

Chlorine-radical Induced Oxidation of Glyoxal and Glyoxal-S(IV) Adducts in the Aqueous Phase

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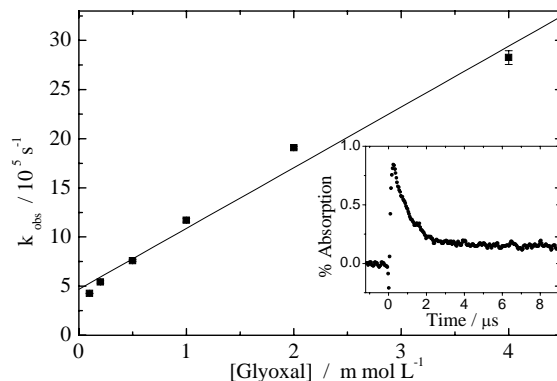
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Abstract: A laser flash photolysis study of the reactivity of Cl[·] with glyoxal, glyoxal mono- and dibisulfite adducts, 1-hydroxy-2, 2-diol-ethanesulfonate and 1, 2-dihydroxy-1, 2-ethanedi sulfonate in the aqueous phase was carried out. The obtained rate constants can be used for atmospheric modeling.

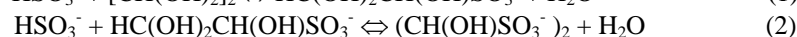
Keywords: Chlorine-radical, glyoxal, glyoxal mono- and dibisulfite adducts, aqueous phase rate constants.

The important role in stabilizing SO₂ in the aqueous phase by the reaction of aldehydes with S(IV) to form hydroxyalkanesulfonate salts has been recognized¹. Since aldehydes are the major carbonyl compounds in polluted environments in the gas phase with large effective Henry's law constants, they are also the most abundant in the droplet phase¹⁻⁴. Glyoxal, an α -dicarbonyl compound, has been identified in cloud water with a mean concentration of 2 $\mu\text{mol L}^{-1}$ ². Aldehyde substrates which meet this criterion and which also form highly stable aldehyde-bisulfite adducts represent potentially important S(IV) reservoirs. On the basis of these criteria, formaldehyde-, glyoxal-, and methylglyoxal-bisulfite adducts have been found to be important species in clouds and fogs². However, the oxidation of S(IV) in clouds might also occur by a free-radical chain process initiated by $\cdot\text{OH}$ and other radicals^{7,8}. Information on the reactivity of $\cdot\text{OH}$ and other radicals with formaldehyde-, glyoxal-, and methylglyoxal-bisulfite adducts is therefore important for assessing their influence on the chain oxidation of SO₂ in the atmosphere. The Cl[·] radical may be formed in cloud droplets by the reactions of chloride with strongly oxidizing radicals such as NO₃[·], SO₄^{·-} and $\cdot\text{OH}$, which are well known atmospheric species^{9,10}. The oxidation of hydroxy-methanesulfonate, the addition product of S(IV) with formaldehyde, in a free radical initiated chain process has been studied³⁻⁶. However, to date, there is no report about the study of the reaction of the free radicals with glyoxal-bisulfite adducts. The addition products of bisulphite with glyoxal are formed *via* the following reactions:

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Figure 1 Dependence of k_{obs} for the reaction of $\text{Cl}^\cdot + [\text{CH}(\text{OH})_2]_2$ on $[[\text{CH}(\text{OH})_2]_2]$ 

Time-absorbance trace for the reaction of Cl^\cdot with glyoxal at 320 nm. $[\text{Glyoxal}] = 1 \text{ mmol L}^{-1}$
 $\text{pH} = 4.5$, $[\text{Chloroacetone}] = 0.02 \text{ mol L}^{-1}$; Ar saturated, 248 nm laser light.



The glyoxal mono- and disulfite adducts, 1-hydroxy-2, 2-diol-ethanesulfonate and 1, 2-dihydroxy-1, 2-ethanedithionate are hereafter respectively denoted with the acronyms GMBS and GDBS.

Experimental setup was described in detail in ref.6. The optical pathlength of the cell was 1 cm. To improve signal quality, recorded traces were an average of four separate flashes to freshly flushed samples. All the kinetics experiments were carried out under pseudo-first-order conditions with $[\text{glyoxal}] \gg [\text{radicals}]_0$ at ambient temperature. All errors are reported as 2σ from linear regression fits. Cl^\cdot was produced in the absence of Cl^\cdot by 248 nm laser photolysis of chloroacetone⁶. The reaction of Cl^\cdot with glyoxal, reaction (3), was investigated in argon-saturated solutions of 0.02 mol L^{-1} chloroacetone and $(0.1-4) \text{ mmol L}^{-1}$ glyoxal at $\text{pH} = 4.5$ using 248 nm laser light.

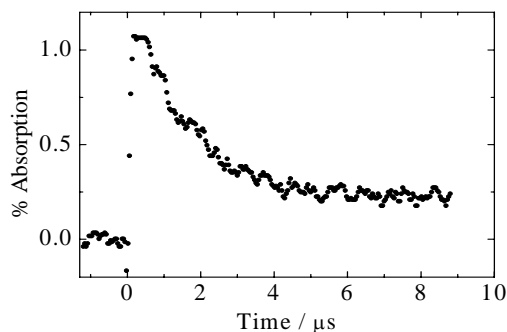


Absorption signals monitored at 320 nm decayed by first-order kinetics to a plateau (see inset to **Figure 1**). At room temperature ($292 \pm 2 \text{ K}$), a plot of k_{obs} against $[[\text{CH}(\text{OH})_2]_2]$ is shown in **Figure 1**. The slope of the straight line yields a rate constant of $k_3 = (6.2 \pm 0.4) \times 10^8 \text{ L}^3 \text{ mol}^{-1} \text{ s}^{-1}$. At the moment, there is no literature value for comparison.

Similar to the study of Cl^\cdot with glyoxal, the reactions of Cl^\cdot with GMBS and GDBS, reactions (4 and 5), were also investigated in argon-saturated solutions of 0.02 mol L^{-1} chloroacetone and $(0.1-4) \text{ mmol L}^{-1}$ glyoxal-sodium bisulphate addition compound at $\text{pH} = 4.3$ using 248 nm laser. A pseudo-first order trace is shown in **Figure 2**.



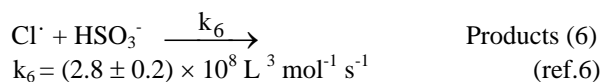
Figure 2 Time-absorbance trace for the reaction of Cl[·] with GMBS and GDBS



[Chloroacetone] = 0.02 mol L⁻³, pH = 4.3, Ar saturated.
 [GDBS]₀ = 1 mmol L⁻³, λ = 320 nm, 248 nm laser light.

Due to the two equilibria: (1) and (2), it is necessary to know the concentration of each species present in this system at a given initial concentration of glyoxal- sodium bisulfite addition compound ([GDBS]₀). They were calculated using a FACSIMILE program (The detail will be sent upon request).

The observed rate constants, k_{obs}(Cl[·]) for the decay of Cl[·] in this system were corrected for the reactions of Cl[·] with glyoxal (reaction (3)) and HSO₃⁻ (reaction (6)), which are in equilibrium with the addition compounds, reaction (1) and (2).



These processes accounted for ~ 15% of k_{obs} at the studied [GDBS]₀ range. The corrected k_{obs}(Cl[·]) was named as k_{dif}(Cl[·]) which can be calculated *via* Eq.1:

$$k_{\text{dif}}(\text{Cl}^{\cdot}) = k_{\text{obs}}(\text{Cl}^{\cdot}) - k_1[\text{Glyoxal}] - k_6[\text{HSO}_3^-] \quad \text{Eq.1}$$

where k_{obs}(Cl[·]) is observed rate constant for the decay of Cl[·].

In order to distinguish the reactivity of the two complexes, the obtained data were treated using the Microcal Software Inc. 3-D ORIGIN curve-fitting package where the dependence of k_{dif}(Cl[·]) on [GMBS] and [GDBS] was treated *via* Eq.2 (**Figure 3**):

$$k_{\text{dif}}(\text{Cl}^{\cdot}) = k_4[\text{GMBS}] + k_5[\text{GDBS}] + k_c \quad \text{Eq.2}$$

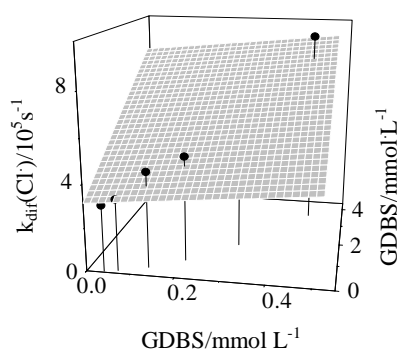
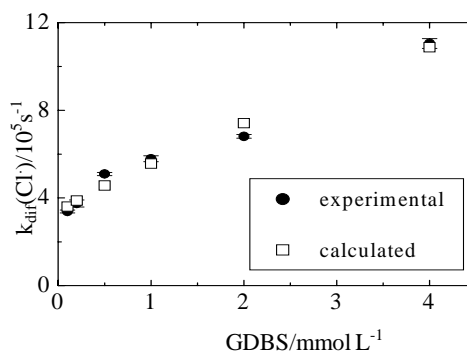
where k₄, k₅ are the rate constants for the reactions of Cl[·] with the mono- (4) and di-complex (5), respectively;

[GMBS] and [GDBS] are the concentrations of mono- and di-complex, respectively;

k_c is the sum of the rate constants for the reactions of Cl[·] with H₂O and ClCH₂COCH₃.

The obtained values are:

$$k_4 = (1.92 \pm 0.65) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}, k_5 = (1.48 \pm 0.42) \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$$

Figure 3 3-D plot of variation of $k_{\text{dir}}(\text{Cl}^\cdot)$ with [GMBS] and [GDBS].**Figure 4** Comparison of experimental and calculated $k_{\text{obs}}(\text{Cl}^\cdot)$ 

[Chloroacetone] = 0.02 mol L^{-3} , pH = 4.3
Ar saturated, 248 nm laser light.

These two rate constants were used to calculate back the $k_{\text{obs}}(\text{Cl}^\cdot)$ and compared with the experimental $k_{\text{obs}}(\text{Cl}^\cdot)$, the results are shown in **Figure 4**. It is seen that the calculated values agree very well with the experimental values.

Acknowledgments

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