Characterization of chlorine atom adducts of dimethyl and diphenyl sulfide in CCl_4

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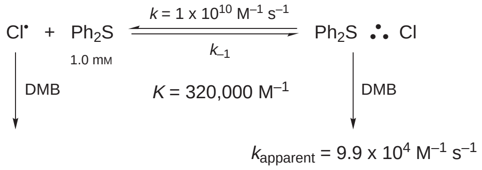
The equilibrium constants for the association of chlorine atom with dimethyl and diphenyl sulfide to form chlorine atom adducts have been determined spectroscopically and indicate that both adducts should be considered three electron bond complexes.

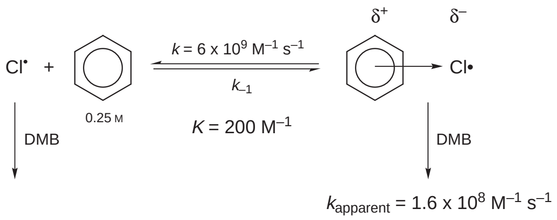
Dimethyl sulfide (Me_2S) is known to be the major natural source of sulfur in the atmosphere.[1] Removal of Me_2S from the atmosphere is believed to occur by the reaction of Me_2S with photolytically generated free radicals and halogen atoms. Therefore, there has been considerable interest recently in kinetic and mechanistic investigations of halogen atom reactivity with sulfur containing species.[2–6] An important aspect of these investigations is the possibility of forming chlorine atom adducts to sulfides. It is also important to understand the physiochemical nature of the chlorine adducts in differing physical environments, *e.g.* gas, interfacial and liquid phases. This report presents a spectroscopic and kinetic methodology for the determination of equilibrium constants (K_{eq}) for the formation of chlorine atom molecular complexes in carbon tetrachloride solution. The equilibrium constants determined in this work were compared to values of K_{eq} for known π- and σ-chlorine atom complexes to determine the bonding nature of the dimethyl sulfide and diphenyl sulfide chlorine atom adducts.

The reason it is important to understand the strength of interaction of chlorine atom adducts is that K_{eq} will influence subsequent reactivity of the individual components of the system. Recently, in reports describing the photochemistry of the diphenyl sulfide/chlorine atom adduct ($Ph_2S/Cl^•$), the complex was assigned to a π-molecular complex[7] owing to similarities in its absorption spectrum to $Cl^•$/arene π-complexes.[8] The assignment is extremely intriguing in that the dimethyl sulfide/chlorine adduct ($Me_2S\therefore Cl$) has been characterized as a sulfur–chlorine three electron bond (2c–3e) adduct by matrix isolation EPR spectroscopy,[9] and in aqueous solution by pulse radiolysis.[10] Therefore, the question arises as to whether $Ph_2S/Cl^•$ may demonstrate dual complexation, that is, π-interaction of $Cl^•$ with the aromatic rings and σ-bond formation with the sulfur center. This question may be addressed by measuring the apparent reactivity of the $Ph_2S/Cl^•$ adduct with 2,3-dimethylbutane (DMB) at low concentrations of complexing agent,[11,12] and in turn determining K_{eq}. The results obtained then may be compared with the reactivity of the known $Cl^•$/benzene π-complex[8] and the $Cl^•$/pyridine σ-complex.[11,12]

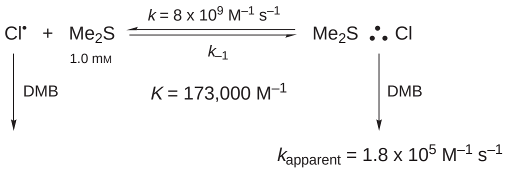
Chlorine atoms, and in turn $Ph_2S/Cl^•$, were independently generated by both pulse radiolysis† and 266 nm laser flash photolysis (LFP) of CCl_4‡ containing 1×10^{-3} M Ph_2S. Each method of generation produced the same result, namely absorption spectra containing two absorption bands (λ_{max} = 340 nm, 500 nm; see graphical abstract) that were consistent with the absorption spectrum of $Ph_2S/Cl^•$ previously reported.[7] Also consistent with the previous report was 1×10^{10} M^{-1} s^{-1} rate of formation of the $Ph_2S/Cl^•$ complex and the 340 nm and 500 nm absorption bands of the $Ph_2S/Cl^•$ complex demonstrated identical kinetic behavior. From a detailed kinetic analysis of selectivity in the photochlorination of DMB in the presence and absence of benzene, Ingold and coworkers[8] determined K_{eq} = 200 M^{-1} for the $Cl^•$/benzene π-complex, *i.e.* $K_{benzene}$ = 200 M^{-1}. It has been demonstrated[11,12] that K_{eq} of other $Cl^•$ complexes ($Cl^•/M$) may then be determined by monitoring the apparent reactivity ($k_{apparent}$) of the complex with DMB using time resolved spectroscopy and the relationship, $K_M = K_{benzene} \times k_{apparent}(\text{benzene})/k_{apparent}(M)$. By directly monitoring the formed complex, $Cl^•/M$, the apparent reactivity reflects the extent of reversible dissociation§ to free $Cl^•$, which then may be scavenged by DMB. The $Ph_2S/Cl^•$ complex demonstrated little reactivity towards DMB, $k_{apparent} = 9.9 \times 10^4$ M^{-1} s^{-1}. This results in K_{eq} for formation of the adduct (K_{Ph_2S}) to be 3.2×10^{-5} M^{-1} according to Scheme 1 and the equation above with $K_{benzene}$ and $k_{apparent}$(benzene), see Scheme 2, being 200 M^{-1} and 1.6×10^8 M^{-1} s^{-1}, respectively. For comparison, K_{eq} for formation of the $Cl^•$/pyridine σ-complex is 1.2×10^5 M^{-1} and $k_{apparent}$(pyridine) = 2.6×10^5 M^{-1} s^{-1}.[11] The $Me_2S/Cl^•$ adduct was also generated by both pulse radiolysis and LFP of CCl_4 (λ_{max} = 365 nm, see graphical abstract). Similar to the $Ph_2S/Cl^•$ results, $Me_2S/Cl^•$ also demonstrted little reactivity toward DMB, $k_{apparent} = 1.8 \times 10^{-5}$ M^{-1} s^{-1}, yielding $K_{eq} = 1.73 \times 10^5$ M^{-1}, Scheme 3. This is true even at $[Me_2S] = 5 \times 10^{-4}$ M. It should also be noted that in aqueous solution K for neutral disssociation of $Me_2S\therefore Cl \rightarrow Me_2S + Cl^•$ is $\ll 10^{-10}$ M^{-1}, whereas $K \approx 4$ M^{-1} for the ionic dissociation to $Me_2S^{•+} + Cl^-$.[10] In CCl_4 there was no spectroscopic evidence of $Me_2S^{•+}$



Scheme 1



Scheme 2



Scheme 3

formation, owing to the lack of solvating power of this solvent.

In summary, the values of K_{eq} for the $Cl^{\bullet}$ adducts with benzene, pyridine, Me_2S and Ph_2S in CCl_4 are: 200 M^{-1}, 120000 M^{-1}, 173000 M^{-1} and 320000 M^{-1}, respectively. Gratifyingly, these results are in accordance with recent theoretical determinations of the 0 K binding energies[5,6] of 11.4 kcal mol^{-1} for the $Cl^{\bullet}$/pyridine complex [Table 2 in ref 5; method used G2 (MP2, SVP)] and 12.32 kcal mol^{-1} for the $Me_2S\therefore Cl$ complex [Table 5 in ref. 6; method used QCISD (T)/DZP + ZPC]. The results presented demonstrate that the bonding nature of the Ph_2S/Cl adduct is not consistent with a loosely bound π-molecular complex, and should be considered a three-electron bond $Ph_2S\therefore Cl$ adduct, as is the $Me_2S\therefore Cl$ complex. The methodology presented may prove useful in future characterizations of $R_2S\therefore Cl$ complexes in interfacial and mixed-solvent systems.

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Notes and References

† Pulse radiolysis experiments were performed using a 10 ns pulse of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator (LINAC). The pulse radiolysis apparatus has been described elsewhere.[13]

‡ CCl_4 (Fisher Spectranalyzed) was distilled from K_2CO_3 (35 cm Vigreux column) prior to use.

§ This methodology is only valid in the absence of radical chain regeneration of $Cl^{\bullet}$ which is not possible in the present experiments.

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