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The Nature of the Active Species in the Chlorinating System Sulphur(I) Chloride–Aluminium Chloride–Sulphuryl Chloride

C. GLIDEWELL

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

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The system S_2Cl_2–$AlCl_3$–SO_2Cl_2 has been extensively employed, although with the reagents in various molar proportions, as a chlorinating agent [1–5]. The pattern of reactivity observed [5] indicated that the active species contained an electrophile, and the suggestion was made that it could be either $SO_2Cl^+AlCl_4^-$ or $SCl_3^+AlCl_4^-$ [5]. Although no distinction was made between SO_2Cl^+ and SCl_3^+ [5] as the active electrophile, tentative mechanisms for the reactivity of a generalised species SX_2Cl^+ (for X = O or Cl) were proposed. If the active agent were $SO_2Cl^+AlCl_4^-$, formed by chloride transfer from SO_2Cl_2 to $AlCl_3$, then the presence of S_2Cl_2 or indeed of any other sulphur-containing additive should be unnecessary: if, on the other hand, the active agent in this mixture is $SCl_3^+AlCl_4^-$, formed by oxidation of S_2Cl_2 by SO_2Cl_2 [5], eqn. (1):

$$3SO_2Cl_2 + S_2Cl_2 + 2AlCl_3 \longrightarrow 3SO_2 + 2SCl_3^+AlCl_4^- \tag{1}$$

then the S_2Cl_2 should be replaceable, either by SCl_2 or even by elemental sulphur, since both SCl_2 and S_8 can be oxidised, for example by elemental chlorine, to yield sulphur(IV) [6, 7].

Here we report the results of experiments designed to clarify the nature of the active species in such S_2Cl_2–$AlCl_3$–SO_2Cl_2 mixtures, and to explore the range of analogous systems which behave chemically in similar ways. In order to standardise these experiments, bromobenzene was chosen as the common target for chlorination, as it gives a readily characterised product, C_6Cl_5Br, in high yield (90%) under the conditions previously employed [5]. Except for the variations in the reaction mixture noted below, the general experimental procedure was as described previously [5].

When elemental sulphur of SCl_2 was employed instead of S_2Cl_2, the yield of the chlorination product C_6Cl_5Br was unchanged from that previously observed [5]; however, if sulphur or one of the sulphur chlorides SCl_2 and S_2Cl_2 was omitted entirely, the resulting mixture consisting of $AlCl_3$ and SO_2Cl_2 only, had no chlorinating ability whatever. These observations suggested that S_8, S_2Cl_2 and SCl_2 react via a common reactive intermediate and, further, strongly indicated that $SO_2Cl^+AlCl_4^-$ cannot be the active species. This was further confirmed by the observations firstly that the salt $SCl_3^+AlCl_4^-$ in the presence of elemental chlorine acted as a powerful chlorinating agent [8], and secondly by the isolation of $SCl_3^+AlCl_4^-$ from mixtures of $AlCl_3$ and SO_2Cl_2 with both SCl_2 [9], and with elemental sulphur, as here. That the salt $SCl_3^+AlCl_4^-$ was both isolable from the reaction mixture, and itself active with elemental chlorine as the sole additional chlorine source, provides excellent evidence, when taken with the foregoing observations that the active chlorinating species in S_2Cl_2–$AlCl_3$–SO_2Cl_2 and similar mixtures is indeed $SCl_3^+AlCl_4^-$, formed from any one of S_8, S_2Cl_2 or SCl_2, rather than $SO_2Cl^+AlCl_4^-$. There is in fact no real evidence that any compound formation occurs between SO_2Cl_2 and $AlCl_3$, in the absence of other reagents, the solubility of $AlCl_3$ in SO_2Cl_2 is very low [10]. On the other hand, compound formation is well established between $SOCl_2$ and $AlCl_3$, although the data from different physical measurements have been interpreted in terms of both ionic and molecular constitutions, including $SOCl^+AlCl_4^-$ [11]; Cl_2SO–$AlCl_3$ [12]; and $ClS(O)Cl$–$AlCl_3$ [13], but this combination, despite compound formation, is not an effective electrophilic chlorinating agent. The mechanism suggested earlier [5] envisaged a role for the $AlCl_4^-$ anion in the electrophilic chlorination of hydrocarbons: some rather circumstantial evidence for this was obtained by replacing $AlCl_3$ in the reaction mixture with other molecular chlorides such as PCl_5 or $SbCl_5$. With either elemental sulphur or S_2Cl_2, in SO_2Cl_2 in each case, chlorination was certainly effected in the presence of PCl_6^- or $SbCl_6^-$ as counter-ion, but in each case reaction was much slower than when the counter-ion was $AlCl_4^-$: neither PCl_5 nor $SbCl_5$ effected chlorination in SO_2Cl_2 in the absence of sulphur or a sulphur chloride. This latter observation implies that PCl_4^+ cannot take the place of SCl_3^+ as a chlorinating species: confirmation of this point was derived from the reaction system PCl_3–$AlCl_3$–SO_2Cl_2 (which yields $PCl_4^+AlCl_4^-$) which even with a prolonged reaction time did not effect any chlorination of bromobenzene.

Finally, substitution of elemental selenium or tellurium for elemental sulphur in mixtures with $AlCl_3$ and SO_2Cl_2 again yielded systems which were active as chlorinating agents towards the standard substrate bromobenzene, and which presumably contained the known [14, 15] compounds $SeCl_3^+AlCl_4^-$ and $TeCl_3^+AlCl_4^-$ respectively, although this is not proven. Whatever the exact nature of these solutions, their efficacy as chlorinating agents was less than that of $SCl_3^+AlCl_4^-$ solutions, in that, with bromobenzene, they reacted rather slowly to yield

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inseparable mixtures of, possibly isomeric, partially chlorinated products.

Thus, these observations have not only indicated that $SCl_3^+AlCl_4^-$ is the active reagent in the system [1–5] S_2Cl_2–$AlCl_3$–SO_2Cl_2, but they have enabled this system to be simplified to comprise S_8–$AlCl_3$–SO_2Cl_2, so obviating the need for the noxious S_2Cl_2 in this system.

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