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Kinetics of sulfur-transfer from titanocene (poly) sulfides to sulfenyl chlorides: rapid metal-assisted concerted substitution†‡

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The kinetics of sulfur transfer from titanocene (poly)sulfides ($^{R}Cp_2TiS_5$, $Cp_2TiS_4CMe_2$, $Cp_2Ti(SAr)_2$, $Cp_2TiCl(SAr)$) to sulfenyl chlorides (S_2Cl_2, RSCl) have been investigated by a combination of stopped-flow UV-Vis/NMR reaction monitoring, titration assays, numerical kinetic modelling and KS-DFT calculations. The reactions are rapid, proceeding to completion over timescales of milliseconds to minutes, *via* a sequence of two S–S bond-forming steps (k_1, k_2). The archetypical polysulfides Cp_2TiS_5 (**1a**) and $Cp_2TiS_4C(Me_2)$ (**2a**) react with disulfur dichloride (S_2Cl_2) through rate-limiting intermolecular S–S bond formation (k_1) followed by a rapid intramolecular cyclization (k_2, with $k_2 \gg k_1$ [RSCl]). The monofunctional sulfenyl chlorides (RSCl) studied herein react in two intermolecular S–S bond forming steps proceeding at similar rates ($k_1 \approx k_2$). Reactions of titanocene bisthiophenolates, $Cp_2Ti(SAr)_2$ (**5**), with both mono- and di-functional sulfenyl chlorides result in rapid accumulation of the monothiophenolate, $Cp_2TiCl(SAr)$ (**6**) ($k_1 > k_2$). Across the range of reactants studied, the rates are relatively insensitive to changes in temperature and in the electronics of the sulfenyl chloride, moderately sensitive to the electronics of the titanocene (poly)sulfide ($\rho_{(Ti-(SAr))} \approx -2.0$), and highly sensitive to the solvent polarity, with non-polar solvents (CS_2, CCl_4) leading to the slowest rates. The combined sensitivities are the result of a concerted, polarized and late transition state for the rate-limiting S–S bond forming step, accompanied by a large entropic penalty. Each substitution step {[Ti]–SR′ + Cl–SR → [Ti]–Cl + RS–SR′} proceeds *via* titanium-assisted Cl–S cleavage to generate a transient pentacoordinate complex, Cl–[Cp_2TiX]–S(R′)–SR, which then undergoes rapid Ti–S dissociation.

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Introduction

Titanocene pentasulfide, Cp_2TiS_5 (**1a**, Scheme 1), is a bench-stable and easily handled pentasulfide dianion surrogate.[1,2] Pentasulfide **1a**, and related polysulfides, (*e.g.* $Cp_2TiS_4C(Me)_2$, **2a**),[2a] allow the selective preparation of sulfur homocycles (S_n),[3] heterocycles (E_2S_n),[4] and polysulfanes (R_2S_n)[5] from sulfenyl chlorides (S_xCl_2, RS_xCl). Titanocene bis and mono-thiolates, $Cp_2Ti(SR)_2$ and $Cp_2TiCl(SR)$, are also efficient sulfide anion surrogates.[3c,6,7] These S–S bond-forming reactions generally proceed quantitatively under mild conditions (≤25 °C) making pentasulfide **1a** and analogues one of the central platforms for the synthesis of polysulfides.[3d,8,9] Despite this widespread application, studies of the mechanism(s) of these sulfur transfer processes are scarce,[2a,7a,10,11] and as far as we are aware the kinetics of the general process in Scheme 1 have not been investigated.

The reaction of pentasulfide **1a** with RSCl species is generally accepted to proceed in two steps, *via* a chlorotitanocene intermediate (**Int**), Scheme 1. Support for this includes the isolation of intermediates from the slow reactions of the sterically hindered sulfenyl chloride Ph_3CSCl with $Cp_2TiS_4CMe_2$ (**2a**) and with Cp_2TiS_4(cyclo-C_6H_{10}).[7a] Münchow and Steudel proposed that nucleophilic attack by the chlorine atom in RSCl at the titanium atom opens the metallacycle (mechanism I).[7a]

However, sulfur compounds can react ambiphilically and several alternative mechanisms can also be considered for the S–S bond forming steps. For example, concerted or step-wise S_N2-at-sulfur reactions are feasible,[12–14] with **1a** acting as the nucleophile (mechanism II). Alternatively, the S–S bond

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† Dedicated to the memory of Prof. Dr Ralf Steudel (March 25, 1937–February 12, 2021) a life-long pioneer in the chemistry of sulfur.

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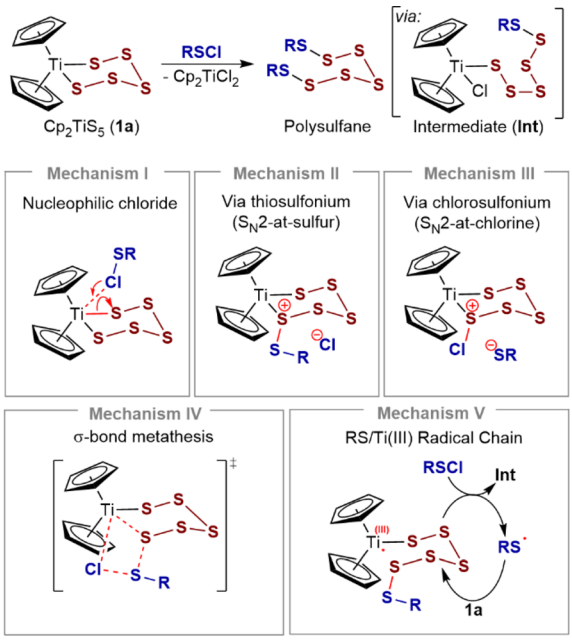


Scheme 1 Reaction of titanocene pentasulfide (**1a**) with sulfur(II) chlorides: general features and potential reaction mechanisms (I–V).

forming steps could involve formation of chlorosulfonium ions (mechanism III), concerted σ-bond metathesis (mechanism IV), or mechanisms involving sulfenyl radicals[15] and Ti(III)[16] chain carriers (mechanism V), or analogous chain processes. There is also the possibility that **1a** acts as a reservoir to reactive ring-opened species.[17] Depending on specific kinetic parameters, these last two possibilities are unlikely to result in simple bimolecular kinetics (see ESI, Section S9‡).

Results and discussion

Herein, we report on the kinetics of sulfur transfer from titanacyles (**1** and **2**) to sulfenyl chlorides S_2Cl_2 and to RSCl reagents (**3** and **4**), including analysis of the effects of solvent and temperature on the rate. The experimental kinetic data are complemented with KS-DFT calculations to assess the feasibility of proposed reaction pathways and elucidate the key role of the titanocene in these nucleophilic substitutions. We also briefly report on the reactions of acyclic Ti-thiophenolates with S_2Cl_2. The overall insight to the kinetics and mechanism allows the identification of parameters that can be used to tune the rate and selectivity.

Kinetics of the reaction of S_2Cl_2 with titanacycle 1a

We began by investigating of the reaction of S_2Cl_2 with Cp_2TiS_5 (**1a**). Preliminary analysis by ^{1}H NMR spectroscopy confirmed quantitative conversion within seconds in CH_2Cl_2 solution, accompanied by a characteristic change in colour from deep-red (Cp_2TiS_5 **1a**, λ_{max} 490 nm) to light-orange (Cp_2TiCl_2, λ_{max} 393 nm).[17b,c] Stopped-flow UV-Vis analysis (SF-UV) of the reactions of **1a**, at initial concentrations in the range 0.05–0.15 mM, with

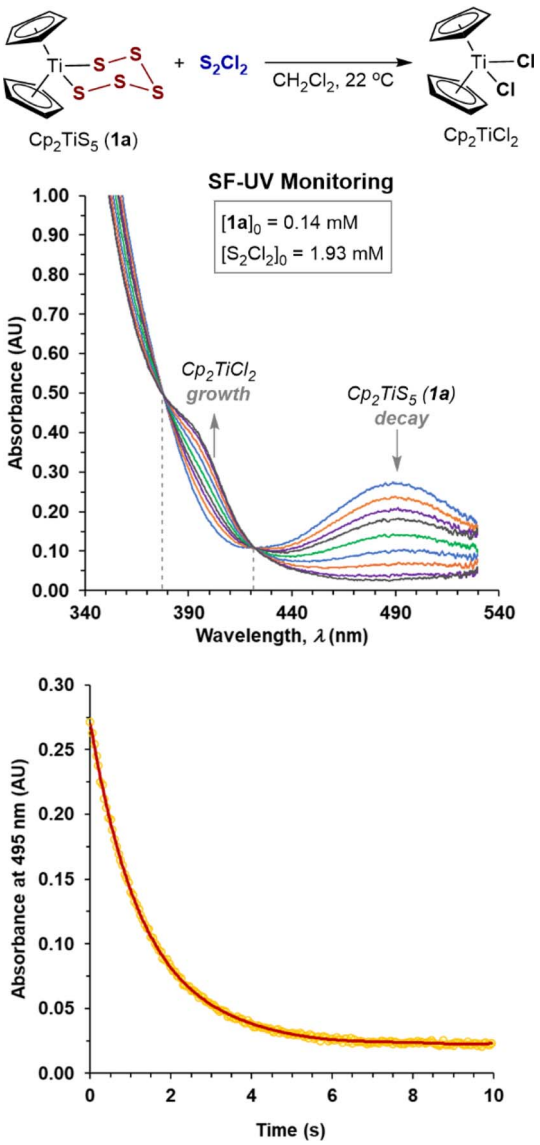


Fig. 1 Stopped-flow UV-Vis temporal evolution of spectra and exponential decay in absorbance of **1a** at 495 nm on reaction with excess S_2Cl_2 in CH_2Cl_2 at 22 °C.

a large excess of S_2Cl_2 (for conditions, see the ESI, Section S2‡) were in agreement with pseudo first-order kinetics, with two clear isosbestic points (λ = 378, 422 nm, *e.g.* Fig. 1). The data correlated with the same exponent ($-k_{obs}t$) when the initial concentrations of the limiting reagent $[\mathbf{1a}]_0$ were doubled or halved (see Section S2 in the ESI‡) confirming the first-order[18] kinetic dependency on the titanium complex **1a** in the rate-limiting event. Extraction of k_{obs} from exponential decays in absorption at 495 nm afforded linear correlations against $[S_2Cl_2]_0$ (see Section S2 in the ESI‡) confirming first-order kinetic dependency on S_2Cl_2. The overall process {**1a** + S_2Cl_2} is thus governed by second order kinetics, first order in both components, *i.e.*, $-d[\mathbf{1a}]/dt = k_1[\mathbf{1a}][S_2Cl_2]$, with the empirical[19] bimolecular rate constant, k_1 = 320 M^{-1} s^{-1} at 22 °C (Table 1, entry 1).

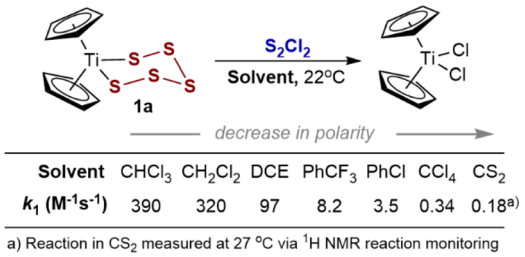


Fig. 2 Solvent effects on the empirical[19] rate constant (k_1) values for the pseudo first-order reaction of **1a** with excess S_2Cl_2 at 22 °C.

Effects of solvent on the rate of reaction of S_2Cl_2 with 1a

The ability to conduct SF-UV kinetic assays at low concentrations of **1a** allowed exploration of a range of solvents without issues relating to solubility of the reactants, intermediates, and titanocene dichloride and cycloheptasulfur products. Solvent polarity substantially affects the rate (k_1, Fig. 2) and there is a reasonable correlation with Catalán's polarity parameters: $\log(k_1) = 49.5\{0.97 \times SA + 0.03 \times SdP\} + 0.56$; $R^2 = 0.98$; see Section 2.3 in the ESI.† [20] The three orders of magnitude range in rate across the series of solvents spanning from CS_2 (slowest) to $CHCl_3$ (fastest) is indicative of development in polar character on approach to the rate limiting transition state.

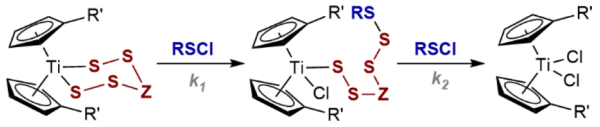
The kinetics of the reaction in CS_2 (ref. 3a) and in CCl_4, were slow enough ($k_1 = 0.18$ and 0.34 M^{-1} s^{-1}, respectively) to allow *in situ* continuous ^{1}H NMR spectroscopic reaction monitoring.[21] The NMR profiles (see ESI, Section S5‡) showed no evidence for accumulation of intermediates, and remained consistent with bimolecular kinetics, *i.e.*, $-d[\mathbf{1a}]/dt = k_1[\mathbf{1a}][S_2Cl_2]$, across a range of concentrations. Overall, the analyses eliminate radical chain (mechanism V) and slow irreversible Ti–S predissociation mechanisms.

Kinetics of the reactions of S_2Cl_2 with related titanacycles 1b–e and 2a

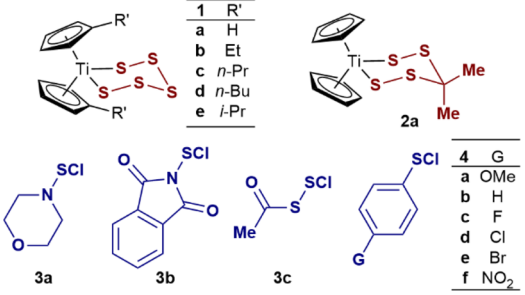
Reactions of S_2Cl_2 in CH_2Cl_2 with structurally related titanacycles **1b–e** and **2a** also gave bimolecular kinetics, *i.e.*, first order in both S_2Cl_2 and the titanacycle (Table 1, entries 2–6). Alkyl substitution of the cyclopentadienyl groups increases the solubility of titanocene (poly)sulfides in organic solvents.[1a,2b] The rates of reaction of the alkylated analogues **1b–e** were all slightly slower than **1a** (Table 1, entries 2–5) with the relative rates ranging from 0.8 (**1b**, Et) to 0.3 (**1e**, i-Pr).

While compensating steric/electronic contributions cannot be discarded, it is reported that the donor effects of cyclopentadienyl substituents do not significantly affect the electron density on Ti in the titanapentasulfide group.[22] The similar inductive effects of the alkyl substituents (*e.g.* Et, i-Pr, $\sigma_p = -0.15$)[23] suggest these changes to result primarily from steric hindrance. However, attempts to correlate these small differences against reported steric parameters, such as angle-descriptions for η^5-cyclopentadienide ligands,[24] did not show a clear trend (see ESI, Section S2.4‡). In contrast to the negligible differences in reactivity of **1a–e**, replacing the sulfur atom at position 4 in the pentasulfide ring had a profound effect, with the rate of $Cp_2TiS_4C(Me)_2$ (**2a**) being two orders of magnitude faster (Table 1, entry 6) than with titanacycle **1a** (Table 1, entry 1). The kinetics were again first order in both components, leading to the same overall bimolecular empirical rate relationship: $-d[\mathbf{2a}]/dt = k_1[\mathbf{2a}][S_2Cl_2]$.

Table 1 Empirical[19] bimolecular rate constants for the reaction of titanacycles **1a–e** and **2a** with S_2Cl_2 and sulfenyl chlorides **3a–c** and **4a–f** in CH_2Cl_2 at 22 °C



Entry	Titanocene	RSCl	k_1 (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1})
1	**1a**	S_2Cl_2	3.2×10^2	—[a]
2	**1b**	S_2Cl_2	2.4×10^2	—[a]
3	**1c**	S_2Cl_2	2.4×10^2	—[a]
4	**1d**	S_2Cl_2	2.0×10^2	—[a]
5	**1e**	S_2Cl_2	0.9×10^2	—[a]
6	**2a**	S_2Cl_2	3.4×10^4	—[a]
7	**1a**	**3a**	4.8×10^1	6.8×10^1
8	**1a**	**3b**	1.7×10^3	6.9×10^3
9	**1a**	**3c**	4.4×10^3	9.8×10^3
10	**1a**	**4a**	4.4×10^4	5.7×10^4
11	**1a**	**4b**	4.2×10^4	5.0×10^4
12	**1a**	**4c**	4.9×10^4	5.0×10^4
13	**1a**	**4d**	4.1×10^4	4.6×10^4
14	**1a**	**4e**	4.5×10^4	4.3×10^4
15	**1a**	**4f**	1.9×10^4	6.8×10^3



[a] No accumulation of an intermediate is observed in these processes, $k_2 > 10^2 k_1$.

Kinetics of the reactions of monofunctional sulfur chlorides (RSCl) 3a–c and 4a–f with titanacycle 1a

The SF-UV analyses of the reactions of monofunctional RSCl reagents **3a–c** and **4a–f** with **1a** showed distinctly different temporal UV-Vis absorption profiles (Fig. 3) to those with S_2Cl_2 (Fig. 1). The absence of isosbestic points accompanied by an increase then decay in absorbance at 495 nm indicates accumulation of a UV-Vis absorbing reactive intermediate (Fig. 3). The difference between the reactions involving the monofunctional RSCl reagents compared to S_2Cl_2 is attributed to the $Cp_2TiCl(S_7Cl)$ intermediate generated by the latter undergoing rapid intramolecular S–S bond formation, *vide infra*.

Stopped-flow ^{1}H NMR spectroscopic (SF-NMR)[25] analysis of the reaction of **1a** with the least reactive monofunctional reagent, *N*-morpholinosulfenyl chloride **3a**, confirmed the generation of a transient species. This was tentatively assigned as the polysulfanido intermediate $Cp_2TiCl(S_6R)$, consistent with Münchow and Steudel's proposal.[7a] In this case the values for k_1 and k_2 (Table 1, entry 7) were independently determined by numerical methods fitting of both the NMR and SF-UV data (Fig. 3). The rate constants for the much more reactive RSCl reagents **3b**, **c** and **4a–f** (Table 1, entries 8–15) were extracted from numerical modelling of the UV-Vis data only, because the reactions were too fast to monitor by SF-NMR.

Each model employed multiple averaged data sets, varying $[RSCl]_0$ (see, ESI, Section S3‡) with the net absorbance assumed to arise from Beer–Lambert additivity of all species. The temporal evolution of the SF-UV data then depends on the initial reactant concentrations, the rate constants k_1 and k_2, and the molar absorption coefficients (ε) of **1a**, Cp_2TiCl_2, and $Cp_2TiCl(S_6R)$. However, without being able to independently determine ε_{int}, we instead used the rate ratio (k_2/k_1) as a dimensionless constraint to find unique solutions to the data. These constraints were determined using analytical solutions to rapid-mixing NMR titration data[26] (see, ESI Section S4.2‡).

The identity of the sulfur electrophile has a major impact on the rates of reaction of **1a** with **3a–c** and **4a–f**, with k_1 and k_2 spanning three orders of magnitude (Table 1, entries 1, 7–15). The rate ratios (k_2/k_1) are also dependent on the identity of RSCl. For example **3b** is significantly more reactive towards the corresponding $Cp_2TiCl(S_6R)$ intermediate than the pentasulfide (**1a**), $k_2/k_1 = 4$. These results confirm that generation of the polysulfido intermediates in high yield from the reaction of titanacycles (**1** and **2**) with monofunctional sulfenyl chlorides is challenging.[7a] The aryl sulfenyl chlorides (ArSCl, **4a–f**, Table 1, entries 10–15) showed the highest reactivity towards **1a**, with rate constants indicative of millisecond reaction timescales at typical concentrations employed for synthetic procedures (0.05–0.1 M).[3] However, within the series, which spans classic electron-donating (*p*-OMe, **5a**) through electron-withdrawing (*p*-NO_2, **5f**) substituents, there is no meaningful correlation against Hammett substituent parameters (see ESI, Section S3.15‡). An analogous lack of correlation has previously been used to invoke concerted, S_N2-like, mechanisms for nucleophilic substitutions at sulfur, rather than step-wise addition–elimination processes.[27]

Activation parameters for the reactions of S_2Cl_2 and 3a with titanacycles 1a and 2a in CH_2Cl_2

The kinetics of the first S–S bond forming step[19] (k_1) in the reaction of **1a**, and of **2a**, with S_2Cl_2, and both S–S bond forming steps (k_1 and k_2) in the reaction of **1a** with *N*-morpholinosulfenyl chloride **3a**, were investigated by variable temperature SF-UV kinetics. Overall, the rates are insensitive to temperature changes, showing small increases or decreases, or no change at all, depending on the identity of the titanacycle and sulfenyl chloride reagent (Fig. 4).

The rate constants for the reaction of **1a** with S_2Cl_2 remain invariant, within experimental error, between 10 and 26 °C. The reaction of S_2Cl_2 with titanacycle **2a** slightly increases in rate on

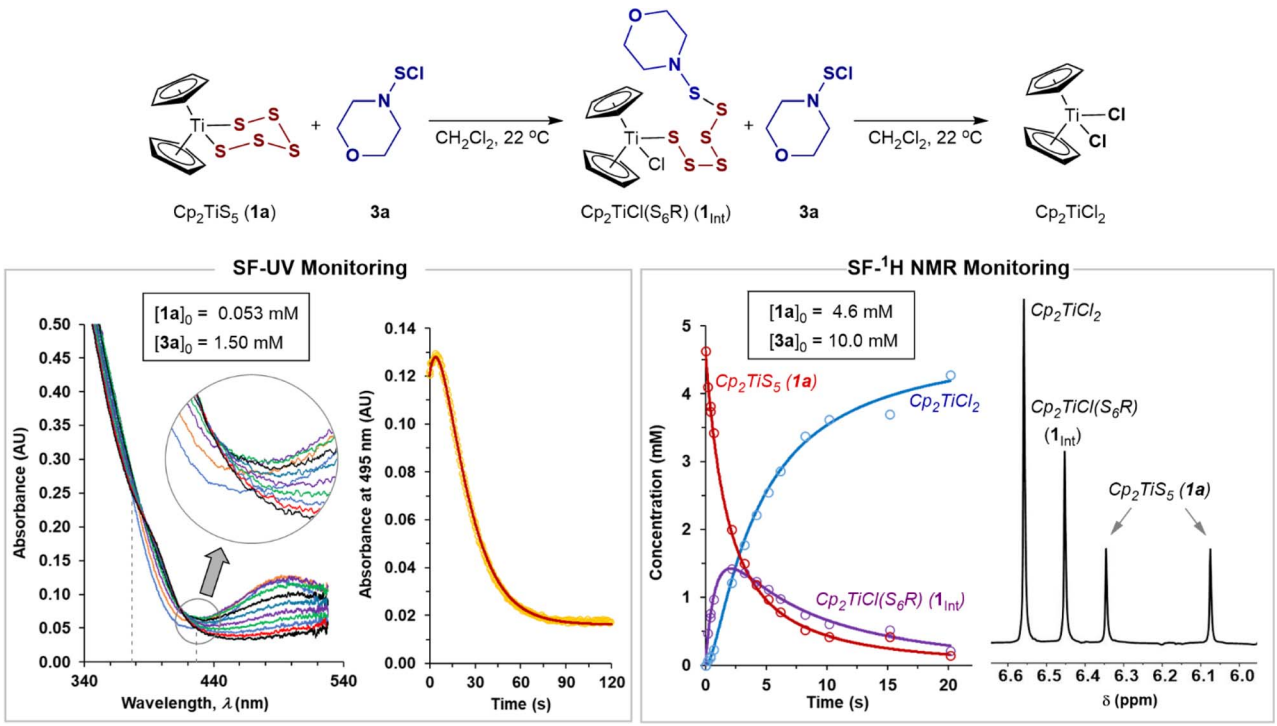


Fig. 3 Stopped-flow UV and ^{1}H NMR monitored evolution of the reaction of **1a** with excess sulfenyl chloride **3a**. Fitted models: solid lines; experimental data: circles.

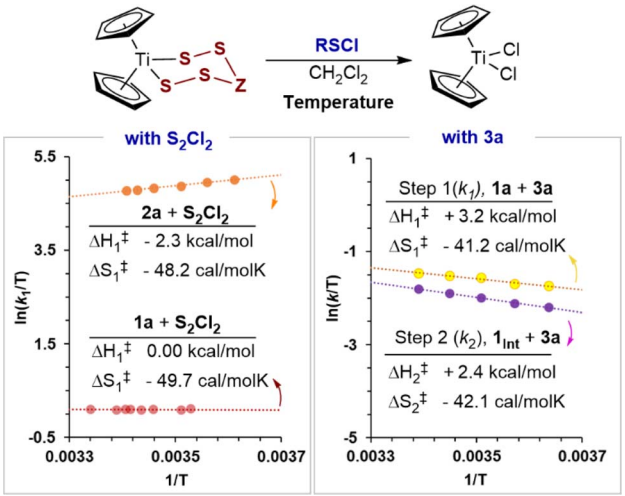


Fig. 4 Eyring analyses using process rate constants for the reaction of titanacycles with chlorosulfanes. The calculated activation parameters correspond to the microkinetic S–S bond forming events.[19]

cooling, ($k_{277K} \approx 1.2k_{295K}$). Conversely, both of the empirical[19] rate constants (k_1, k_2) for the reaction of **1a** with **4a** slightly decrease on cooling ($k_{275K} \approx 0.8k_{295K}$). Eyring analyses (Fig. 4) showed all these effects arise from activation barriers that are dominated by large negative changes in entropy, with only minor enthalpic contributions (*i.e.*, $\Delta G^‡/RT \approx -\Delta S^‡/R$). Large negative entropies of activation can arise from significant solvent reorganisation around the transition state. However, this is more commonly observed in polar protic solvents and is unlikely to be significant in CH_2Cl_2. Overall, the results are indicative of highly organised associative transition states which result in large losses in translational degrees of freedom in the reactants, relative to the ground state.

Computational interrogation of the reaction of S_2Cl_2 with titanacycles 1a and 2a

The reaction of **1a** with S_2Cl_2 was selected for initial assessment of various computational methods.[28] Hybrid density functionals and DLPNO-CCSD(T) failed to qualitatively describe experimental trends, likely due to a significant multideterminant character in some calculated species (see ESI, Section S11.2‡). Based on these preliminary computational assays, the meta-GGA functional, r^{2}SCAN,[29] was chosen for further investigations.

Free energy profiles of sulfur transfer reactions of S_2Cl_2 with **1a** and **2a** are shown in Fig. 5A. Both profiles qualitatively agree with

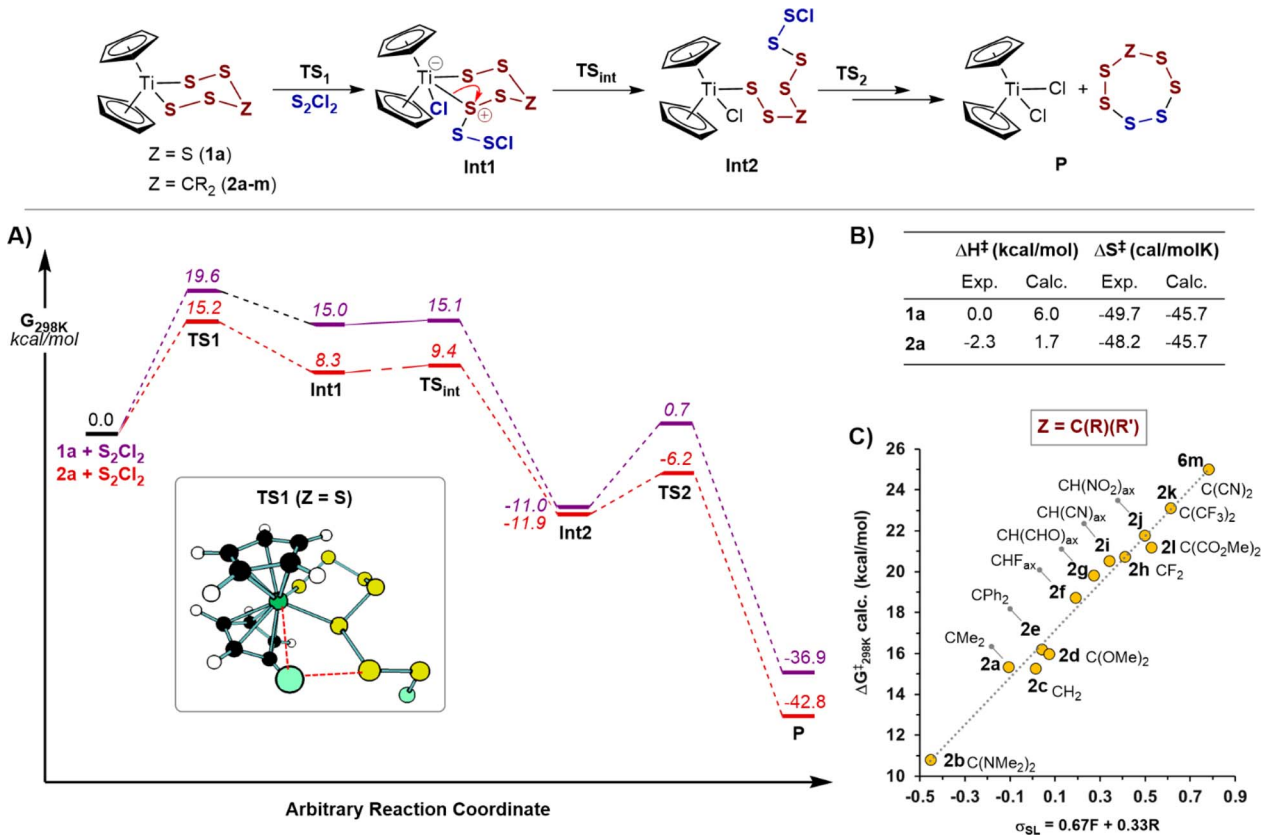


Fig. 5 (A) Computed free energy reaction profile of **1a** and **2a** with S_2Cl_2 including transition state geometry **TS1** for {**1a** + S_2Cl_2}. (B) Comparison of experimental (295 K) and computed values of activation parameters of the rate limiting transition state (TS1) for the reaction of **1a** and **2a** with S_2Cl_2. (C) Virtual reaction of other titanacycles Cp_2TiS_4Z (**2b–m**) with S_2Cl_2: correlation of microkinetic free energy barriers for TS1 against Swain–Lupton substituent constants. Computational calculations performed with: r^{2}SCAN-D4-SMD(CH_2Cl_2)/ma-def2-QZVPP(Ti); ma-def2-TZVPP(C, H, S, Cl, O, N, F)//r^{2}SCAN-3c, T = 298.15 K, p = 1.0 atm, qRRHO cutoff = 50 cm^{-1}, c = 1.0 M.

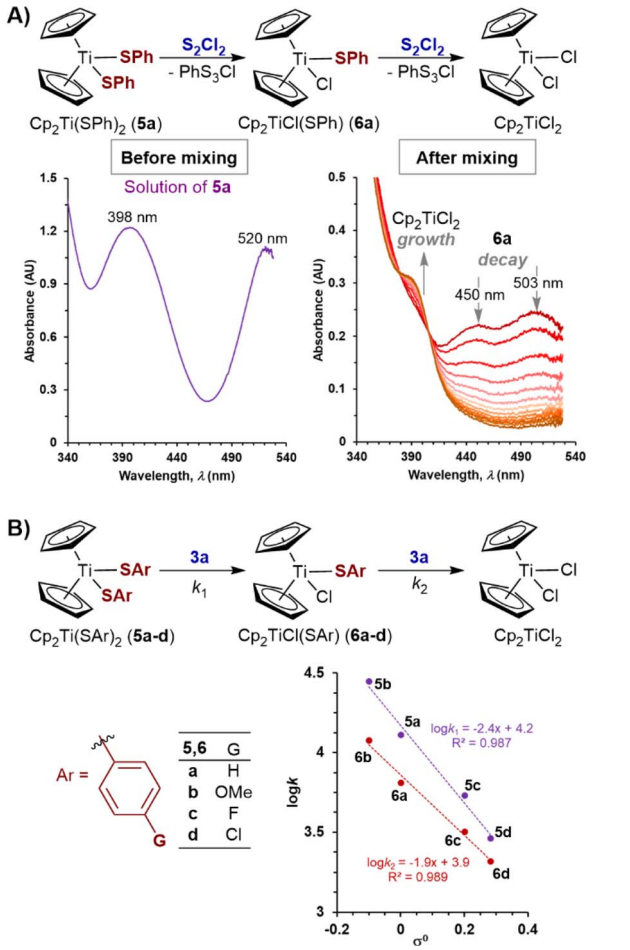


Fig. 6 (A) SF-UV monitoring of the reaction of titanocene bisthiophenolate **5a** with S_2Cl_2 at 22 °C. (B) Yukawa–Tsuno linear free energy correlation for thiophenolates **5a–d** and **6a–d** in reaction with **3a**.

experimental results in that the initial sulfur transfer is rate-limiting, and that titanacycle **2a** is significantly more reactive than **1a**. Sulfur transfer from the titanocene to the sulfur chloride were found to proceed through a four-membered transition state, similar to mechanism IV, but without accompanying dissociation of the Ti–S bond. The transfer initially leads to a coordinatively saturated 18-electron titanium complex (Fig. 5, **Int1**), prior to this opening into a 16-electron polysulfide intermediate (Fig. 5, **Int2**). Other pathways explored computationally (*e.g.* mechanism III) were much less favourable than the process discussed above (see ESI Section S11.3‡), and no appropriate local minimum could be found resulting from the attack of the chlorine atom of S_2Cl_2 at titanium (mechanism I).[7a]

Comparison of the computational activation parameters for the rate controlling barriers with those determined experimentally are shown in Fig. 5B. Considering statistical corrections,[19] the computational predictions are in reasonable agreement with results from experiment. The negligible changes in enthalpy and the large entropy of activation values for the reaction of **1a** ($|\Delta S^{\ddagger}_{exp} - \Delta S^{\ddagger}_{calc}| = 4.0$ cal mol^{-1} K^{-1}) and **2a** ($|\Delta S^{\ddagger}_{exp} - \Delta S^{\ddagger}_{calc}| = 2.5$ cal mol^{-1} K^{-1}) further support a concerted metathesis-like mechanism.[30] These results also reinforce the conclusion that the large entropic barriers are not caused by solvent reorganisation.

The qualitative correlations found for trends in the reactions of other titanocenes (see ESI, Section S11.4‡) prompted us to further investigate the electronic effects caused by replacing the distal sulfur in **1a** with carbon groups (**2a** and analogues **2b–m**, Fig. 5C). The microkinetic free energies of activation correlated well with inductive-weighted Swain–Lupton parameters ($\rho_{SL} = +11.5$; $R^2 = 0.98$),[23,31] with electron-donating groups resulting in lower reaction barriers. That the correlation includes substituents of various sizes, and ground state geometries (**2b**, **2k** and **2l** have a twist-boat like geometry), suggests that steric factors, and other effects such as angle strain, only play a minor role on the relative reaction rates.

Kinetics of the reaction of S_2Cl_2 with titanoncene thiophenolates 5a–d and 6a–d

To expand the study to acyclic titanocene sulfide di-anion surrogates, we analysed the kinetics of the reactions of thiophenolato complexes, $Cp_2Ti(SAr)_2$ (**5a–d**) and $Cp_2TiCl(SAr)$ (**6a–d**) with S_2Cl_2, and with *N*-morpholinosulfenyl chloride **3a**. ^{1}H NMR spectroscopic analysis confirmed that complexes **5a** and **6a** are stable in CH_2Cl_2 solution at room temperature for at least 24 hours in the dark.

Complexes **6a–d** are however sensitive to ambient light, especially **6a** (see ESI Section S8‡), and additional precautions were taken to avoid visible light exposure when preparing and handling their solutions.[32] SF-UV analyses of the reactions of bis(thiophenolato) titanocenes **5a–d** with excess of S_2Cl_2 showed this class of substrate to be exceptionally reactive. Indeed, **5a–d** are converted into **6a–d** within the deadtime (<10 ms) of the measurement method. This is then followed by exponential decay of the monothiolates **6a–d** to Cp_2TiCl_2 (Fig. 6A). The same empirical rate constant (k_2), within experimental error, was independently determined using an isolated sample of **6a**. These features are indicative of a consecutive process for **5a–d**, with the first step being significantly faster than the second ($k_1/k_2 \geq 100$).

The high reactivity of the bis(thiophenolato) titanocenes **5a–d** is consistent with findings of Osakada and Yamamoto on the relatively slow kinetics of transmetallation of PtClMe(COD) with titanocene monothiolate **6a** in THF.[11b] However, in contrast to the second order kinetics observed for the reactions with sulfenyl chlorides studied herein, Osakada and Yamamoto found that monothiolate **6a** undergoes indirect reaction with PtClMe(COD) *via* **5a** generated through reversible disproportionation, resulting in overall third-order kinetics.[11b]

Direct comparison of the empirical rate constants for the reactions of titanacycles **1** and **2** with S_2Cl_2 (Table 1) against the same process for thiolate derivatives **6a–d** is not possible because the sulfenyl chloride co-product (PhS_3Cl) from the latter is highly susceptible to spontaneous desulfuration.[33] This phenomenon results in the observed decay rates of **6a–d** being the net effect of several simultaneous substitution processes. Nevertheless, similarly to titanacycles **1** and **2**, the rates of reaction of **6a** with S_2Cl_2 show a low sensitivity to temperature

($k_{281K} \approx 1.1k_{297K}$). Qualitative assessment of effects of *para*-substitution in the aromatic ring in thiophenolate derivatives **6a–d**, shows that electron-donating groups accelerate the substitution processes.[34]

To make quantitative comparisons, SF-UV analyses of the reactions of **5a–d** with the less reactive *N*-morpholinosulfenyl chloride **3a** were conducted. The spectra showed the distinctive features of a sequential reaction: lack of isosbestic points and initial increase then decay in absorbance. Deconvolution of data showed moderate selectivity of **3a** for the bisthiolate complexes (k_1/k_2 = 1.4 to 2.5),[19] with the greater the electron donating ability of the thiolate, the higher the selectivity. Linear free energy relationships using Hammett substituent constants[23,30] showed moderate curvature (see ESI Section S3.15‡), for both experimental and computational data, despite the known correlation of nucleophilicity parameters for thiolates.[35] Better correlations for both steps (k_1, $\rho = -2.4$; k_2, $\rho = -1.9$) were obtained using the method of Yukawa and Tsuno,[36] (Fig. 6B). Both analyses indicate significant development of positive charge at the nucleophilic Ar–S–Ti sulfur atom during the transition state,[37] consistent with that found in computational analysis of the reaction of S_2Cl_2 with **2a–m** (Fig. 5C).

Conclusions

Using a combination of stopped-flow UV-Vis and stopped-flow NMR techniques, kinetic analyses, numerical modelling, and KS-DFT-computations, we have investigated the reactions of titanocene (poly)sulfides with a variety of sulfenyl chlorides to generate sulfur homocycles (S_n), heterocycles (E_2S_n), and polysulfanes (R_2S_n). Systematic variations in the structure of the reactants, reaction temperature, and solvent polarity have served to kinetically characterise key parameters influencing the phenomenological[19] process rates. Collectively, the study provides data that supports a different mechanism to that previously proposed.[7a] The process has all of the characteristics of a nucleophilic substitution at R–S–Cl by the titanium-bound sulfur, in a concerted, late, and metathesis-like four-membered transition state, in which chloride departure is assisted by the metal (Fig. 5).

Titanocene pentasulfide **1a** is about two orders of magnitude less reactive than the isopropylidene analogue **2a**, and about three orders of magnitude less reactive than monosulfide analogues **5a–d** and **6a–d**, to intermolecular attack of sulfenyl chlorides. In other words, the nucleophilicity of the titanium-bound sulfur is progressively attenuated by the increasing number of concatenated sulfur atoms, with the effect greatest in pentasulfide **1a**. The results also rationalise the challenges in isolating titanocene polysulfido complexes in high yields using monofunctional sulfur chlorides as electrophiles, due to consecutive processes (k_1, k_2) having similar rates. Two key outcomes from these investigations inform practical protocols for sulfur transfer from titanocenes:

(1) The low sensitivity of the process rates to temperature makes cooling useful for the preparation of thermally sensitive organic (poly)sulfides without sacrificing reactivity. Solvent polarity can also be used to tune process rates, and incorporation of alkyl substituents on the titanocenes used to enhance solubility and thus process concentrations without a significant decrease in nucleophilicity.

(2) Titanocene thiolates undergo very rapid reactions with sulfenyl chlorides. They can be stored indefinitely as solids in the dark at −40 °C, are stable in solution for hours, and can generally be handled under air but do require protection from exposure to ambient light. Compared to the mono(thiolato) titanocenes, the bis(thiolates) are easier to access and more stable to visible light, but retain high nucleophilicity, thus making them the more practical sulfur transfer reagents.

Overall, the mechanistic features elucidated can be considered for other nucleophilic substitutions involving transition metal polysulfides, electrophiles or titanocene nucleophiles under non-aqueous conditions.

Data availability

Experimental kinetic data, NMR spectra, UV-Vis spectra, SF-methods, kinetic analyses, computational methodologies, energies, and further discussion and analysis can be found in the ESI.‡ Cartesian coordinates of optimised geometries are available in the OptimisedGeometries.xyz file.

Author contributions

AGD and GCL-J directed the investigation. PHHO and AGD conducted all experimental work, except for the synthesis of **1b–1f** which was carried out by GH. PHHO conducted the computational studies. PHHO, AGD, PJB and GCL-J analysed the data. All authors contributed to the preparation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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