*Journal of Organometallic Chemistry* 161 (1978) 183—195

# KINETICS AND MECHANISM OF INVERSION AT SULPHUR AND OF LIGAND EXCHANGE IN SOME SULPHIDE COMPLEXES OF CHROMIUM AND TUNGSTEN PENTACARBONYL. A CASE OF DIASTEREOMERIC FLUXIONALITY

J.H. EEKHOF, H. HOGEVEEN *, R.M. KELLOGG, * and E. KLEI

*Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)*

(Received May 23rd, 1978)

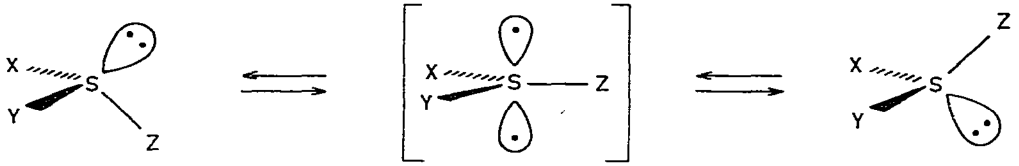
## Summary

The chromium and tungsten pentacarbonyl complexes of 2,5-dihydrothiophene and β-phenethylmethyl sulphide have been prepared. The β-phenethylmethyl sulphide complexes can be shown by $^{13}C$ and $^{1}H$ NMR spectroscopy at —100°C to consist of two diastereomers, consistent with nonplanarity of the sulphur atom. For the case of the β-phenethylmethyl sulphide chromium pentacarbonyl $\Delta H^{\ddagger}$ 10.0 kcal/mol and $\Delta S^{\ddagger}$ 2.4 e.u. as derived from line-broadening experiments. Inversion barriers in other complexes lie in the same range. Mechanisms for the inversion process are considered. Ligand exchange takes place at higher temperatures than those required for line coalescence for the inversion process. The kinetics of this process were investigated for the exchange between the 2,5-dihydrothiophenechromium pentacarbonyl and β-phenethylmethyl sulphide. The kinetic data are interpreted in terms of a rate-determining dissociation of the sulphide ligand from the chromium atom.

---

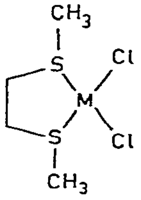
Bivalent sulphur in dialkyl sulphides is readily changed to trivalency by, for example, alkylation to form a sulphonium salt or by oxidation to form a sulphoxide. Two important chemical consequences of such transformations may be emphasized. First, owing to the increased electron deficiency at the sulphur atom, the acidity of carbon-bound protons adjacent to this center is enhanced. Abstraction of such protons by strong bases produces nucleophilic carbon anions used extensively in synthesis [1]. Second, trivalent sulphur atoms, at least in the compounds known to date, are nonplanar. This raises the possibility, among other things, of the generation of chiral species [2]. Trivalent sulphur compounds undergo pyramidal inversion (scheme 1). The barriers rarely exceed 50 kcal/mol [3] and are usually lower. Fairly detailed information is available regarding the

SCHEME 1

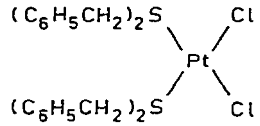


relationship of structure to the height of the inversion barrier [4]. A thorough knowledge of such factors combined with the development of new synthetic techniques has allowed, for example, the transfer of chirality from sulphur to carbon in certain synthetic operations [5].

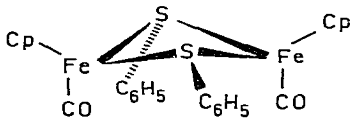
Trivalent sulphur compounds are also obtained readily by complexation of alkyl sulphides with metal carbonyls [6]. Relatively little work has been done with such complexes although attractive synthetic possibilities can be envisaged. In view of the unexploited possibilities, we have initiated a program to study the properties of such compounds. This report deals with the stereochemical aspects and ligand exchange reactions of some chromium and tungsten carbonyl complexes of sulphides. At the beginning of this work the only precedents available to us were the platinum and palladium complexes Ia, Ib [7] and II [8] and the iron complex III [9] (the other geometrical isomers are known but only for III are crystallographic data available). In I—III the sulphur atoms are pyramidal and the heights of the inversional barriers have been measured.



a) M= Pt
(I) b) M= Pd



(II)



(III)

## Results and discussion

### A. *The averaging process*

We chose to examine chromium and tungsten pentacarbonyl complexes of sulphides because the octahedral geometry about the metal atom precludes the complication of pseudorotation found in iron carbonyl complexes [10]. The sulphide ligands chosen were 2,5-dihydrothiophene, used because of the simplicity of its NMR spectrum and its synthetic utility, and $\beta$-phenethylmethyl sulphide, because of its stereochemical properties (see below). The complexes IVa, IVb and Va, Vb were prepared.

At the normal probe temperature (ca. 35°C) the absorptions of the 2,5 protons of IVa, IVb and of the $S$-$CH_3$ protons in Va, Vb were singlets. If the sulphur atom is pyramidal and configurationally stable the 2,5-protons of the dihydrothiophene ring in IVa, IVb should be nonequivalent as in 2,5-dihydrothiophene sulphoxide. This is clearly not the case. Furthermore in various solvents and at various concentrations these protons of IVa, IVb remained equivalent. Consider now Va, Vb. If the sulphur were pyramidal and configurationally stable the $SCH_3$ absorptions (for example) would be expected to consist of two peaks of unequal height corresponding to the two diastereomers produced on generation of a new asymmetric center. There is no indication for the existence of diastereomers in the $^1$H NMR spectra at room temperature. These observations were disconcerting.

Low temperature spectra revealed a pattern more consistent with expectation. The absorption of the ligand 2,5 protons in IVa, IVb broadened and separated into an AB quartet at sufficiently low temperature: similar behaviour is observed for the absorption of the *S*-$CH_3$ protons in Va, Vb, which separated into two peaks of unequal height (Fig. 1). That the latter phenomenon is due to the exis-

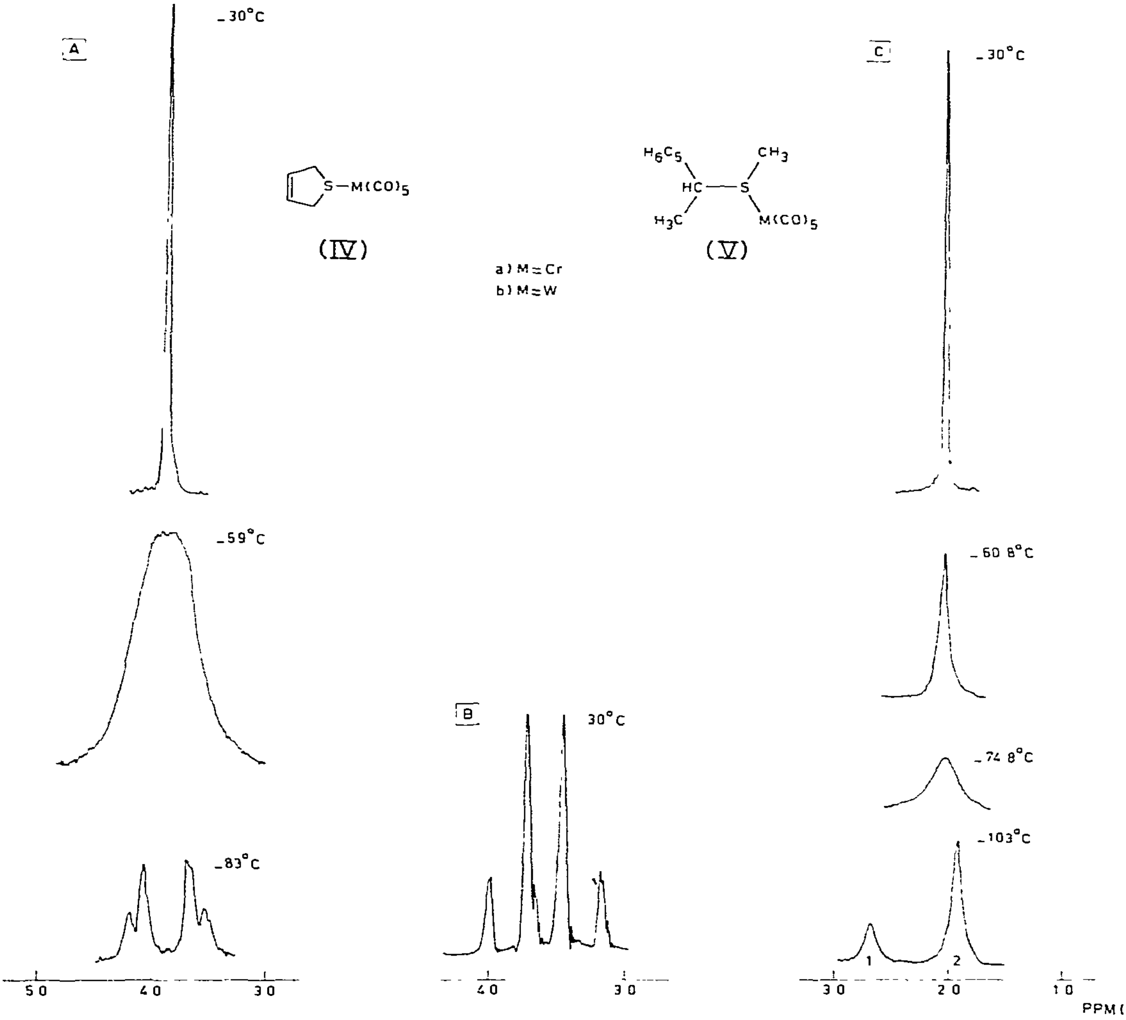
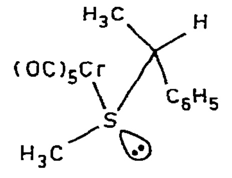


Fig. 1. The $^1$H NMR spectra in the methylene region of IVa (A, in $CS_2$) and 2,5-dihydrothiophene-1-oxide (B, in $CDCl_3$) and of the *S*-$CH_3$ absorptions in Va (C, in $CS_2$).

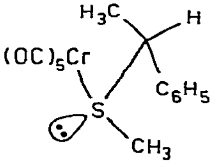
tence of diastereomers Va', Va'' present in a ratio of 62 to 38 is adequately confirmed by the low temperature $^{13}C$ NMR spectrum (Fig. 2). To our knowledge this is the first demonstration of the existence of such diastereomeric complexes.

The $\Delta G^{\ddagger}$ values for the averaging processes in these complexes were calculated from [11]:

$$\Delta G^{\ddagger} = 4.57\, T_c(9.97 + \log T_c A^{-1})$$



(Va')



(Va'')

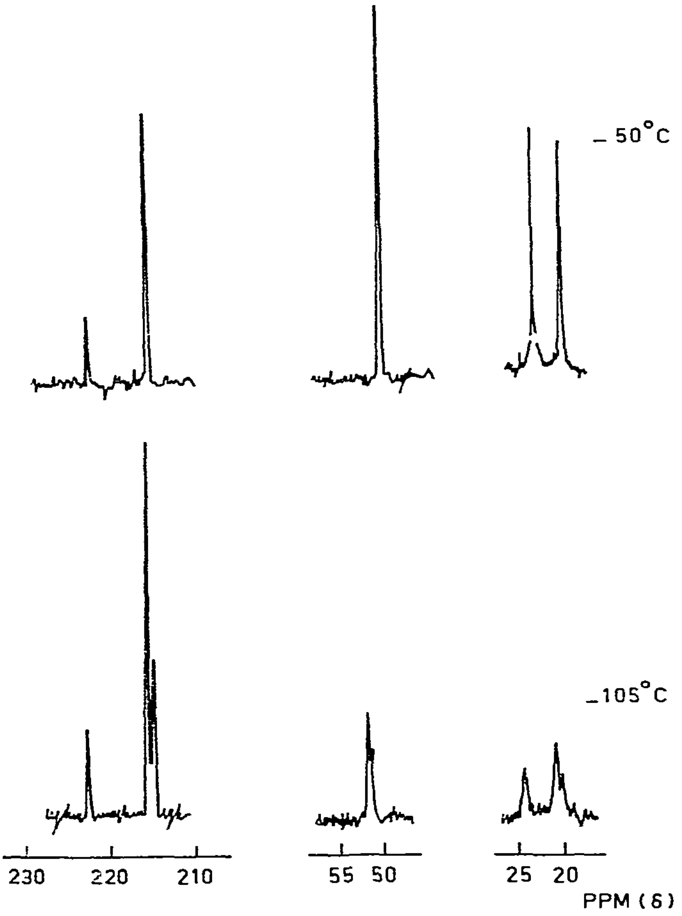


Fig. 2. The diastereomeric forms of Va. Absorptions have not been assigned to specific diastereomers; only one enantiomer of each diastereomer is shown. The $^{13}C$ NMR spectra of Va in $CD_3COCD_3$ (the absorptions of the aromatic carbons have been omitted).

where $T_c$ is the coalescence temperature (in K) and $A$ is the chemical shift difference (in Hz): $A = \delta\nu$ for two singlets as with the $SCH_3$ absorptions in Va, Vb; for the AB quartet of IVa, IVb $A = [(\nu_a - \nu_b)^2 + J_{ab}^2]^{1/2}$. The results are given in Table 1.

The equation used has been derived for the averaging of two processes in a 1/1 ratio. For the β-phenethylmethyl sulphide complex Va the $SCH_3$ peaks are present in a ratio of 38/62 measured from the integration of the different peaks below coalescence temperature. To ensure that the calculation of $\Delta G^{\ddagger}$ for the averaging process in the complexes Va, Vb with the aid of this equation was valid, a more careful study was performed. The line width of the $S$-$CH_3$ signal in Va of both diastereomers was measured at different temperatures in the slow and rapid exchange region. With the formulas for the rapid and slow exchange [11] an Eyring plot was set up (Fig. 3) for both signals 1 and 2 (Fig. 1c) according to:

$$\log k/T = 10.32 - (\Delta H^{\ddagger}/4.57\ T) + (\Delta S^{\ddagger}/4.57)$$

From this plot the following activation parameters were calculated:

$\Delta G_2^{\ddagger} = 9.6 \pm 0.2$ kcal/mol (—60.8°C) $\quad \Delta G_1^{\ddagger} = 9.4 \pm 0.2$ kcal/mol (—60.8°C)
$\Delta H_2^{\ddagger} = 10.0 \pm 0.2$ kcal/mol $\quad \Delta H_1^{\ddagger} = 10.0 \pm 0.2$ kcal/mol
$\Delta S_2^{\ddagger} = 1.7 \pm 2$ e.u. $\quad \Delta S_1^{\ddagger} = 3.0 \pm 2$ e.u.

The rate constants for inversion at —60.8°C are for process 2 → 1 551 $sec^{-1}$ and for process 1 → 2 881 $sec^{-1}$.

A question that must be answered is whether the averaging process being measured by NMR corresponds to pyramidal inversion at sulphur. Elimination of alternative mechanisms is the most profitable line of attack on this problem.

One can begin by considering tunneling. However this is estimated to be of little importance in view of the height of the potential barrier in these complexes [12]. Chemical reactions such as occur in allyl sulphoxides [13] and/or rotational isomerism [14] are also essentially ruled out, since the quantitative data for IVa, IVb, Va, Vb indicate that the inversional barrier is independent of the presence and position of unsaturation in the organic ligand.

A possible explanation of the averaging process is bimolecular exchange [15] (scheme 2), although the entropy of activation of near zero for Va would argue

TABLE 1

COALESCENCE TEMPERATURES AND FREE ENTHALPIES OF ACTIVATION FOR THE AVERAGING PROCESS IN IV, Va AND Vb

| Formula | $T_c$ | $\Delta\nu$ [a] | $\Delta G^{\ddagger}(T_c)$ [b] | solvent | $J_{ab}$ [a] |
|---|---|---|---|---|---|
| $(C_4H_6S)\ Cr(CO)_5$ | —59 | 48 | 10.3 | $C_3D_6O/CS_2$ | 14 |
| $(C_4H_6S)\ W(CO)_5$ | —49 | 30 | 10.9 | $C_3D_6O$ | 14 |
| $(H_5C_6CHCH_3SCH_3)$ [c] $Cr(CO)_5$ | —76 | 38 | 9.6 | $CS_2$ | |
| $(H_5C_6CHCH_3SCH_3)$ [c] $W(CO)_5$ | —76.5 | 27 | 6.7 | $CS_2$ | |

[a] In Hz. [b] The free enthalpy of activation at coalescence temperature in kcal/mol. [c] For the purpose of calculation the diastereomeric complexes are assumed to be present in a 1/1 ratio (see text).

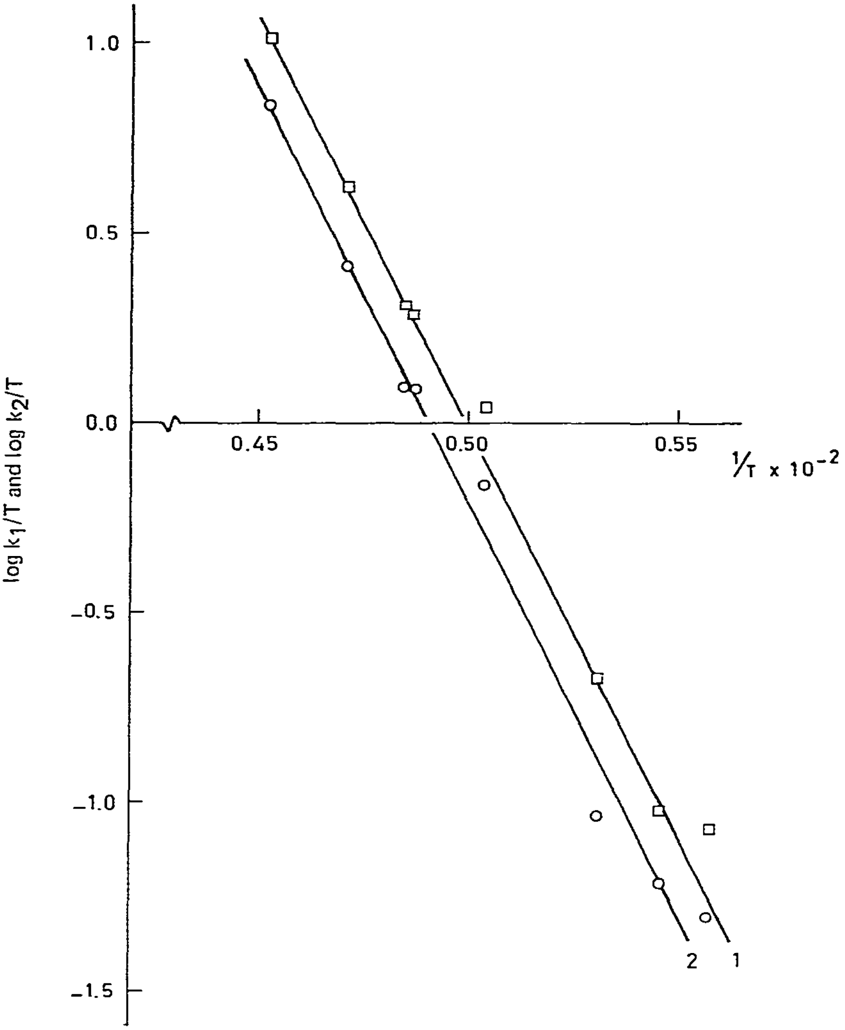
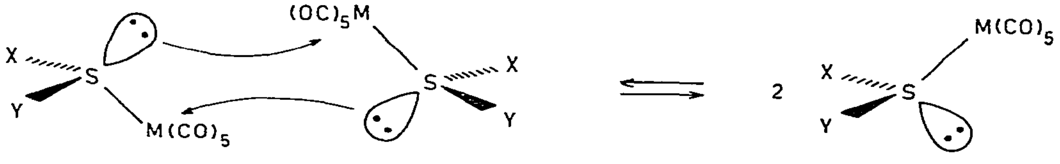


Fig. 3. Eyring plot of the line-broadening experiments of absorptions 1 and 2 (Fig. 1c) of β-phenethylmethyl sulphide chromium pentacarbonyl (Va).

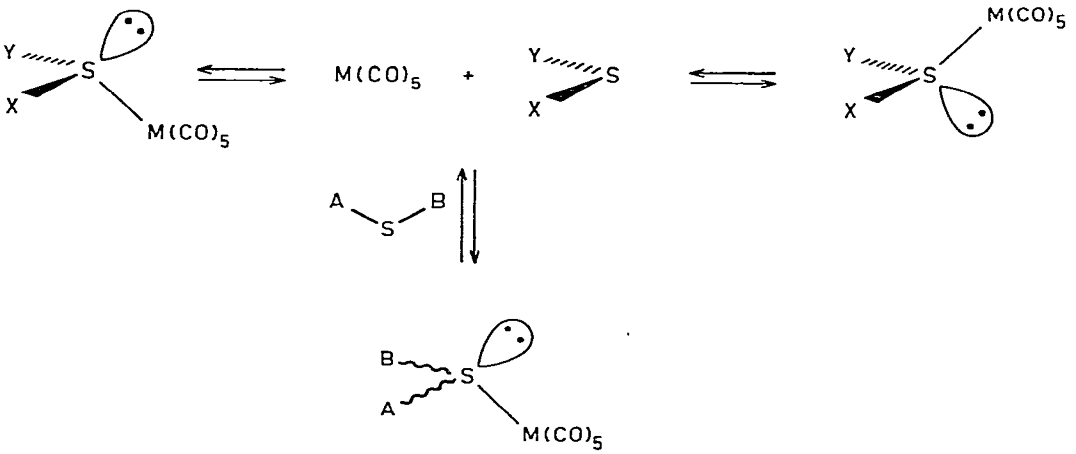
more for an unimolecular process. However the coalescence temperature for the averaging process was not changed within experimental error on doubling or halving the concentration of the complex, which is inconsistent with the bimolecular mechanism implied by scheme 2.

SCHEME 2



Dissociation-recombination (scheme 3) represents another possible mechanism to explain the averaging process. If such is the case trapping of the coordinatively unsaturated metal pentacarbonyl moiety should be possible. On adding β-phenethylmethyl sulphide to IVa at room temperature in $CS_2$, there was indeed observed ligand exchange. This exchange reaction was, however, strongly inhibited by lowering the reaction temperature. At about —50°C (that is 10 degrees above the coalescence temperature) no exchange could be detected in a period of more than 2 h. A similar reaction was also performed with 2,5-dihydrothiophenechromium pentacarbonyl and tetrahydrothiophene; again (at —50°C over a period of more than 2 h) there was no detectable exchange. At —59°C the rate of averaging process for IVa is 106 $s^{-1}$. Hence the low temperature averaging process is unimolecular and unrelated to the ligand exchange at higher temperatures (see below).

SCHEME 3



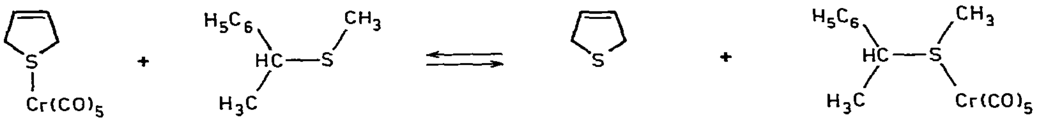
The low temperature averaging process must therefore correspond to an unimolecular change whereby the configuration at pyramidal sulphur inverts. We emphasize, however, that this need not correspond to pyramidal inversion at sulphur, such as occurs in, for example, aliphatic sulphoxides (barrier ranges typically 35—43 kcal/mol [3a,b]) or aliphatic sulphonium salts (barrier ranges typically 25—29 kcal/mol [3c]). Increasing the electronegativity of a substituent on a heteroatom, specifically in the case of phosphines, leads to a raising of the inversion barrier [16]. The chromium tricarbonyl substituent is known to be electron-withdrawing [17] and the same is apparently true for chromium pentacarbonyl [18]. On these a priori grounds one could anticipate that at least for chromium complexes, the inversion barriers would be higher than for aliphatic sulphonium ions. This line of argument clearly leads to an incorrect conclusion. The inversion barriers are at least 15 kcal/mol lower than for aliphatic sulphonium ions. Although the data base is limited, low barriers (<18 kcal/mol) for pyramidal inversion have been found in all palladium, platinum, chromium, and tungsten carbonyl complexes studied to date. For the platinum sulphide complex II, Haake and Turley [19] using related arguments suggested that metal *d*-orbitals are in some way involved. It appears also to us that true sulphur pyramidal inversion is probably not involved. In view of the apparent generality of the lowering of the barrier by metals, a detailed theoretical investigation of this problem could be rewarding *.

### B. *The exchange reaction*

The ligand exchange reactions of octahedral metal carbonyls are of great interest [22] because of their relationship to compounds important in industrial processes. From kinetic studies of various exchange reactions, both associative [23,24] and dissociative [25] mechanisms have been proposed. In the case of chromium complexes, Strohmeier and coworkers studied the exchange reactions between complexed and isotopically labelled uncomplexed ligands. Benzene [26,27] and cycloheptatrienechromium tricarbonyls [28] were used. These reactions are thermal processes with a half life of several hours at high temperatures (100—160°C). The exchange reactions we observed are much faster, with half lives of 10—15 min at room temperature.

We investigated in more detail the exchange depicted in scheme 4. By integrating in the ${}^1$H NMR spectrum the appearance of the S-$CH_3$ absorption of $\beta$-phenethylmethyl sulphide chromium pentacarbonyl (Va) and the disappearance of the same absorption of the free ligand VII the exchange reaction was followed in $CS_2$ at 20°C. Although we were aware that exchange reactions being studied did not completely fulfil the conditions Harris [29] has defined for an isotopic exchange reaction with a non-negligible isotopic effect, we calculated the order of our exchange reaction from the equation:

SCHEME 4



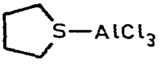
(IVa) (VII) (VI) (Va)

$$R = \frac{-2.303 \cdot [\mathrm{IVa}]_{t=0} \cdot [\mathrm{VII}]_{t=0}}{t([\mathrm{IVa}]_{t=0} + [\mathrm{VII}]_{t=0})} \log(1 - x_t/x_\infty)$$

where $R$ is the gross rate of exchange which may be any function of [IVa] and [VII], $x_t$ and $x_\infty$ are the rates of exchange from VII to Va at $t = t$ and $t = \infty$

---

* Comparison of the geometry about sulphur in a chromium pentacarbonyl complex (available from X-ray structural determination) [6b] with that in sulphonium ions [20] revealed no abnormal flattening of the sulphur atom. In an attempt to assess the importance of possible metal $d$-orbital participation we prepared the thiolane-$AlCl_3$ [21] adduct (VIII), m.p. 31.5°C. (2,5-Dihydrothiophene could not be used because it polymerized in the presence of the strong Lewis acid.) The room temperature ${}^1$H-NMR spectra definitely appear to agree with rapid (on the ${}^1$H NMR time scale) inversion at sulphur. However, owing to technical difficulties we were unable to lower the temperature sufficiently to obtain the expected separation of the methylene protons $\alpha$ to the sulphur atom.

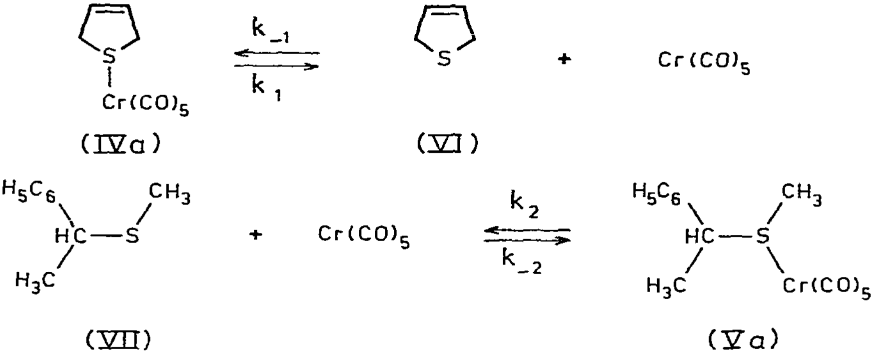


(VIII)

(equilibrium after more than ten half lives). From the graph $\log(1 - x_t/x_\infty)$ vs. $t$ the gross rate of exchange $R$ can be calculated. Experimental results are given in Table 2. The gross rate of exchange $R$ is a function of the concentrations of the starting components: $R = k[\text{IVa}]^m\,[\text{VII}]^n$. The reaction orders $m$ and $n$ were calculated from this equation, and found to be 1 and 0, respectively. For these values a margin of error of 15% was taken as an approximation of experimental errors in integration, etc.

This kinetic result can be explained by a dissociative mechanism as shown in scheme 5. The dissociation rate constant $k_1$ in this reaction is calculated to be $1.3 \times 10^{-4}\ \text{s}^{-1}$ at 20°C.

SCHEME 5



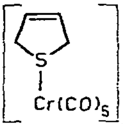
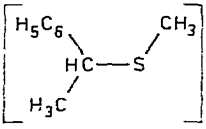
The theoretical rate expression for scheme 5 with the steady state approximation for $Cr(CO)_5$ is:

$$\frac{d[\text{Va}]}{dt} = k_{-2}[\text{VII}]\,\frac{k_2[\text{Va}] + k_1[\text{IVa}]}{k_{-2}[\text{VII}] + k_{-1}[\text{VI}]} - k_2[\text{Va}]$$

In the beginning of the reaction [VII] >> [VI]; the association rate constants

TABLE 2

THE OVERALL RATE OF EXCHANGE $R$ AS A FUNCTION OF THE CONCENTRATIONS OF STARTING COMPONENTS IN $CS_2$ AT 20°C

|  (mol/l) |  (mol/l) | $10^4 \times R$ (mol/l) | $X_\infty$ (in %) |
|---|---|---|---|
| 0.50 | 0.25 | 0.60 | 50.9 |
| 0.375 | 0.25 | 0.44 | 46.8 |
| 0.25 | 0.25 | 0.37 | 35.1 |
| 0.25 | 0.313 | 0.37 | 33.6 |
| 0.25 | 0.375 | 0.34 | 31.4 |

($k_{-1}$ and $k_{-2}$) are very large and of comparable magnitude. Since the amount of consumed IVa with time is equal to the concentration of formed Va (an experimental confirmation of the steady state approximation), for the beginning of the reaction a first order rate expression is obtained:

$$-\frac{\mathrm{d}[\mathrm{IVa}]}{[\mathrm{IVa}]} = k_1 \mathrm{d}t$$

For the overall reaction, the kinetic equation becomes extremely complicated and cannot be treated readily. A study of the initial rates of conversion ($-d[\mathrm{IVa}]/\mathrm{d}t$ as a function of [IVa]) revealed that the reaction is first order in the concentration of IVa within experimental error (fault limit 15%). Various concentrations of added VII did not influence the rate. The rate constant $k_1$ was calculated to be $1.6 \times 10^{-4}\ \mathrm{s}^{-1}$ at 20°C.

Thus the rate of the exchange reaction (scheme 4), derived not only by use of the formula for isotopic exchange but also with that based on the initial rate of conversion, was found to depend only on the concentration of starting complex IVa, and the values for the dissociation constants obtained by both methods are in fairly good agreement with each other ($1.3 \times 10^{-4}$ vs. $1.6 \times 10^{-4}\ \mathrm{s}^{-1}$). It is possible that the coordinatively unsaturated species $Cr(CO)_5$ could be stabilized by solvents possessing free electron pairs like $CS_2$, acetone, or ether [30] (the exchange experiments were carried out in $CS_2$). This would be in agreement with the enhanced stability of these types of complexes in these solvents compared with solvents like pentane. The observed first-order kinetics may therefore be pseudo-first order kinetics involving solvent.

## General conclusions

The sulphur atoms in sulphide complexes of chromium and tungsten pentacarbonyl are demonstrably pyramidal but the barriers to inversion of configuration of sulphur are remarkably low. The exact mechanism by which inversion of configuration occurs is difficult to ascertain.

The ligands are not strongly bound, and exchange between complexed sulphide ligand and free ligand occurs readily at room temperature. A dissociative mechanism, strongly reminiscent of that involved in $S_N1$ solvolysis of carbon compounds, is clearly involved.

## Experimental

Melting points were determined on a Mettler FP 2 melting point apparatus equipped with a Mettler FP 52 microscope. Microanalyses were performed in the Microanalytical Department of this laboratory by Mr. H. Draayer, Mr. J. Ebels, Mr. A.F. Hamminga, Mr. J. Hommes, Mr. A. Meetsma and Mr. J.E. Vos. NMR spectra were recorded on a Varian A-60 D or a Perkin—Elmer R-24 B spectrometer, with use of acetone-$d_6$ as the solvent (unless otherwise indicated) and TMS ($\delta = 0$) as an internal reference. A Varian XL-100 was used for the carbon-13 and 100 MHz proton line-broadening spectra. These spectra were recorded by and discussed with Ir. P.B.J. Driessen and Dr. H. Hiemstra. The kinetic experiments were performed on a JEOL C-60 HL spectrometer equipped with variable temperature probes. Infrared spectra were recorded on a Perkin—Elmer 257, a Perkin—Elmer 125 or a Hitachi EPI-G spectrophotometer. Mass spectra were obtained on an AEI-902 by Mr. A. Kiewiet.

The irradiations were carried out with an S81 quartz lamp under dry nitrogen. Commercial chromium hexacarbonyl and tungsten hexacarbonyl were used without purification. The starting materials, 2,5-dihydrothiophene [31] and β-phenethylmethyl sulphide [32] were prepared by known procedures.

The solvents used were purified by distillation from $P_2O_5$ and stored over sodium wire.

### *2,5-Dihydrothiophene $Cr(CO)_5$ (IVa)*

499 mg (5.8 mmol) of 2,5-dihydrothiophene and 1298 mg (5.9 mmol) of $Cr(CO)_6$ in 110 ml of benzene were irradiated at room temperature for 16 h. After filtration and evaporation of the solvent a yellow oil was obtained, and this was purified by short path distillation at 35°C/0.15 mmHg. The yellow oil (m.p. 16.5—17.5°C) was obtained in 984 mg (3.54 mmol, 61% yield). $^1H$ NMR (35°C): $\delta$ 6.01 (s, 2 H, vinyl) and 3.94 ppm (s, 4 H, $CH_2$). $^{13}C$ NMR (—6.5°C): $\delta$ 222.0 (s, ax CO), 215.3 (s, eq. CO), 128.2 (d, vinyl C, $J$ 169 Hz) and 49.4 ppm (t, $CH_2$, $J$ 146 Hz). IR (KBr): 3065, 2930, 2850, 2070, 1990, 1920 (vs br), 1635, 1115, 1026, 964, 920, 670, 664, 648, 548, 444 $cm^{-1}$. Mass spectrum: $M^+$ 278 with successive losses of 5 carbonyl fragments. Analysis: Found: C, 38.94; H, 2.26; Cr, 18.49; S, 11.21. $C_9H_6O_5CrS$ calcd.: C, 38.86; H, 2.17; Cr, 18.69; S, 11.52%.

### *β-Phenethylmethyl sulphide $Cr(CO)_5$ (Va)*

304 mg (2 mmol) of β-phenethylmethyl sulphide and 550 mg (2.5 mmol) of $Cr(CO)_6$ were irradiated in 100 ml of benzene for 23 h. After filtration and evaporation of the solvent the yellow oil obtained was purified by crystallization at —40°C from pentane. The yield was 189 mg (0.55 mmol, 27.5%). $^1H$ NMR (35°C): $\delta$ 7.52—7.16 (m, 5 H, phenyl), 4.03 (q, 1 H, $J$ 7 Hz, CH), 2.14 (s, 3 H. $S$-$CH_3$) and 1.68 ppm (d, 3 H, $J$ 7 Hz, $C$-$CH_3$). $^{13}C$ NMR (35°C): $\delta$ 221.4 (s, CO, ax), 215.3 (s, CO, eq), 141.0 (s, C of the phenyl group), 129.6, 129.0 and 128.5 (d, phenyl carbons, $J$ 162 Hz), 52.7 (d, CH, $J$ 144 Hz), 23.7 (q, S—$CH_3$, J = 144 Hz) and 20.7 ppm (q, C—$CH_3$, $J$ 132 Hz). $^{13}C$ NMR (—100°C): $\delta$ 222.0 (ax. CO), 215.3 and 214.9 (eq. CO's; in a ratio of 67/33), 141.2 (C of the phenyl group), 129.4, 129.0, 128.6, 128.4, 127.9 (phenyl carbons), 51.7 and 51.5 (CH), 24.3 and 20.0 ppm (S—$CH_3$) and 20.6 (C—$CH_3$). IR (neat): 3022, 2970, 2924, 2065, 1900—1960 (br), 1595, 1488, 1445 $cm^{-1}$. Mass spectrum: $M^+$ 344 with successive losses of 5 carbonyl fragments. The $m/e$ value for $C_{14}H_{12}O_5CrS$ was found to be 343.983 (calcd. 343.980).

### *2,5-Dihydrothiophene $W(CO)_5$ (IVb)*

258 mg (3 mmol) of 2,5-dihydrothiophene and 1162 (3.3 mmol) of $W(CO)_6$ were irradiated in 110 ml of benzene for 16 h. After filtration and evaporation of the solvent the residue was sublimed at room temperature. $W(CO)_6$ was obtained as the first fraction. At a temperature of 40—45°C/0.005 mmHg a yellow-green complex was obtained in 652 mg (1.59 mmol, 53% yield); melting point 54.5—54.6°C. $^1H$ NMR (35°C): $\delta$ 6.02 (s, 2 H, =CH) and 4.19 ppm (s, 4 H, $CH_2$). $^{13}C$ NMR (—40°C): $\delta$ 201.1 (s, ax CO), 197.9 (s, eq CO), 128.1 (d, vinyl C,

*J* 173 Hz) and 52.2 ppm (t, $CH_2$ *J* 146 Hz). IR (KBr): 2960, 2935, 2860, 2075, 1985, 1940—1840 (vs, br), 1635, 1122, 1002, 965, 696, 663, 595, 574 $cm^{-1}$. Mass spectrum: $M^+$ 410 with successive losses of 5 carbonyl fragments. Analysis: Found: C, 26.34; H, 1.50; S, 7.60. $C_9H_6O_5$ SW calcd.: C, 26.37; H, 1.48; S, 7.82%.

*β-Phenethylmethyl sulphide W(CO)$_5$ (Vb)*

304 mg (2 mmol) of β-phenethylmethyl sulphide and 880 mg (2.5 mmol) of $W(CO)_6$ were irradiated in 100 ml of benzene for 16.5 h. After filtration and evaporation of the solvent the green oil obtained was purified by recrystallization at —40°C from pentane. The yield was 343 mg (0.72 mmol, 35.7%). $^1H$ NMR (35°C): δ 7.50—7.18 (m, 5 H, phenyl group), 4.20 (q, 1 H, CH, *J* 7 Hz), 2.49 (s, 3 H, *S*-$CH_3$), 1.69 (d, 3 H, *C*-$CH_3$, *J* 7 Hz). $^{13}C$ NMR ($CS_2$, —10°C): δ 199.2 (s, ax CO), 197.3 (s, eq CO), 139.7 (s, C of the phenyl group), 129.6, 129.2 and 127.8 (d, phenyl carbons, *J* 162 Hz), δ 55.4 (d, CH, *J* 138 Hz), 27.0 (q, $SCH_3$, *J* 150 Hz) and 21.2 ppm (q, $CCH_3$, *J* 138 Hz). IR (neat): 3020, 2970, 2918, 2070, 1870—1950 (br), 1595, 1488, 1445, 1425 $cm^{-1}$. Mass spectrum: $M^+$ 476 with successive losses of 5 carbonyl fragments. Analysis: Found: C, 35.72; H, 2.60; S, 6.62. $C_{14}H_{12}O_5SW$ calcd.: C, 35.32; H, 2.54; S, 6.73%.

*Kinetic measurements*

Solutions of 2,5-dihydrothiophene chromium pentacarbonyl (IVa) of the appropriate concentrations in $CS_2$ were prepared in NMR tubes. At a temperature of 0°C, variable amounts of β-phenethylmethyl sulphide (VII) were added; the tube was then immediately placed in the probe maintained at 20°C. Integration of the *S*-methyl protons of β-phenethylmethyl sulphide chromium pentacarbonyl (Va) and its free ligand (VII) was performed at appropriate time intervals. The way the physical values are calculated is indicated in the text.

## Acknowledgement

This investigation was supported in the form of a fellowship to J.H.E. provided by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Science (Z.W.O.).

## References

1 B.M. Trost and L.S. Melvin, Jr., Sulfur Ylides, Academic Press, Inc., New York, San Francisco, London, 1975.

2 M. Axelrod, P. Bickart, J. Jacobus, M.M. Green and K. Mislow, J. Amer. Chem. Soc., 90 (1968) 4835.

3 (a) D.R. Rayner, E.G. Miller, P. Bickart, A.J. Gordon and K. Mislow, J. Amer. Chem. Soc., 88 (1966) 3138; (b) C.R. Johnson and D.C. Vegh, J. Chem. Soc. Chem. Commun., (1969) 557; (c) D. Darwish, S.H. Hui and R. Tomilson, J. Amer. Chem. Soc., 90 (1968) 5631; (d) D.M. Roush and C.H. Heatcock, ibid., 99 (1977) 2337.

4 J.B. Lambert, Pyramidal Atomic Inversion, in N.L. Allinger and E.L. Eliel (Eds.), Topics in Stereochemistry, Vol. 6, Wiley-Interscience, New York, 1971, p. 19.

5 C.A. Maryanoff, K.S. Hayes and K. Mislow, J. Amer. Chem. Soc., 99 (1977) 4412.

6 (a) M. Dekker, G. Knox and C.G. Robertson, J. Organometal. Chem., 18 (1969) 161; (b) H.G. Raubenheimer, J.C.A. Boeyens and S. Lotz, ibid., 112 (1976) 145.

7 E.W. Abel, R.P. Bush, F.J. Hopton, and C.R. Jenkins, J. Chem. Soc. Chem. Commun., (1966) 58.

8 P. Haake and P.C. Turley, J. Amer. Chem. Soc., 89 (1967) 4611.

9 G. Ferguson, C. Hannaway and K.M.S. Islam, J. Chem. Soc. Chem. Commun., (1968) 1165.

10 R.K. Sheline and H. Mahnke, Angew. Chem. Int. Ed. Engl., 14 (1975) 314.

11 (a) H. Günther, NMR-spektroskopie, Georg Thieme Verlag, Stuttgart, 1973; (b) J.A. Pople, W.G. Schneider and H.J. Bernstein, High-resolution Nuclear Magnetic Resonance, McGraw Hill Book Co., New York, 1959.

12 (a) J.F. Kincaid and F.C. Henriques, Jr., J. Amer. Chem. Soc., 62 (1940) 1474; (b) R.S. Berry, J. Chem. Phys., 32 (1960) 933.

13 R. Tang and K. Mislow, J. Amer. Chem. Soc., 92 (1970) 2100.

14 J.B. Lambert and S.I. Featherman, Chem. Rev. 75 (1975) 611.

15 B. Fontal and H. Goldwhite, Tetrahedron, 22 (1966) 3275.

16 K. Mislow, Trans. N.Y. Acad. Sci., 35 (1973) 227.

17 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551.

18 C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 533.

19 P.C. Turley and P. Haake, J. Amer. Chem. Soc., 89 (1967) 4617.

20 A. Lopez-Castro and M.R. Truter, Acta Cryst., 17 (1964) 465.

21 R.L. Richards and A. Thompson, J. Chem. Soc. A, (1967) 1248.

22 G.R. Dobson, Accounts Chem. Res., 9 (1976) 300.

23 L.D. Cook and K.Y. Wan, Can. J. Chem., 49 (1971) 3315.

24 T. Yoshida and S. Otsuka, J. Amer. Chem. Soc., 99 (1977) 2134.

25 (a) R. Good and A.E. Merbach, Inorg. Chem., 14, 1030 (1975). *b* L.S. Frankel, Inorg. Chem., 10, 814 (1971).

26 W. Strohmeier and D. von Hobe, Z. Naturforschg. B, 18 (1963) 981.

27 W. Strohmeier and H. Mittnacht, Z. Phys. Chem. N.F., 29 (1961) 339.

28 W. Strohmeier and H. Mittnacht, Z. Phys. Chem. N.F., 34 (1962) 82.

29 G.M. Harris, Trans. Faraday Soc., 47 (1951) 716.

30 M. Herberhold, Z. Naturforschg. B, 31 (1976) 1489.

31 (a) S.F. Birch and D.T. McAllan, J. Chem. Soc., (1951) 2556; (b) R.C. Krug and D.E. Boswell, Int. J. Heterocyclic Chem., 4, (1967) 309.

32 (a) H. Rupe and W. Tomi, Chem. Ber., 47 (1914) 3064. (b) S. Siegel and A.F. Graefe, J. Amer. Chem. Soc., 75 (1953) 4521; (c) G.G. Urquhart, J.W. Gates and R. Conner, Org. Synth., 21 (1941) 36.