

Supplementary material (ESI)

for

“A Highly Sensitive Method for Time-Resolved Detection of O(¹D) Applied to Precise Determination of Absolute O(¹D) Reaction Rate Constants and O(³P) yields”

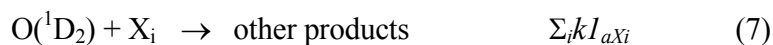
Shaun Avondale Carl

The CH(A²Δ) quasi-steady-state concentration, [CH(A²Δ)]_{ss}, and hence the CH(A²Δ→X²Π) emission intensity at 431 nm, I_{em} , are proportional to the ratio of the [CH(A²Δ)] formation and removal rates. Thus the general equation is:

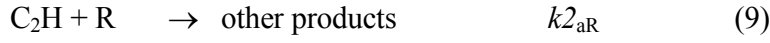
$$I_{em} \propto [CH(A^2\Delta)]_{ss} = B[C_2H] \left([O(^1D_2)] + \frac{[O(^3P_J)]}{3.0} \right) \quad (i)$$

Here, $B = k_{chem}/\{A_{nm} + \sum_i(kI_{bXi}[X_i] + kI_{bR}[R])\}$, where the denominator is the sum of quenching rate constants for CH(A²Δ), kI_{bXi} and kI_{bR} , by species [X_i] and [R], respectively, and the Einstein coefficient, A_{nm} , for spontaneous emission for CH(A²Δ → X²Π). [X_i] represents the concentrations of the photolytic precursors for O(¹D) and C₂H, and that of the buffer gas, [He], whereas [R] represents the concentration of any added reactant. [X_i] and [R] are treated separately because the kinetic effects of [X_i] remain essentially constant, even though [He] is altered slightly to compensate for added [R].

The temporal profile of the CH(A→X) emission depends on the time dependences of [O(¹D₂)], [C₂H], and [O(³P_J)], governed by:



This journal is © the Owner Societies 2005.



Therefore, $[O(^1D_2)]_t = [O(^1D_2)]_0 \exp(-k_1 t)$ and $[C_2H]_t = [C_2H]_0 \exp(-k_2 t)$ where $k_{\delta'} = k_{\delta aR}[R] + k_{\delta bR}[R] + \Sigma_i ((k_{\delta aXi} + k_{\delta bXi})[X_i])$, with $\delta = 1$ or 2 , and

$$\frac{d[O(^3P_J)]}{dt} = [O(^1D_2)]_t k_{1b'} + [C_2H]_t k_{2b'} - [O(^3P_J)]_t k_{3'} \quad (ii)$$

Where the total removal rate of $O(^3P_J)$, $k_{3'} = k_{3R}[R] + \Sigma_i (k_{3Xi}[X_i])$, giving

$$[O(^3P_J)] = \left\{ \frac{k_{1b'}}{k_{1'} - k_{3'}} \right\} [O(^1D_2)]_0 (\exp(-k_{3'} t) - \exp(-k_{1'} t)) + \left\{ \frac{k_{2b'}}{k_{2'} - k_{3'}} \right\} [C_2H]_0 (\exp(-k_{3'} t) - \exp(-k_{2'} t)) \quad (iii)$$

This leads to the full expression for I_{em} of

$$I_{em} \propto B[C_2H]_0 [O(^1D_2)]_0 \left\{ \exp(-(k_{1'} + k_{2'}) t) + \left\{ \frac{1}{3.0} \right\} \left\{ \frac{k_{1b'}}{k_{1'} - k_{3'}} \right\} \left\{ \exp(-(k_{3'} + k_{2'}) t) - \exp(-(k_{1'} + k_{2'}) t) \right\} \right\} \\ + B[C_2H]_0^2 \left\{ \left\{ \frac{1}{3.0} \right\} \left\{ \frac{k_{2b'}}{k_{2'} - k_{3'}} \right\} \left\{ \exp(-(k_{3'} + k_{2'}) t) - \exp(-2k_{2'} t) \right\} \right\} \quad (iv)$$

Two simplifications can be applied leading to a function having only two unknown parameters, k_{1Ra} and k_{1R} ($= k_{1Ra} + k_{1Rb}$). The first is to recognise the general great disparity in the magnitude of rate constants for reactions involving, on the one hand, $O(^1D_2)$ and C_2H , and, on the other, $O(^3P_J)$ with neutral, stable molecules. This leads to elimination of

This journal is © the Owner Societies 2005.

$k3'$ from equation (iv). The second concerns the low yield of $O(^3P_J)$ generated by reactions of C_2H . $O(^3P_J)$ cannot be generated efficiently from the $C_2H + N_2O$ reaction because the *overall* rate constant is low at room temperature and below. If this holds also for R – either because it is void of O-atoms, the rate of reaction of R with C_2H is low, or the branching fraction to $O(^3P_J)$ for $R + C_2H$ is negligible – then the second term of equation (iv) may be neglected, because, $[O^1D_2]_0(kI_b'/kI') \gg [C_2H]_0(k2_b'/k2')$ – assuming $[O^1D_2]_0$ is of the same order as, or greater than, $[C_2H]_0$.

To a very good approximation,

$$I_{em} \propto B[C_2H]_0 [O(^1D)]_0 \left\{ \exp(-(k1'+k2')t) + \left\{ \frac{1}{3.0} \right\} \left\{ \frac{k1_b'}{k1'} \right\} \left\{ \exp(-k2't) - \exp(-(k1'+k2')t) \right\} \right\} \quad (v)$$

Thus at long times, the decay rate is that of $[C_2H]$, given by $A(kI_b'/3kI')\exp(-k2't)$, where A is a constant.

In order to determine the values kI_{aR} and kI_R , the following procedure may be followed. A chemiluminescence profile is recorded in the presence of N_2O , C_2H_2 , and He only. Fitting equation (v) to this profile gives the values for kI' , $k2'$, kI_b'/kI' (*i.e.*, their values when $[R] = 0$) and A . In cases when kI_b'/kI' is less than about 0.03, a second decay is recorded under conditions in which a small fraction of $[He]$ is replaced by either $[Ar]$ or $[N_2]$. This promotes quenching of $O(^1D_2)$, and therefore increases the intensity of the long-time portion of the decay, and in turn increases the precision to which $k2'$ is known. Thus $k2'$ may be determined from the second profile while kI' and kI_b' are always determined from the first.

Once these parameters are known, $[R]$ may be added and equation (v) fit to the new profile, with the only unknown parameters now being kI_{bR} , kI_R , and $(k2_{aR} + k2_{bR})$. Again $(k2_{aR} + k2_{bR})$ may be determined more precisely, if required, by replacement of a small fraction of $[He]$ by $[N_2]$. In practice, several sets of decay profiles are taken with different $[R]$ to determine the values of the desired parameters. If $kI_{bR} \ll kI_{aR}$ these parameters are not strongly coupled, since kI_{bR} affects the long-time *intensity* of the decay profile, whilst kI_{aR} affects its initial *slope*.

This journal is © the Owner Societies 2005.