterioration, the interference of the scattered shock waves, the windows vibration and the effects of the refraction index modulation (“Schlieren effects”) were investigated. It was found that none of these effects, except for the gain reduction by the windows, has any significant impact on the cell performance.

Hydroxyl radicals were monitored using a MW excited OH resonance lamp (ca. 17 strong narrow lines around 308 nm), selected using a narrow band interference filter. The cell was made of a spherical (R=20 cm) and a planar dielectric Mirrors (97.67% and 97.10% reflectance), the cell gain was 38 without the windows and 14 with AR coated windows. Single-shot kinetics with the initial concentration of OH radicals as low as 5x10\textsuperscript{12} molecule cm\textsuperscript{-3} were recorded. The majority of the measurements were performed with the [OH]\textsubscript{0} = (1 – 2)x10\textsuperscript{13} molecule cm\textsuperscript{-3}.

Methyl radicals were detected using strong narrow absorption band near 215 nm. Two Zn resonance line sources (213.9 nm, RF driven and MW driven Zn resonance lamps) as well as a UV enhanced Xe arc lamp with current pulsing (100 A, 7 msec) were evaluated. The cell (96.8% and 97.3% mirrors) has gain of 34 without windows and 14 with V-coat AR windows. The single shot detection limit for CH\textsubscript{3} radicals was 5x10\textsuperscript{13} molecule cm\textsuperscript{-3}, useful kinetic profiles were recorded at [CH\textsubscript{3}]\textsubscript{0} = 5x10\textsuperscript{14} molecule cm\textsuperscript{-3}.

A number of radical precursors were tested and (partially) characterized. For OH, pyrolysis of ethyl iodide/nitrogen dioxide mixtures, C\textsubscript{2}H\textsubscript{5}I/NO\textsubscript{2}, as well as pyrolysis of nitric acid, HNO\textsubscript{3}, were used. To simultaneously produce OH and CH\textsubscript{3}, pyrolysis of t-butyl hydroperoxide, (CH\textsubscript{3})\textsubscript{3}COOH, in mixtures with di-t-butyl peroxide,
(CH$_3$)$_3$COO(CH$_3$)$_3$, or pyrolysis of methanol, CH$_3$OH, were used. Methyl radicals were produced using either pyrolysis of di-t-butyl peroxide, (CH$_3$)$_3$COO(CH$_3$)$_3$, or methyl iodide, CH$_3$I. Methylene, CH$_2$, was produced using the pyrolysis of ketene, CH$_2$CO.

A number of reactions of hydroxyl and methyl radicals were (in some cases, partially) studied:

\[
\begin{align*}
\text{OH} + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O} \\
\text{OH} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H} \\
\text{OH} + \text{C}_2\text{H}_6 & \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5 \\
\text{OH} + \text{CH}_3 & \rightarrow \text{H}_2\text{O} + ^{1}\text{CH}_2 \\
\text{OH} + \text{CH}_2 & \rightarrow \text{H}_2\text{CO} + \text{H} \\
\text{CH}_3 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6
\end{align*}
\]

The results for reactions 2 and 3 are in good agreement with the literature. Reaction of hydroxyl and methyl radicals (reaction 5) was studied in the most detail. The results are shown in Fig. 1. Reaction of methylene with hydroxyl is the major interfering reaction; the rate constant of this reaction was evaluated using ketene as an additional source of methylene.

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