

A Kinetic and Mechanistic Study of the Oxidative Addition of Diaryl Ditellurides to *trans*-Carbonylchlorobis(triphenylphosphine)iridium(I) in Toluene

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The oxidative addition of diaryl ditellurides to $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ in toluene solution has been followed by visible spectrophotometry. The reaction is first order in the concentration of each reagent. An e.s.r. signal can be detected from the reacting solution. An i.r. spectroscopic study of the reaction in carbon tetrachloride shows the relatively rapid formation of an adduct before the final stages of the process occur. Rate constants and activation parameters for four different ditellurides have been determined. These parameters vary widely with the substituents on the aryl rings of the ditellurides. A mechanism is suggested which involves the initial addition of ditelluride to iridium(I), followed by homolytic cleavage of the Te-Te bond and formation of the final *trans* product.

We recently published a study of the oxidation of a diaryl ditelluride by molecular iodine.¹ This paper deals with the same family of tellurium reagents, but now it is their oxidative addition to transition-metal complexes that concerns us. In exploratory studies we considered the three best known complexes which undergo oxidative addition; namely the d^7 pentacyanocobaltate(II) ion,² the square-planar d^8 complex $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ commonly called Vaska's compound,³ and the d^{10} complex tetrakis(triphenylphosphine)platinum(0).⁴ Oxidative additions to these different transition-metal reagents exhibit differing mechanistic requirements, and so a range of investigations might have offered information about the reactivity of the Te-Te bond in ditellurides. In the event we only studied the addition to Vaska's compound. The literature already contains a report of a kinetic study of the oxidative addition of diaryl disulphides to this compound⁵ and so our ability to study the reaction of a tellurium analogue was not surprising.

The most convenient ditelluride with which to work is bis(*p*-ethoxyphenyl) ditelluride. Throughout this paper we will represent this as RTeTeR or R_2Te_2 .

Results

Since ditellurides are insoluble in water, it is necessary to work in mixed-solvent systems when studying their reactions with most ionic reagents. In order to study the reaction with the $[\text{Co}(\text{CN})_5]^{3-}$ ion we worked in aqueous methanol. A methanolic solution of R_2Te_2 was added to a solution of the olive green cobalt(II) complex in aqueous methanol^{6,7} under an inert atmosphere. No precipitation occurred upon mixing when the proportions of water and methanol were chosen to give a final ratio of 1 : 3. Under such circumstances the peak at 967 nm, due to the pentacyanocobaltate ion, disappears rapidly. This is true even when the concentration of the ditelluride is considerably less than that of the cobalt complex. The appearance of a peak at 380 nm accompanies this process. King and Winfield⁷ assigned this peak to $[\text{Co}(\text{CN})_4(\text{OH})]^{3-}$ or $[\text{Co}(\text{CN})_4(\text{OH}_2)]^{2-}$. We were unable to isolate, purify, and characterise completely the cobalt-containing product from such a reaction mixture; but we were able to show that a solid material isolated after reaction contained cobalt but not tellurium. As a result of these findings we decided not to pursue this topic further.

The possibility of investigating oxidative addition to d^{10} platinum(0) was dismissed even more quickly. We could find no easily detectable property which could be monitored to

show the extent of reaction between equimolar quantities of R_2Te_2 and tetrakis(triphenylphosphine)platinum(0) in dry toluene under nitrogen, even after continuous stirring for 1 d.

Vaska's compound offers an advantage over the complexes mentioned above due to its solubility properties. A single, pure solvent can be used, rather than a mixed solvent. We chose to work in dry toluene. When the reagents were present at suitable concentrations for a spectrophotometer to be used to follow the course of the reaction, we found that the reaction required several hours to reach completion at normal temperatures. Most of our experiments were carried out using bis(*p*-ethoxyphenyl) ditelluride. Both this compound and Vaska's compound have minima in their u.v.-visible spectra around 360 nm. Their product exhibits a saddle point, rather than a minimum, in this region. The greatest increase in optical density on passing from reagents to product occurred at 364 nm, and so we followed the reaction at this wavelength.

The variation of optical density with time shows the reaction to be first order in the concentration of each of the two reagents [equation (1)]. Equation (1) holds for all the second-

$$d[\text{Product}]/dt = k_{\text{obs}}[\text{IrCl}(\text{CO})(\text{PPh}_3)_2][\text{R}_2\text{Te}_2] \quad (1)$$

order concentration conditions used (including the case when both reagents are at equal concentrations) for the full period of observation, usually to more than 75% completion of reaction. In Tables 1 and 2 we summarise the values of the observed rate constants, and the activation parameters subsequently computed for the reactions of the various ditellurides are quoted in Table 3.

In addition to studying the reactions by monitoring visible spectral changes, we briefly investigated the changes occurring in the carbonyl-stretching region of the i.r. spectrum for reaction mixtures containing R_2Te_2 . The most convenient experimental conditions for this technique were equimolar quantities of reagents, but at higher concentrations than those used in the spectrophotometric work, and in carbon tetrachloride as solvent rather than the toluene used for the kinetic studies. Vaska's compound shows $\nu(\text{CO})$ at 1959 cm^{-1} . By the time that the reagent solutions had been mixed together at room temperature and the reaction mixture inserted into the i.r. solution cell, the carbonyl band was seen to have shifted to 2065 cm^{-1} . Its intensity had also slightly decreased. A new band at 2080 cm^{-1} subsequently appeared in the spectrum while that at 2065 cm^{-1} declined. Eventually the band at 2080 cm^{-1} becomes dominant and exhibits a shoulder at 2065 cm^{-1} . These changes are illustrated in Figure 1. The product of reaction, prepared and isolated separately, has an

Table 1. Rate data for the reaction between *trans*-[IrCl(CO)(PPh₃)₂] and R₂Te₂ at 50 °C, followed at 364 nm in dry toluene

10 ⁴ [R ₂ Te ₂]	10 ⁴ [IrCl(CO)(PPh ₃) ₂]		
mol dm ⁻³		10 ⁵ <i>k'</i> _{obs.} */s ⁻¹	<i>k</i> _{obs.*/dm³} mol ⁻¹ s ⁻¹
5.00	5.00		0.516
2.50	5.00	1.29	0.515
1.50	4.50	1.50	0.500
1.00	4.00	1.64	0.547
1.00	5.00	2.04	0.510

* *k'*_{obs.} is the composite constant derived from the integrated form of equation (1), i.e. *k*_{obs.*/{[IrCl(CO)(PPh₃)₂]₀ - [R₂Te₂]₀}}.

Table 2. Second-order rate constants, *k*/dm³ mol⁻¹ s⁻¹, for the reactions between ditellurides (*p*-XC₆H₄Te)₂ and Vaska's compound in dry toluene

θ _c /°C	X			
	C ₂ H ₅ O	CH ₃	Cl	H
60.0				1.30
55.0		0.708		1.02
50.0	0.518	0.325		0.508
45.0	0.482	0.208	0.462	0.275
40.0	0.438	0.118	0.428	0.177
35.0	0.397	0.0705	0.320	0.108
30.0	0.363		0.295	
25.0	0.317		0.238	

Table 3. Activation parameters for some oxidative additions to *trans*-[IrCl(CO)(PPh₃)₂]

Additive	Solvent	Δ <i>H</i> [‡] /kJ mol ⁻¹	Δ <i>S</i> [‡] /J K ⁻¹ mol ⁻¹	Ref.
(<i>p</i> -CH ₃ C ₆ H ₄ Te) ₂	Toluene	94 ± 6	+36 ± 2	<i>a</i>
(C ₆ H ₅ Te) ₂	Toluene	87 ± 4	+18 ± 1	<i>a</i>
(<i>p</i> -ClC ₆ H ₄ Te) ₂	Toluene	24 ± 3	-175 ± 20	<i>a</i>
(<i>p</i> -C ₂ H ₅ OC ₆ H ₄ Te) ₂	Toluene	13 ± 0.5	-210 ± 10	<i>a</i>
Various R'SSR'' ^b	Toluene	<i>ca.</i> 70	<i>ca.</i> -80	5
Various R'SH ^b	Benzene	<i>ca.</i> 40	<i>ca.</i> -125	14
CH ₃ I	Benzene	23	-210	9
H ₂	Benzene	45	-96	9
O ₂	Benzene	55	-88	9

^a This work. ^b R'' = 2,4-dinitrophenyl, while R' represents various *p*-substituted phenyl groups.

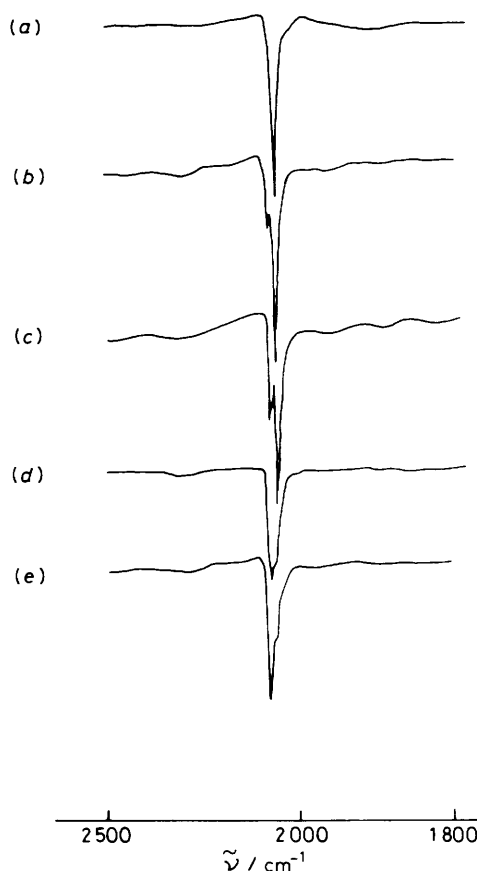
i.r. spectrum indistinguishable from the final spectrum shown in the Figure.

Elemental analytical data obtained from this product, which melts at 70 °C, are consistent with the formula IrCl(TeR)₂(CO)(PPh₃)₂. The ¹H and ¹³C n.m.r. spectra of a solution in deuteriochloroform are complicated, but clearly show the presence of both phenyl and ethoxy-substituted phenyl groups. The ³¹P spectrum shows only a singlet, as does Vaska's compound, but the product's signal is shifted by 99.8 p.p.m. relative to that reagent. The ¹²⁵Te spectrum also shows only one peak, δ = 453.6 ± 1 p.p.m. relative to an external Te(CH₃)₂ reference. This is virtually identical to the signal for the ditelluride reagent, δ = 456 p.p.m.

One final observation is that a very broad e.s.r. signal can be detected for solutions which have not reached completion of reaction.

Discussion

First we consider the nature of the reaction product. Lam and Senoff⁵ reported that the addition of unsymmetrical disul-

**Figure 1.** The variation in i.r. spectrum with time exhibited by an equimolar mixture of [IrCl(CO)(PPh₃)₂] and R₂Te₂ in carbon tetrachloride at room temperature. Times after mixing are 1 (a), 20 (b), 60 (c), 120 (d), and 240 min (e)

phides to Vaska's compound resulted in the formation of dimeric products containing Ir and P in a 1 : 1 ratio. An equivalent formulation would be inconsistent with our analytical data. The products obtained by us are most reasonably formulated as six-co-ordinate iridium(III) complexes with two triphenylphosphine ligands per iridium. According to the ³¹P n.m.r. spectrum, both phosphine ligands are equivalent. Similarly, the ¹²⁵Te spectrum shows the presence of only one type of tellurium nucleus, but one which is indistinguishable from the parent ditelluride reagent. This is a surprising result even though this spectrum was recorded elsewhere, under different conditions from those employed for the other n.m.r. studies.

The 70 °C melting point observed for our product is below that of the parent ditelluride,⁸ 107–108 °C. If heating the compound to this temperature range caused decomposition back to the original reagents such a melting point would be reasonable. It therefore seems likely that the product of the oxidative addition of diaryl ditellurides to Vaska's compound readily reverts to its constituent reagents, under suitable conditions. In Figure 2 we show three feasible structures for a monomeric product.

The observed shift in ν(CO) on changing from Vaska's compound to the final product is very much in line with similar observations reported elsewhere.^{9,10} The unusual feature of our i.r. measurements is the evidence for the rapid formation of an intermediate in carbon tetrachloride. That intermediate has ν(CO) at a very similar frequency to those shown by related six-co-ordinate iridium(III) species.

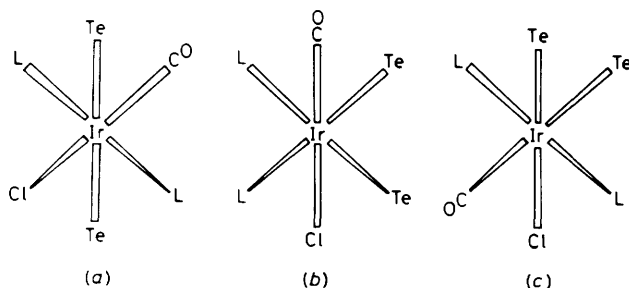


Figure 2. Possible structures for the final product; L = PPh₃

There are suggestions in the literature that ditellurides can add to elemental mercury¹¹ and to copper(I)^{12,13} without breaking the Te-Te bond. The first, but non-discrete, stage in many proposed mechanisms for oxidative addition is a similar addition.^{5,14} We propose such an initial distinct step here. Two alternative descriptions of this step are possible. It could be simply an 'addition' reaction producing six-coordinate Ir^I with bonds to two Te^I atoms; or it could be an 'oxidative addition' yielding Ir^{III} and two donor tellurium(II) ligands. Although precedent indicates the second alternative, since shifts in $\nu(\text{CO})$ to the region of 2050 cm⁻¹ have been associated with the formation of iridium(III) products,^{9,10} we incline to the view that the first step is an 'addition' and not an 'oxidative-addition' reaction.

The rapidly achieved equilibrium in which the four-coordinate iridium(I) reagent is converted into the six-coordinate intermediate, as evidenced by i.r. spectroscopy, is essentially complete under the prevailing conditions, as shown by the disappearance of the bands at 1955 cm⁻¹. The same equilibrium probably plays a part in the kinetic scheme followed by our reaction solutions. At lower concentrations and in a different solvent the degree of completion of reaction may be much less. Certainly, the equilibrium must lie over to the left in order to yield the observed rate equation.

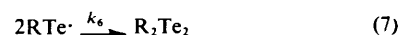
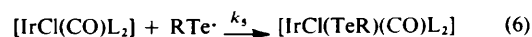
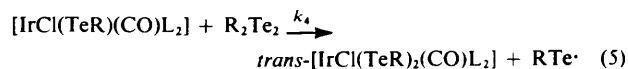
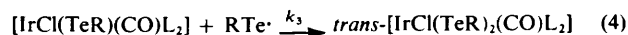
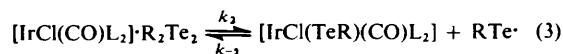
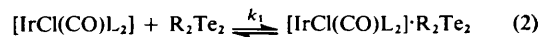
The activation parameters corresponding to the observed rate constants for the addition of various ditellurides are quoted in Table 3, together with selected comparison data from the literature. The most obvious feature is the wide range of activation parameters produced by changing the substituents on the aryl groups of the ditelluride reagent. This is in pronounced contrast to the almost invariant entropy and enthalpy of activation for the oxidative addition of asymmetrical disulphides and substituted benzenethiols.^{5,14} Senoff and co-workers deduce that those reactions do not include the dissociation of the S-H and S-S bonds as distinguishable steps, but rather pass through a three-centre transition state. The added bond is then believed to break giving a *cis* configuration for the first product. The reactions described here seem likely to follow a different pathway. The markedly different patterns of activation parameters in the two instances are most easily explained if changes in the degree of solvation during the steps following the initial equilibrium are very dependent on the aryl group attached to the tellurium.

We have observed an e.s.r. signal during the course of reaction, and have noted elsewhere¹⁵ that tellurium-containing radicals produce very broad e.s.r. signals. Therefore, we presume that some aryltellurium radicals occur during the course of reaction, probably having a place in the main reaction sequence.

Taken together, these speculations indicate that the reaction sequence involves the homolytic cleavage of the relatively weak Te-Te bond. If this were followed by the formation of a *cis* product, one might expect its formation to be sufficiently

rapid to preclude the observation of an e.s.r. signal. Therefore, we conclude that the most likely product is that shown in Figure 2(a).

The Scheme shows the proposed overall process. When the



Scheme. L = PPh₃

initial adduct of a square-planar iridium(I) complex and a ditelluride molecule breaks up to yield a five-coordinate iridium(II) complex and an aryltellurium radical the product pair will be held together within a solvent cage. If escape from such a cage is unlikely, reactions (5)–(7) can be neglected. Then, if equilibrium (2) lies in favour of the reagents, and the steady-state assumption can be applied to the RTe· radical and to the five-coordinate complex, an overall second-order rate equation (8) will occur.

$$k_{\text{obs.}} = K_1 k_2 k_3 / (k_{-2} + k_3) \quad (8)$$

Should it be possible for the products of step (3) to separate, steps (5)–(7) must also be considered. We take the simpler form shown in equation (8) as a basis on which to argue. Similar conclusions are reached when the full Scheme is discussed, as long as reaction (7) is unimportant. The observed rate constant depends on the ratio of k_3 to k_{-2} , which measures the likelihood that the radical pair can move, relative to each other, within their solvent cage. Therefore, one should expect it to show marked changes as the substituents on the aryl groups vary. That variation will be superimposed upon the substituent's influence on k_2 , the rate constant for homolytic cleavage of the Te-Te bond. Table 3 shows that wide variations in activation parameters are observed here.

In summary, we deduce that the oxidative addition of the weak Te-Te bond involves its homolytic cleavage and the transient appearance of an aryltellurium radical. It may well be that elements from the lower reaches of the Periodic Table frequently undergo reaction *via* radical processes.

Experimental

The preparation of diphenyl ditelluride and bis(*p*-ethoxyphenyl) ditelluride have already been reported.¹ The other related compounds were prepared in exactly analogous fashion and gave the expected melting points and analytical results. *trans*-Carbonylchlorobis(triphenylphosphine)iridium(I),⁴ tetrakis(triphenylphosphine)platinum(0),¹⁶ solutions containing pentacyanocobaltate(II),¹⁷ and pure solvents¹⁸ were prepared by literature methods.

Carbonylchlorobis(P-ethoxyphenyltelluro)bis(triphenylphosphine)iridium(III).—The new compound was prepared by adding Vaska's compound (7.79 g) with continuous stirring to

a solution of the ditelluride (4.96 g) in dry toluene (150 cm³) in a flask shielded from all incident light. The mixture was then gently heated and stirred for 2 h under an inert atmosphere. The bulk of the solvent was then distilled off under reduced pressure. A light brown solid precipitated, which was filtered off, washed with dry toluene, and dried under vacuum, m.p. 70 °C (Found: C, 49.1; H, 3.9; Cl, 4.4; P, 6.5; Te, 20.2. C₅₃H₄₈ClIrO₃P₂Te₂ requires C, 49.8; H, 3.8; Cl, 2.8; P, 4.9; Te, 20.0%).

Physical measurements were made using a Pye Unicam SP8-100 spectrophotometer for u.v.-visible measurements, a Perkin-Elmer 225 spectrometer for i.r. studies, a JEOL JES-PE-1 for e.s.r., and a JEOL FX-90Q for ¹H, ¹³C, and ³¹P n.m.r. spectra.

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