# Displacement of Organic Sulphides by Amines in *trans*-Dichlorobis(organic sulphide)palladium(II) Complexes

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The kinetics of nucleophilic displacement of a variety of organic sulphides RSR′ from complexes of the type *trans*-[Pd(RSR′)$_2$Cl$_2$] by amines of different basicity and steric hindrance have been measured in 1,2-dimethoxyethane at 25 °C. The overall reaction occurs in two separate stages, the first being much faster than the second. The investigated processes correspond to the reaction: *trans*-[Pd(RSR′)$_2$Cl$_2$] + amine $\longrightarrow$ *trans*-[Pd(RSR′)(amine)Cl$_2$] + RSR′ (amine = pyridine or substituted pyridine). The nucleophilic substitutions obey the usual two-term rate equation. The rate of the reactions, the discrimination of one complex against the individual entering amines, and the lability of the individual sulphides when they are displaced by a given amine are compared and discussed.

THE lability of organic sulphides co-ordinated to $d^8$ transition-metal ions (planar four-co-ordinate complexes) has been mainly investigated in platinum(II) derivatives.[1] Palladium(II) complexes are known to be more reactive than the corresponding platinum(II) species and for this reason previous studies have dealt only with relatively inert chelating [2-4] or sterically hindered sulphides.[5] The presently available techniques for studying fast reactions (stopped flow) allow us to investigate systems (1) in 1,2-dimethoxyethane at 25 °C (amine = pyridine or substituted pyridine).

$$trans\text{-}[\mathrm{Pd(RSR')_2Cl_2}] + \text{amine} \longrightarrow trans\text{-}[\mathrm{Pd(RSR')(amine)Cl_2}] + \mathrm{RSR'} \quad (1)$$

## EXPERIMENTAL

*Materials.*—The sulphides were pure commercial samples. Standard methods were used for the purification of the

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[1] L. Cattalini, G. Marangoni, S. Degetto, and M. Brunelli, *Inorg. Chem.*, 1971, **10**, 1545.

[2] M. Martelli, G. Marangoni, and L. Cattalini, *Gazzetta*, 1968, **98**, 1031.

[3] L. Cattalini, G. Marangoni, J. S. Coe, M. Vidali, and M. Martelli, *J. Chem. Soc. (A)*, 1971, 593.

[4] L. Cattalini, M. Martelli, and G. Marangoni, *Inorg. Chim. Acta*, 1968, **2**, 405.

[5] G. Marangoni, M. Martelli, and L. Cattalini, *Gazzetta*, 1968, **98**, 1038.

amines. The solvent, 1,2-dimethoxyethane, was distilled over sodium before use. Disodium tetrachloropalladate(II) and the complexes *trans*-[Pd(RSR′)$_2$Cl$_2$] were obtained by following the procedures reported in the literature.[6-8] Analytical data are in Table 1.

*Kinetics.*—Preliminary measurements were made with an Optica CF4R double-beam recording spectrophotometer in the near-u.v. region of the spectrum. By mixing a solution containing one of the palladium(II) complexes in 1,2-dimethoxyethane with a solution of the amine in the same solvent at the appropriate concentration, directly in the thermostatted cells of the instrument, one can observe a fast reaction leading to the formation of an intermediate species. A second slower stage occurs, and the final spectra correspond to those of the *trans*-[Pd(amine)$_2$Cl$_2$] complexes. The rate of the first stage was measured with a Durrum–Gibson stopped-flow instrument at 330 nm in the same solvent at 25 °C. The kinetic runs were carried out under pseudo-first-order conditions, in the presence of an excess of amine. The first-order rate constants are summarized in Supplementary Publication No. SUP 22138 (4 pp.).* No variations in the rate constants were observed on recording the optical-density changes at different wavelengths.

TABLE 1

Analytical data (%) for the complexes *trans*-[Pd(RSR′)$_2$Cl$_2$]

| | C | | H | | S | | Cl | |
|---|---|---|---|---|---|---|---|---|
| RSR′ | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. |
| R = Ph, R′ = Me | 39.4 | 39.5 | 3.8 | 3.75 | 14.6 | 15.05 | 16.3 | 16.65 |
| R = R′ = PhCH$_2$ | 55.6 | 55.5 | 4.6 | 4.60 | 10.6 | 10.6 | 11.6 | 11.7 |
| R = Me, R′ = Pr$^i$ | 26.6 | 26.85 | 5.4 | 5.60 | 17.6 | 17.95 | 19.6 | 19.85 |
| R = Et, R′ = Me | 21.9 | 21.85 | 4.9 | 4.85 | 19.2 | 19.45 | 21.2 | 21.5 |
| R = R′ = Et | 26.6 | 26.85 | 5.7 | 5.60 | 17.2 | 17.95 | 19.4 | 19.85 |
| R = R′ = Ph | 52.0 | 52.4 | 3.2 | 3.65 | 11.5 | 11.65 | 12.9 | 12.9 |

TABLE 2

Second-order rate constants, $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$, for reaction (1) in 1,2-dimethoxyethane at 25 °C

| Amine | p$K_a$ [b] | R = Ph R′ = Me (−0.6) [c] | R = R′ = PhCH$_2$ (−0.43) | R = Me R′ = Pr$^i$ (+0.19) | R = Et R′ = Me (+0.1) | R = R′ = Et (+0.2) | R = R′ = Ph (−1.2) | R = R′ = Pr$^i$ [a] (+0.38) |
|---|---|---|---|---|---|---|---|---|
| 2,4-Dimethylpyridine | 6.99 | | 27.3 | 5.62 | 5.92 | 3.5 | 1.41 | 0.59 |
| 3,4-Dimethylpyridine | 6.44 | 23 290 | 2 700 | 457 | 405 | 377 | 122 | |
| 3,5-Dimethylpyridine | 6.34 | | 2 280 | 336 | 338 | 241 | 100 | 100 |
| 2-Methylpyridine | 6.10 | 109 | 16.4 | 1.69 | 2.09 | 1.23 | 0.54 | 0.43 |
| 4-Methylpyridine | 6.02 | 22 370 | 1 880 | 444 | 393 | 306 | 100 | |
| Pyridine | 5.17 | | 1 530 | 261 | 269 | 210 | 69.2 | 74 |
| 3-Chloropyridine | 2.84 | 6 475 | | 102 | 118 | 85.8 | 52.6 | 31.5 |
| 4-Cyanopyridine | 1.90 | | 485 | 91.7 | 88.8 | 81.3 | 42.8 | 26 |
| 3-Cyanopyridine | 1.38 | 4 770 | 417 | 63.8 | 55.5 | 51.1 | 31.8 | 20 |

[a] Values from ref. 5. [b] Relative to the acid Ham$^+$ in water. [c] Values in parentheses are the sum of the Taft σ* values, −Σσ*, relative to the inductive effects of the radical R and R′ in RSR′.

## RESULTS AND DISCUSSION

The observation that the overall reaction (2) occurs in

$$trans\text{-}[Pd(RSR')_2Cl_2] + 2\ amine \longrightarrow trans\text{-}[Pd(amine)_2Cl_2] + 2\ RSR' \quad (2)$$

two separate stages, the first being much faster than the second, is strong evidence of the fact that the investigated processes correspond to reaction (1). This is confirmed also by the spectra of the transient intermediates which correspond closely to those observed on studying the reverse reaction [9] (3).

$$trans\text{-}[Pd(amine)_2Cl_2] + RSR' \longrightarrow trans\text{-}[Pd(RSR')(amine)Cl_2] + amine \quad (3)$$

The greater lability of the first displaced sulphide can be reasonably explained as a consequence of the larger *trans*-labilizing effect of sulphides compared to amino-groups. Moreover, since it is known that in square-planar substitution the *trans*-labilizing effect usually parallels the nucleophilicity, it should be noted that, as a rule, sulphides are by far better nucleophiles than amines towards complexes of Pt$^{II}$, Pd$^{II}$, and Au$^{III}$.[10] On plotting the values of $k_{obs.}$ against the concentration of the entering nucleophile a straight line was obtained, indicating that the processes investigated obey the rate equation $k_{obs.} = k_2$[amine], corresponding to that expected for nucleophilic substitution at square-planar complexes, *i.e.* $k_{obs.} = k_1 + k_2$[amine], but with a negligible contribution of the $k_1$ term. Values of $k_2$ were calculated with the least-squares method from the data in SUP 22138 and are summarized in Table 2.

The data in Table 2 can be discussed in two ways, *i.e.* either by examining (*i*) the discrimination of one complex against the individual entering amines, or (*ii*) the different labilities of the individual sulphides when the complexes react with a given amine.

In order to discuss the discriminating ability we refer

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[6] G. B. Kauffmann and J. H. Tsai, *Inorg. Synth.*, 1966, **8**, 236.

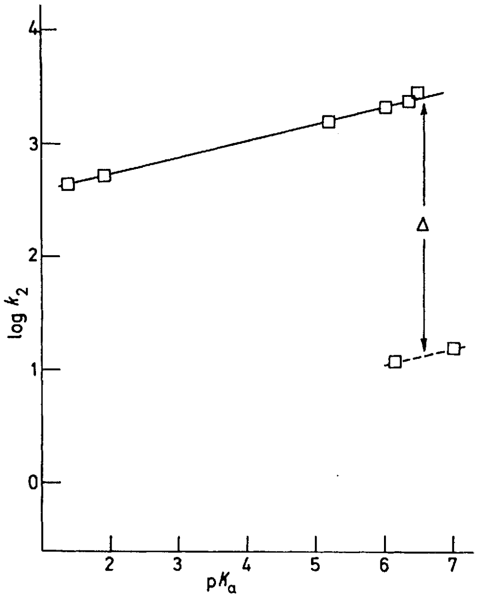
[7] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1935, 1558.

[8] 'Gmelins Handbuch der Anorganischen Chemie,' 1957, N.68, Teil D.

[9] L. Cattalini, G. Marangoni, and M. Martelli, *Inorg. Chem.*, 1968, **7**, 1495.

[10] L. Cattalini, 'Inorganic Reaction Mechanisms,' ed. J. O. Edwards, Wiley, New York, 1971.

to diagrams of the type in the Figure where values of log $k_2$ are plotted against the p$K_a$ of the amine. It is known that, for heterocyclic amines having no (or the same amount of) steric hindrance and different basicity, a free-energy relation of the general type log $k_2 = \alpha(\mathrm{p}K) +$ constant exists in a number of cases and in various solvents,[10] the parameter α being a measure of the ability of the substrates to discriminate against the individual amines, *i.e.* a measure of the sensitivity of the system with respect to proton basicity. It is also known that one can change the steric hindrance of the entering substituted pyridines by using 2-methylpyridine and its derivatives. The values of Δ, obtained as in the Figure, are a measure of the kinetic retardation due to steric hindrance in these bimolecular processes. Values of α and Δ measured during this work are in Table 3. These data, which also include values obtained from the literature (for the complex with R = R′ = Pr$^i$), clearly show that the values of both α and Δ remain fairly constant (*ca.* 0.16 and 2.15 respectively) for a group of five complexes. This seems to suggest that bond formation between the palladium atom and the entering amine is sensibly constant on changing the nature of the sulphides which are at the same time leaving groups and *trans* partners. Independence of the bond-making and -breaking aspects of the substitution is common in platinum(II) complexes and this also seems to be true in this case. In the case of R = R′ = Pr$^i$ the relatively small value of α (0.132), and large value of Δ (2.35), seem to reflect a relatively large steric hindrance of the substrate. In the case of R = R′ = Ph the same could be true, even though the relatively small value of α (0.1) is accompanied by a value of Δ = 2.



Free-energy relation between the reactivity of *trans*-[Pd(SPh$_2$)$_2$Cl$_2$] and the basicity of the entering amine

TABLE 3

Nucleophilic-discrimination factors (α) and steric-retardation parameters (Δ) for reaction (1) in 1,2-dimethoxyethane at 25 °C

| R,R′ | α | Δ [a] |
|---|---|---|
| R = R′ = Ph | 0.1 | 2 |
| R = R′ = Et | 0.16 | 2.1 |
| R = Et, R′ = Me | 0.15 | 2.1 |
| R = Pr$^i$, R′ = Me | 0.17 | 2.2 |
| R = R′ = PhCH$_2$ | 0.16 | 2.2 |
| R = Ph, R′ = Me | 0.15 | 2.2 |
| R = R′ = Pr$^i$ | 0.132 [b] | 2.35 [b] |

[a] Evaluated graphically (as indicated in the Figure in the case of R = R′ = Ph) and are therefore approximate. [b] From ref. 5.

As far as the relative lability is concerned, we observe that, apart from these two cases, there is a regular decrease in reactivity on increasing the values of the σ* constants [11,12] for R and therefore the donor ability of the sulphur atom. These features clearly indicate that the lability decreases as the bond strength increases, suggesting a role of the bond-breaking aspects in these bimolecular substitutions; however, we also point out that in these cases there is no linear free-energy relation between log $k_2$ and $-\Sigma\sigma^*$, so that the above observation simply indicates a general trend.

The cases in which R = R′ = Ph and Pr$^i$ show that the reactivity is much lower than that expected on the basis of comparison with the other systems investigated. This can be easily explained by considering the essential role of steric hindrance. Thus, it seems reasonable that, whereas the S–Pd–Cl angles are expected to remain approximately the same (90°) in the initial and transition states, the increase in the co-ordination number from four to five on forming the activated complex would give rise to an overcrowded situation and therefore to an extra destabilization of the transition state.

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