Reactivity of Sulphuryl Chloride in Acetonitrile with the Elements†

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Sulphuryl chloride in MeCN reacts with all but the most refractory elements to give mainly solvated chlorides at or below 300 K in contrast with SO_2Cl_2 alone which requires at least twice this temperature. There is evidence for an ionic mechanism based on analogy, thermochemistry, transport measurements and additive effects. The instability of these solutions leading to polymerization, together with its inhibition, is described. Sulphur dioxide formed in reactions seldom plays a reductive role apart from influencing formation of the mixed-valence Tl_4Cl_6. Semiquantitative kinetic measurements in different solvents emphasize the uniqueness of MeCN. For most elements attack is diffusion controlled across surface films giving a parabolic dependence on time which can be linearized if film growth is prevented by changing the solvent mix. The varied nature of these surface films vitiates any simple relation between rate and periodicity. Some applications are indicated.

The halogenating propensity of SO_2Cl_2 should be comparable with that of the dihalides E_3AX_2 (E = a bond or lone pair; A = main group 15–18 element, X = Cl) which heterolyse to electrophilic halogen with suitable donor and or acceptor additions.[1] Indeed, some organic reactions with SO_2Cl_2 in donor solvents seem to have ionic, rather than the usual radical, mechanisms,[2] according to indirect evidence from the position of substitution[3–6] or kinetics.[7–9] The Silberrad,[10] Watson[11] and Ballester–Molinet–Castaner[12] reagents, consisting of SO_2Cl_2 with a Lewis acid and catalytic amounts of sulphur or its compounds, exemplify ionic reactivity *via* chlorosulphonium salts.

The reactions of SO_2Cl_2 in donor solvents with the elements have been examined in this study. Few elements react with SO_2Cl_2 at ambient temperature[13–15] but in the presence of MeCN all but the most refractory ones do. An alternative polar mechanism to the high-temperature radical one is proposed, although instability of the electrophile to self-chlorination of the donor hinders definitive identification.

Experimental

Commercial SO_2Cl_2 was refluxed over Hg, fractionated and the mid-fraction kept over copper foil in the dark. (This traps chlorine leaving traces of SO_2 which will not affect reactivity.) Acetonitrile (HPLC quality) stored over molecular sieves (4A) was distilled as required. Elements were used in consolidated form where possible and surfaces cleaned chemically or mechanically. Preliminary corrosion experiments were carried out in B24 stoppered boiling tubes (50 cm^3) shaken horizontally at ambient temperature. Products were identified separately using a vacuum-line technique to avoid any hydrolysis and contamination with H_2SO_4.[16] A weighed sample was placed in a cylindrical vessel (35–50 cm^3) fitted with a B14 side arm and closed by a Young's Teflon tap (diameter 1 cm). The requisite SO_2Cl_2 was distilled into a measuring tube (4 cm^3), also fitted with a Teflon tap, and weighed before and after vacuum transfer to the reaction flask. Finally, MeCN was distilled in before agitating the contents magnetically, or ultrasonically in a thermostat. Excess of liquid was carefully distilled off after reaction, stirring constantly to avoid bumping. The remaining solid was analysed for chlorine (gravimetrically as AgCl) and metal content (from the metal dissolved or by standard methods; some valency states were found by redox titrimetry). Acetonitrile in adducts was identified by IR spectroscopy but not determined directly since most adducts are known.[17,18] Raman spectra were recorded on a Coderg spectrometer using an argon-ion laser. The results are summarized in Table 1; more detail is given on starred elements.

Thallium. Freshly cut metal placed in a 1.95 mol dm^{-3} solution having SO_2Cl_2:Tl 2.83:1 was partly covered by a yellow film in a colourless solution after 1 d and dissolved completely in 3 d at an average rate of 10 mg h^{-1}. A mixed white and yellow powder remained on evaporation, only the white portion ($TlCl_3$) being water soluble, the remaining citron-yellow solid contained Tl, Cl and no S as shown by electron-microprobe analysis. Its composition was $TlCl_{1.5}$ corresponding to the mixed-valence compound Tl_4Cl_6. The ratio $TlCl_{1.5}$:$TlCl_3$ was 1.20:1. Addition of SO_2 at Tl:SO_2Cl_2:SO_2 1:2.19:2.33 increased the ratio to 1.53:1. Addition of KF at Tl:SO_2Cl_2:KF 1:3.21:3.87 increased the solution rate to 59 mg h^{-1} over 18 h and no surface film was observed.

Sulphur. Powdered sulphur (0.40 g) was equilibrated with SO_2Cl_2 (0.5–2 cm^3) in MeCN (10 cm^3) for 6 h to form yellow solutions with undissolved S. The solubility increased initially but remained constant above a unit ratio SO_2Cl_2:S indicating a maximum take up of one Cl_2 per S (Ph_2S also takes up one Cl_2 from SO_2Cl_2 in MeCN to form Ph_2SCl_2 provided the solution is kept cool to avoid ring chlorination).

SO_2Cl_2:S	0.199	0.646	1.11	1.92	2.07:1
Molality (mol kg^{-1}) of S in solution	0.36	0.50	0.87	0.87	0.87

Iodine. In a 1.36 mol dm^{-3} solution (SO_2Cl_2:I 2.87:1) the iodine colour became orange-yellow within 0.5 h. A yellow solid sublimed on evaporation and crystals separated which liquefied to a brown-red residue indicating decomposition of ICl_3 to ICl. Oxidation to I^{III} was demonstrated by the quantitative conversion of CsI into Cs[ICl_4] with excess of SO_2Cl_2 (Cs[ICl_2] can be isolated with equimolar CsI and SO_2Cl_2 in MeCN).

Effect of NMe_4Cl *on Rate*.—The low solubility of NMe_4Cl in MeCN increased on adding SO_2Cl_2.

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† *Non-SI units employed*: cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J.

Table 1 Products from elements and SO_2Cl_2–MeCN solutions with some relative rates

Groups 1, 2, 11 and 12	Product
Li	LiCl (Ref. 19)
Mg	$MgCl_2\cdot 2MeCN$
Ca	$CaCl_2$
Cu	$CuCl_2\cdot MeCN$
Ag	AgCl
Au	$AuCl_3\cdot MeCN$
Zn	$ZnCl_2\cdot 2MeCN$
Cd	$CdCl_2\cdot 2MeCN$
Hg	$HgCl_2$
Au > Cu ≫ Ag, Hg > Zn ≫ Cd	
Groups 3 and 13	
B	Inert
Al	$AlCl_3\cdot 2.6MeCN$
Ga	$GaCl_3\cdot 1.5MeCN$
In	$InCl_3\cdot 3MeCN$
Tl*	Tl_4Cl_6, $TlCl_3$
Y	$YCl_3\cdot 0.2MeCN$
Tl > Al ≫ In	
Group 14	
C, Si	Inert
Ge	$GeCl_4$
Sn	$SnCl_4\cdot 2MeCN$
Pb	$PbCl_2$
Sn ≫ Ge > Pb	
Group 15	
P	PCl_3
As	$AsCl_3$
Sb	$SbCl_3$
Bi	$BiCl_3$
Bi ≈ Sb ≫ As > P	
Group 16	
S*	Solution
Se	$SeCl_4$
Te	$TeCl_4\cdot 0.4MeCN$
Te > Se > S	
Group 17	I^{III} in solution
First transition-metal series	
Ti	$TiCl_4\cdot 2MeCN$
V	$VCl_3\cdot 4MeCN$
Cr	$CrCl_3\cdot 3MeCN$
Mn	$MnCl_2\cdot 2MeCN$
Fe	$FeCl_2\cdot 2MeCN$
Co	$CoCl_2\cdot 3MeCN$
Ni	$NiCl_2\cdot 2MeCN$
Fe ≫ Ni > Co, Cr, V, Ti > Mn[a]	
Second and third transition-metal series	
Zr	Chlorides of Zr^{III} and Zr^{IV}
Nb, Mo, Ru	Inert
Rh	$RhCl_3\cdot 3.7MeCN$
Pd	$PdCl_2\cdot 2MeCN$
Ta, W, Os, Ir	Inert
Pt	$PtCl_4\cdot x MeCN$
Pd ≫ Rh > Pt	
U	$UCl_4\cdot 4MeCN$

[a] A quantitative rate comparison using bulk specimens of nearly the same area gave $Lt^{-\frac{1}{2}}c^{-1}$ (see Table 3) constants for Fe, Ni, Co and Mn of 14.7, 5.80, 2.75 and 0.257 respectively.

10^3 (SO_2Cl_2:MeCN)	0	9.62	24.4	203.3:1
Solubility (mol kg^{-1})	0.003 26	0.315	0.568	0.924

Table 2 Dissolution of Ge in MeCN solutions of SO_2Cl_2 with ammonium salt additions

Salt	Ge dissolved (as % of maximum) in 1 d	Relative[a] rate	SO_2Cl_2:Ge:chloride
None[b]	1.8	1	1.82:1
$NBu^n{}_4Cl$	6.3	3.7	5.27:1:1.90
NH_4Cl	9.8	6.1	3.32:1:2.39
NH_3Bu^tCl	19.2	6.9	2.54:1:2.02
NMe_4Cl[b]	37.8	39.6	3.39:1:1.44

[a] Corrected for different SO_2Cl_2 concentrations. [b] The last experiment was made using the lump specimen left from the first.

Pellets of Zn dissolved at >1 g h^{-1} in 0.5 h using SO_2Cl_2:Zn:NMe_4Cl 2.91:1:2.14 compared to 7.6 mg h^{-1} in 46 h without NMe_4Cl. The $ZnCl_4{}^{2-}$ salt, identified from the Raman spectrum, could be isolated. At SO_2Cl_2:Zn:NMe_4Cl 3.74:1:1 the solid was $ZnCl_3{}^-$ without any $ZnCl_2$. At NMe_4Cl:Zn 3:1 attack was even faster (> 3 g h^{-1}). The product was a mixture of $ZnCl_4{}^{2-}$ and Cl^- without any $ZnCl_5{}^{3-}$. Guanidinium chloride addition at a 2:1 ratio dissolved Zn at lower rates (130 mg h^{-1}) yielding a $ZnCl_4{}^{2-}$ salt.

Cadmium at SO_2Cl_2:Cd:NMe_4Cl 1:1:1 dissolved at 3.3 mg h^{-1} over 45 h compared with 1.8 mg h^{-1} over 96 h without NMe_4Cl. Results with Ge are given in Table 2.

Example of a Quantitative Preparation of $[NMe_4]_2[GeCl_6]$.—Powdered Ge (0.25 g), NMe_4Cl (0.76 g), SO_2Cl_2 (2 cm^3) and MeCN (15 cm^3) were heated with stirring for 5.5 h at 70 °C in a Teflon-lined screw-capped pressure vessel. After vacuum evaporation, 1.49 g of white product remained (calc. for $2NMe_4Cl\cdot GeCl_4$: 1.49 g) identified as the $GeCl_6{}^{2-}$ salt from the Raman spectrum. A similar experiment at Ge:NMe_4Cl 1:1 gave the same salt *via* a quantitative disproportionation $[NMe_4][GeCl_5] \longrightarrow 0.5[NMe_4]_2[GeCl_6] + 0.5GeCl_4$.

Effect of Lewis acids on Rate.—A lump of Cd in a $FeCl_3$ solution in MeCN (0.69 mol kg^{-1}) containing SO_2Cl_2 at $FeCl_3$:SO_2Cl_2 1.97:1 turned the brown solution pale green and precipitated white $CdCl_2\cdot MeCN$. The rate of dissolution became constant after a rapid initial attack. A different product ($CdCl_2\cdot 2MeCN$) formed more slowly in the absence of $FeCl_3$. Similarly, a silver disc was attacked more rapidly until a film of AgCl formed. Further addition of $FeCl_3$ increased the rate temporarily.

Additions of $AlCl_3$ to SO_2Cl_2 did not increase the rate of attack on Ge, Nb or W but did with Cd (× 5), Mn (× 8) and Pb which was not attacked without $AlCl_3$ present. No $AlCl_4{}^-$ salts could be isolated.

Kinetic Measurements.—In preliminary experiments conditions for comparative rate measurements were delineated. Rectangular specimens cut from a single nickel sheet (99.9%, 0.055 mm thick) were immersed in solution and mechanically shaken at constant speed. The metal was removed at intervals, washed (water, Me_2CO), dried and reweighed within 2–3 min. This cleaning should not affect the kinetics because the surface film reforms at once while the bulk of $NiCl_2\cdot 2MeCN$ separates. Measurements were limited to 1 d to avoid solvent chlorination. Sulphuryl chloride alone did not attack Ni (>1 month) and neither did solutions in chlorocarbons (*e.g.* CH_2Cl_2) or liquid SO_2. Results of % weight loss L with time t at a variety of SO_2Cl_2 concentrations c, and the parameter $Lt^{-\frac{1}{2}}c^{-1}$ are given in Table 3. Duplicate specimens having twice the surface area (28.3 cm^2) in an 0.345 mol dm^3 solution were sampled alternately to give nine values from 1 to 9 h. The average $Lt^{-\frac{1}{2}}c^{-1}$ was 53.4 ± 2, about twice the above value. Duplicate experiments at 21 and 4 °C (in a cold room) gave $Lt^{-\frac{1}{2}}c^{-1}$ 65.8 ± 1.3 using 0.473 mol dm^{-3} solution at 21 °C and 65.5 ± 0.2 using 0.457 mol m^{-3} solution at 4 °C. Hence further experiments used 28.3 cm^2 specimens at ambient temperature allowing for different SO_2Cl_2 concentrations in the constant.

Table 3 Effect of SO_2Cl_2 concentration on the dissolution rate of Ni (21 ± 1 °C)

Concentration of SO_2Cl_2 in MeCN, c/mol dm^{-3}	Time/h	Weight loss (L) as % of maximum *	$Lt^{-\frac{1}{2}}$ (mean)	$Lt^{-\frac{1}{2}} c^{-1}$
0.363	2.43	15.1	9.7	27.6
	4.65	21.6	10.0 (10.0 ± 0.35)	
	6.65	26.8	10.4	
0.525	2.43	18.3	11.7	24.2
	4.65	27.8	12.5 (12.7 ± 1)	
	6.65	35.2	13.6	
1.175	2.43	49.4	31.7	26.2
	3.50	57.6	30.8 (30.8 ± 0.5)	
	4.65	64.7	30.0	
				Mean 25.7 ± 1.3

* The maximum is calculated on the initial amount of SO_2Cl_2.

Table 4 Effect of base additions on the rate of attack on Ni in 0.574 mol dm^{-3} SO_2Cl_2 in MeCN

Base	Mole ratio Base:SO_2Cl_2	$Lt^{-\frac{1}{2}}c^{-1}$	L at 23 h (%)
Pyridine	1:1	36.8	36
	1:1 *	1.5	12
	0.5:1	31.4	60
	2.0:1	10.1	12
1-Methylpyridine	1:1	69.5	65
2-Methylpyridine	1:1	33.3	59
2,6-Dimethylpyridine	1:1	26.8	43
3,5-Dimethylpyridine	1:1	38.2	62
3,4-Dimethylpyridine	1:1	55.2	59
2,4,6-Trimethylpyridine	1:1	25.1	33
2,6-Dichloropyridine	1:1	32.5	95
3,5-Dichloropyridine	1:1	69.9	85
Quinoline	1:1	38.3	56
Isoquinoline	1:1	1.07	15
Piperidine	1:1	26.5	57
Morpholine	1:1	11.9	20
Dioxane	1:1	44.3	94
Imidazole	1:1	No attack	
No base addition		53	96

* Solution aged for 1 d before use. L at 23 h > 95% shows complete reaction with Ni since sampling losses total about 5%. There are large isomer differences, *e.g.* with isoquinoline there is hardly any attack and the specimen remains polished, unlike with quinoline.

Table 5 Analysis of hydrolysed solutions of MeCN–SO_2Cl_2 after ageing

Solution molality (mol kg^{-1})	Time/d	% of original acidity *	% SO_2Cl_2 converted into SO_2
2.45	1.27	99.6	1.0
2.04	3.04	98.5	5.0
2.18	6.79	93.0	28.0

* 1 mol hydrolysed SO_2Cl_2 ≡ $4H^+$.

Table 6 Raman intensities in CH_2ClCN–MeCN–SO_2Cl_2 mixtures on ageing

	CH_2ClCN	MeCN	SO_2Cl_2	SO_2
Composition/mmol	15.4	38.3	12.4	—
Measured line/cm^{-1}	746	923	410	1150
Peak height at 0.5 h	51.5	36.5	162	4
Peak height at 6 h	8	9.5	5	41

ν(C≡N) shifts from 2259 to 2250 cm^{-1} the value for CCl_3CN.

Effect of Solvents on Rate.—Approximately molar solutions of SO_2Cl_2 were used at SO_2Cl_2:Ni 0.69:1 and the rate order found was EtCN > MeCN > dimethylsulphoxide (dmso) > dimethylformamide (dmf) > $MeNO_2$ > tetrahydrothiophene 1,1-dioxide (sulpholane) > Me_2CO > Et_2O, ethyl acetate *e.g.* $Lt^{-\frac{1}{2}}c^{-1}$ for EtCN, MeCN and $MeNO_2$ was 77.9, 54.8 and 0.43. Similar orders were obtained with tin (MeCN ≫ sulfolane > Et_2O). Dissolution of SO_2Cl_2 in dmf and dmso was exothermic, requiring cooling during make-up. The effect of mixed solvents on the rate is described later.

Effect of Additives.—The compounds PhI, Ph_2S and PPh_3 added to SO_2Cl_2 gave $Lt^{-\frac{1}{2}}c^{-1}$ values of 26.7, 13.2 and 11.1 respectively. Addition of $SnCl_4$ to the PhI did not increase the rate. Tetrabutylammonium iodide added at 1:2 ratio to SO_2Cl_2 gave a rate constant of 9.8 ($[NBu_4][ICl_4]$ can be isolated from this solution although it self-chlorinates and liquefies in daylight).

The effect of base additives is summarized in Table 4.

Stability of MeCN–SO_2Cl_2 *Solutions.*—Under ambient conditions these solutions acquire a brown tinge in a few days which slowly changes to black and a black solid is precipitated. The aged solutions are still corrosive, ruling out a number of instrumental methods apart from Raman spectroscopy which is particularly suitable since all fundamental frequencies can be seen. Changes in composition (Table 5) were followed by hydrolysing vacuum-prepared solutions after standing, the acidity being determined alkalimetrically and SO_2 content iodimetrically.

The acidity decreases to 3 equivalents of H^+ on substitution. Thus in the last run the acid equivalent is 28 × 3 + 0.72 × 4 = 3.72 or 93% of the original $4H^+$, in agreement with the alkalimetric value. The symmetrical stretch of Cl_2 at 546 cm^{-1} was never seen.

A 2.61 mol kg^{-1} solution after 10 d left a small amount of a brown oil under an aqueous layer on hydrolysis. The oil precipitated a black solid on dilution, amounting to 5% of the original solution weight. The aqueous extracts had 73% of the original acidity and 50% of the chlorine in the original SO_2Cl_2 was precipitated as AgCl.

Raman intensities (Table 6) were referenced to CCl_3CH_3 lines after showing the inertness of the latter compound. Thus, SO_2Cl_2 in CCl_3CH_3 (0.278:1) remained colourless over 40 d and the ratio SO_2Cl_2:CCl_3CH_3, as measured by the 410:530 cm^{-1} lines, remained at 1.63 ± 0.01:1 over 27 d. A ternary solution SO_2Cl_2:CCl_3CH_3:MeCN was examined up to 15 d when darkening obscured the spectrum. The results (Fig. 1) conform with the chemical analyses. The degree of substitution exceeds unity because CH_2ClCN additions accelerate decomposition. Most of the SO_2Cl_2 is used up in 6 h. Decomposition is photochemically promoted (see Table 7).

Stabilization of MeCN–SO_2Cl_2 *Solutions.*—(*a*) *Addition of* SO_2 *at* SO_2:SO_2Cl_2 1.94:1. The intensity ratio remained at 1.42 ± 0.01:1 over 10 d. After 25 d it increased to 3.55:1 and the line of CCl_3CN at 490 cm^{-1} appeared.

(*b*) *Addition of* $S_2O_8^{2-}$. This was judged by the time for the

Table 7 Effect of light on ageing of SO_2Cl_2–MeCN solutions

		Ratio of Raman intensities		
Solution mole fraction of SO_2Cl_2	Time/d	SO_2Cl_2:MeCN* 410:920 cm^{-1}	SO_2:MeCN* 1150:920 cm^{-1}	SO_2:SO_2Cl_2
0.0810 (exposed to 100 W lamp)	0.083	2.63	0.15	0.056
	1.92	0.84	0.45	0.585
	2.92	0.44	1.10	2.52
0.123 (in dark)	0.083	2.07	0.13	0.063
	1.83	1.97	0.12	0.061
	4.00	2.00	0.14	0.070

* Chlorination of MeCN has only a small effect on the intensity of the band at 920 cm^{-1} since MeCN is present in 7–11 fold excess over SO_2Cl_2.

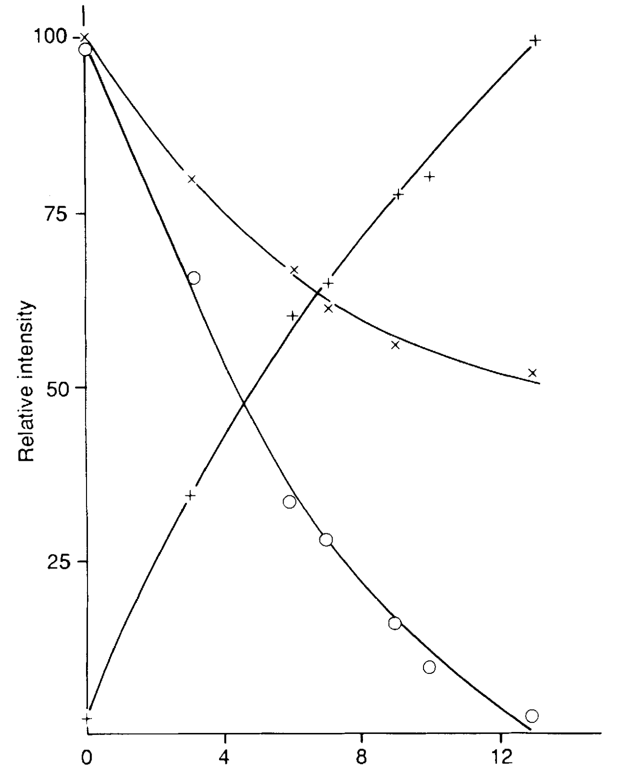


Fig. 1 Raman intensities of an ageing CCl_3CH_3–SO_2Cl_2–MeCN solution (5:2:3) referenced to the intensity of the band of CCl_3CH_3 at 526 cm^{-1} [intensities of SO_2Cl_2 (○), SO_2 (+) and MeCN (×) measured at 410, 1150 and 2257 cm^{-1} respectively]

solutions to darken. At $S_2O_8^{2-}$:SO_2Cl_2 0.076:1 the solution became faint brown in 19 d under ambient conditions, whereas for $S_2O_8^{2-}$:SO_2Cl_2 0.150:1 in the dark it took 99 d.

(*c*) *Addition of* Cl^- *in the form of* KCl. This kept a solution 14 d and a saturated NMe_4Cl solution 20 d before colouration. Addition of Na_2CO_3 at CO_3^{2-}:SO_2Cl_2 0.869:1 yielded a colourless solution after 56 d. The Na_2CO_3 was partly converted into NaCl.

Detection of Ionization.—The conductivity, measured in a cell with tungsten electrodes, increased continuously over days when SO_2Cl_2 was distilled into MeCN. (Results using platinum electrodes were discounted because Pt was not inert as seen by removal of platinum black.) Transport measurements were made in an H-shaped cell with vertical compartments isolated by a sintered glass disc in the horizontal arm. Silver-rod electrodes removed discharged chlorine as AgCl. The low conductivity of an 0.328 molal solution limited the current and it needed 2 d at 40 V to pass 0.01 F of electricity. Solutions from each compartment were analysed after electrolysis for SO_2 (adding to excess of I_2, back titration with $S_2O_3^{2-}$) and total S (SO_2 + SO_2Cl_2 after oxidation with H_2O_2 and precipitation as $BaSO_4$). The amount of the anolyte SO_2 became greater than that of the catholyte and *vice versa* for SO_2Cl_2. The electrolysis efficiency was only 60% due to ohmic loss and non-electrolytic reactions common to both compartments. The loss in SO_2Cl_2 when compared with the starting solution balanced the gain in SO_2 to within 10%.

Results and Discussion

The enhanced reactivity of SO_2Cl_2 in MeCN, comparable with that of N_2O_4 in organic solvents towards metals,[20] suggests an ionic mechanism. The extent of ionization is minute, and not detectable in Raman or NMR spectra of fresh solutions, but the presence of ions is detectable from the conductivity increase. Possible gas-phase ionizations (1)–(3) can be compared.

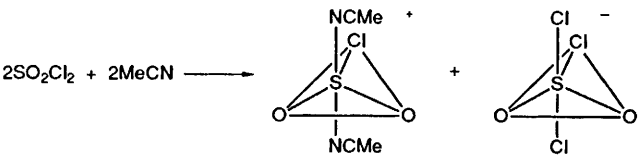
$$SO_2Cl_2 \longrightarrow SO_2Cl^+ + Cl^- \tag{1}$$

$$SO_2Cl_2 \longrightarrow Cl^+ + SO_2Cl^- \tag{2}$$

$$2SO_2Cl_2 \longrightarrow SO_2Cl^+ + SO_2Cl_3^- \tag{3}$$

A minimum neglect of differential overlap (MNDO)[21] calculation gave $\Delta H_f(SO_2Cl^-)$ −63.8 and $\Delta H_f(SO_2Cl^+)$ +341.3 kcal mol^{-1}. An experimental value of $\Delta H_f(SO_2Cl^-)$ −135 kcal mol^{-1} has been found[22] and hence $\Delta H_f(SO_2Cl^+)$ can be corrected to 270 kcal mol^{-1} which is reasonable since the negative and positive ions are stabilized by 10 or 12 kcal over the sum of SO_2 + Cl^- or Cl^+ values. Ionization (1) is then favoured by 32 kcal over (2). Further stabilization arises in (3) using the experimental[22] $\Delta H_f(SO_2Cl_3^-)$ of −149 to −157 kcal mol^{-1} which is 10–14 kcal more stable than the values for SO_2Cl_2 + Cl^- or SO_2 + Cl_3^-.[23] In solution extra stabilization by solvation favours the 'softer' SO_2Cl^+ over Cl^+ cation. (Following Pearson's[24] measure of hardness, (ionization energy − electron affinity)/2, the values 19.7 and 11.1 eV can be assigned to Cl^+ to SO_2Cl^- respectively using the MNDO calculated ionization energies of 5.61 and 19.50 eV for SO_2Cl^- and SO_2Cl^+.)

Qualitatively, analogies between SO_2Cl_2 and SO_2ClF support the thermochemical results. The compound SO_2ClF, like SO_2Cl_2, needs high temperatures to attack metals,[25] whereas in MeCN attack occurs at room temperature to give mixtures of chloride and fluoride.[26] It is bound to polarize with positive chlorine and since lithium alkyls yield sulfonyl chlorides with both SO_2Cl_2[27] and SO_2ClF[28] the common electrophile must be SO_2Cl^+. More directly, a simple transport experiment using silver electrodes to trap discharged chlorine shows that SO_2 is transported with the positive species, and SO_2Cl_2 with the negative, in accord with the symmetry-allowed chloride-ion transfer. This ionization explains the effect of NMe_4Cl additions, which produce 'basic' solutions,[29] on



reactivity. Wasif and co-workers[30,31] have measured the stability of $SO_2Cl_3^-$ in MeCN, with a large excess of NMe_4Cl which preserves these solutions. The $SO_2Cl_2 \cdots Cl^-$ complex is weak and was considered to be formed by charge transfer. Nevertheless, the solubility of NMe_4Cl in MeCN can be enhanced 100 fold by SO_2Cl_2 addition. The rate of dissolution of zinc also increases 100 fold at unit $NMe_4Cl:SO_2Cl_2$ ratio and chlorozincates can be isolated from solution. By contrast Cd is almost unaffected. The dissolution rates of Al and In are similarly enhanced, the latter spectacularly by a factor of more than 10 000 if ultrasonic agitation is used. Enhancements of up to 40 fold were found for Ge and the basicity order $NMe_4Cl > NH_3Bu^tCl > NBu_4Cl > NH_4Cl$ established.

The complementary 'acid' behaviour with Lewis acids was obscured because they partly ionize in MeCN. Thus $AlCl_3$ in MeCN forms solid 1:1, 2:3 and 1:2 adducts, the last with a structure $[AlCl(MeCN)_5][AlCl_4]_2 \cdot MeCN$.[32] Some increase in rate is probably due to chlorine liberated *via* $SO_2Cl_2 + AlCl_3 \rightleftharpoons Cl_2 + AlCl_3 \cdot SO_2$.[33] Iron trichloride similarly autoionizes to $FeCl_4^-$ anions.[34] However, addition of $FeCl_3$ substantially increases the rate of dissolution of Cd in spite of the absence of Lewis acidity, because of the redox reaction $Cd + 2Fe^{3+} \longrightarrow Cd^{2+} + 2Fe^{2+}$.

The SO_2, formed during chlorination with SO_2Cl_2, only seems to affect reaction with Tl which is incompletely oxidized to Tl^{III}. Stable $Tl^ITl^{III}Cl_6$[35–37] is formed on the surface and $TlCl_3$ in solution. Addition of SO_2 increases the $Tl_4Cl_6:TlCl_3$ ratio whereas addition of KF, which complexes SO_2 as SO_2F^-, eliminates the surface film and considerably increases the rate of attack. There is no evidence for the radical ion $SO_2^{\bullet -}$ responsible for the attack on metals in dmso–SO_2.[38]

Most heterogeneous reactions are diffusion controlled through surface films rather than chemically controlled at the metal–solution interface. Hence there is only a broad division between refractory elements, with high melting point or hardness, and the rest which parallel aqueous reactivities. This is shown in the periodic variation of reactivity with atomization energies. The transition elements with values above 150 kcal mol^{-1} [Ta, Nb; W, Mo; Re, Tc(?); Os, Ru and Ir] are inert. Similarly the main-group elements with higher atomization energies (C, B, Si) are also inert. Low-melting elements which form chlorides soluble in MeCN, *e.g.* Sn, Se, Bi, dissolve rapidly even in SO_2Cl_2 alone, but elements forming unsolvated chloride films, *e.g.* Ag, Pb, Li, Ca, are passivated. However, atomically dispersed Pb, as in Pb–Sn alloys, is rapidly and completely converted into $PbCl_2$.

Kinetic measurements were made to examine these rates and the effect of additives and solvents. Nickel foil was a convenient substrate, thinning uniformally and clearly showing film formation of yellow $NiCl_2 \cdot 2MeCN$. The solution rate, measured in terms of the % of the maximum loss (L) allowed by the SO_2Cl_2 content, varied parabolically with time (t) and was proportional to the SO_2Cl_2 molarity (c). It also depended on the surface area but not on the temperature (from 4 to 22 °C). For comparative purposes, rate constants $Lt^{-\frac{1}{2}}c^{-1}$ obtained on standard-sized foils were used. (A parabolic relation is characteristic of diffusion control in metal oxidation.) Vigorous agitation eliminated any transport control *via* the liquid.[39] No reaction was observed using Ni in chlorinated solvents, or in Et_2O and ethyl acetate. The rate order found was EtCN > MeCN > dmso > dmf > $MeNO_2$ > tetrahydrothiophene 1,1-dioxide > Me_2CO which is not that of the relative permittivity or donor number. The superiority of nitriles suggests a specific $N \longrightarrow S$ stabilization of SO_2Cl^+ ions since all the other solvents are oxygen donors. An attempt to probe this interaction by addition of nitrogen bases, mainly pyridine derivatives, was inconclusive because the strongest bases precipitated 2:1 complexes with SO_2Cl_2[40–42] and others self-chlorinated to a greater extent than with MeCN. This was shown by incomplete reaction of SO_2Cl_2 with the equivalent amount of Ni, as well as by the greater stability of chlorinated pyridines. A more regular series was observed on addition of equivalent amounts of PhI, Ph_2S and PPh_3, which form $PhICl_2$, Ph_2SCl_2 and $Ph_3PSO_2Cl_2$ *in situ*. A rate order $SO_2Cl_2 > PhI > Ph_2S > PPh_3$ agrees with the previously derived order based on oxidation couples.[43]

The specificity of MeCN is encountered with mixed solvents. Solutions of SO_2Cl_2 in $MeNO_2$, with a high permittivity but low donor number, mixed with diethyl ether of opposite properties, failed to attack Ni whereas addition of MeCN to $MeNO_2$ at a $MeCN:SO_2Cl_2$ ratio of 1.6:1 was enough to increase the rate 20 fold over that of $MeNO_2$ alone. Similarly, CH_2Cl_2–SO_2Cl_2 solutions which are inert to Ni required less than a unit $MeCN:SO_2Cl_2$ ratio to initiate attack. Interestingly, CH_2Cl_2–MeCN (1:1 v/v) attacks Ni faster than with MeCN as solvent. The attack was linear because a surface film was absent. Results with dmf–MeCN mixtures, in which the rate decreased with increasing dmf:SO_2Cl_2 ratio, indicates that the electrophile $[Me_2N{=}CHCl]^+$[44] is less effective than SO_2Cl^+ as expected since Vilsmeier-type reagents formylate rather than chlorinate.

Before discussing reactions with platinum metals some comment on the stability of MeCN–SO_2Cl_2 solutions is needed. Conductivities increase as soon as the components mix and the change can be followed within 1 d by conventional analysis since SO_2 forms and ionizable chlorine decreases. Solutions (2–3 mol dm^3) lose *ca.* 1% of SO_2Cl_2 in 1 d accelerating to about 30% within a week when the solution acquires a brown tinge. This darkens with deposition of a black solid. The change can also be monitored from Raman intensities using CCl_3CH_3 as an internal standard. Fig. 1 shows the growth of SO_2 at the expense of SO_2Cl_2 and the MeCN present in excess. The distinctive ν(C≡N) of CCl_3CN is detectable towards the end. The average degree of chlorine substitution cannot be determined from the ionizable chlorine on hydrolysis, which is limited to 50% according to $MeCN + nSO_2Cl_2 \longrightarrow CH_{(3-n)}Cl_nCN + nSO_2 + nHCl$, but it is greater than monosubstitution because CH_2ClCN–SO_2Cl_2 solutions change more rapidly.

The HCl released does not increase the acidity. It is neutralized in 'adducts' such as $MeCN \cdot nHCl$ (n = 1 or 2). The latter, as a solid, is $MeCCl{=}NH_2^+Cl^-$;[45] the former probably exists as an equilibrium between MeCCl=NH and $MeCNH^+Cl^-$. Since the imidyl chloride is analogous to an acyl chloride it hydrolyses and titrates as ionizable chloride. Condensation reactions can occur in the presence of HCl. Thus MeCCl=N–C=NHMe and its hydrochloride can be isolated in high yield.[46]

Further polymerization would produce a conjugated chain, akin to that in black paracyanogen, $(CN)_x$, and would explain the observed darkening. High-temperature polymerization of MeCN in adducts with Lewis-acid chlorides has been reported[47] and this behaviour could hinder desolvation of some metal chlorides. Deterioration occurs to some extent by radical chlorination since it is quicker in the light than in the dark and solutions stabilize in the presence of $S_2O_8^{2-}$ presumably *via* radical capture by $SO_4^{\bullet -}$. Chlorides such as NMe_4Cl also stabilize solutions by suppression of the SO_2Cl^+ electrophile, as does Na_2CO_3 by neutralization of HCl. Sulphuryl chloride itself is dissociated by daylight but can be kept unchanged in CCl_3CH_3 for over 1 month. Hence the simplest stabilization procedure would be to add MeCN to this solution immediately before use.

There is a diagonal pattern of reactivity among Group 8 and 9 metals with Rh, Os and Ir inert in SO_2Cl_2–MeCN. Palladium is the most reactive, the powder giving an immediate brown solution at the melting point of MeCN before precipitating yellow

$PdCl_2 \cdot 2MeCN$. If the reaction is prolonged for more than 1 d, as may be required for complete dissolution of consolidated specimens, a much higher-molecular-weight product with a high organic content results. Possibly Pd^{II} interacts with the conjugated –C=N– system from the $MeCN–SO_2Cl_2$ decomposition and may even catalyse the latter. The same difficulty arises with Pt which needed days to dissolve. The organic content increases with reaction time whilst the Cl:Pt ratio remains near 4:1. Rhodium powder reacts, at a hundredth the rate of Pd, to give $RhCl_3 \cdot xMeCN$. The dissolution of Pt is speeded up by NMe_4Cl additions to give a $PtCl_6^{2-}$ salt but still with an organic content. Palladium(II) is oxidized to Pd^{IV} with a diminution in rate but the oxidation state Rh^{III} is unchanged with NMe_4Cl present. Even the inert Ru slowly dissolves. A more detailed study is required to resolve the organic chemistry involved in dissolution of Pd and Pt.

Conclusion

The SO_2Cl_2–MeCN reagent should be useful for quantitative small-scale preparations of solvated chlorides (*e.g.* $PdCl_2 \cdot 2MeCN$) or unsolvated ones ($SeCl_4$ and Tl_4Cl_6) as well as complex salts (*e.g.* $ZnCl_3^-$, $ZnCl_4^{2-}$ or $GeCl_6^{2-}$). Some convenient analytical separations are possible such as Pb from solders, Pd from other platinum metals or of refractory carbides and nitrides from steels.[48] Finally, etching or surface finishing of metals, alloys and semiconducting materials is possible and will be reported elsewhere.

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