KINETICS OF SUBSTITUTION REACTIONS OF DIACIDODICYCLOPENTADIENYLTITANIUM(IV) COMPOUNDS IN ACETONE*

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The kinetics of the halide substitution reaction (eqn. 1) of $(C_5H_5)_2TiBr_2$ with various chlorides were first examined by Jensen and Basolo[1].

$$(C_5H_5)_2TiX_2 + 2Y^- \longrightarrow (C_5H_5)_2TiY_2 + 2X^- \qquad (1)$$

Subsequently, Jensen[2] has made a detailed investigation of the reactions of $(C_5H_5)_2$-$TiBr_2$ and $(C_5H_5)_2Ti(SCN)_2$ with LiCl and LiSCN in acetone. In the earlier report, different rate laws were found for different sources of chloride. When the chloride was introduced as benzyldimethyloctadecylammonium chloride, the reaction was nearly first order in chloride. With LiCl the reaction was found to be nearly zero order in chloride; with $(CH_3)_4NCl$ the reaction was found to be approximately one-half order in chloride. In his later paper, Jensen assumed that the lithium halide reactions with the complex in acetone could be resolved into a first order and a second order process. The observed reactions were pseudo first order (first order in complex) and the LiCl dependence was treated in terms of eqn. (2).

$$k_{observed} = k_1 + k_2[LiCl^-] \qquad (2)$$

Plotting $k_{observed}$ against concentration of LiCl, the intercept is taken as k_1 and the slope as k_2. Jensen devoted most of his discussion of the reaction mechanism to interpretation of k_1 and largely ignored k_2 since it was fairly small. At the time, we had completed a series of similar experiments using tetraphenylarsonium salts as sources of the entering anion. In these experiments, k_1 was much smaller than Jensen's value and k_2 was much larger. We had been tempted to essay a mechanistic analysis of k_2 and ignore k_1. The most obvious difference between the procedure followed by Jensen[3] and our own was that we were at greater pains to exclude water from the solvent. We have now examined the dependence of k_1 and k_2 on the water content of the acetone using both types of salts and have studied the substitution reactions using a wider variety of halides so that the dependence of the reaction rate on the nature of the entering group is elucidated.

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RESULTS

Reactions in "dry" acetone

The experiments reported in this section were carried out with an excess of the salt of the entering anion (pseudo first-order conditions). The complex concentration was typically 2–3 × 10^{-2} *M* and the salt concentration 2 × 10^{-3} *M* to 1.0 × 10^{-2} *M*. In general, good first order plots were obtained for the overall conversion $(C_5H_5)_2TiX_2$ to $(C_5H_5)_2TiY_2$. Presumably, the first step is rate-determining. In the following sub-sections, general characteristics of the reactions of the various complexes under these conditions are described. (1) *$(C_6H_5)_2TiBr_2$*. This complex reacted with LiCl and $(C_6H_5)_4AsCl$ to give $(C_6H_5)_2TiCl_2$ in a reaction that was kinetically first order in bromo complex, went to completion, and yielded the same rate constant from absorbance data at the wavelength of the peak in the spectrum associated with $(C_6H_5)_2TiCl_2$ and at the $(C_6H_5)_2TiBr_2$ wavelength of maximum absorbance. The reactions of $(C_6H_5)_2$-$TiBr_2$ with $(C_6H_5)_4AsSCN$ and tetra-*n*-butylammonium thiocyanate were similar. The reaction with $(C_6H_5)_4AsN_3$ also went to completion but was too fast to measure; only a lower limit for the reaction rate can be assigned. (2) *$(C_6H_5)_2TiCl_2$*. This compound also reacted rapidly with $(C_6H_5)_4AsN_3$ to give $(C_6H_5)_2Ti(N_3)_2$. The reaction with tetraphenylarsonium bromide proceeds slowly to an equilibrium position with the main titanium species still $(C_6H_5)_2TiCl_2$. The reaction with $(C_6H_5)_4AsSCN$ goes to completion only at the highest of the thiocyanate concentrations studied. Kinetic data were obtained for the reaction going to completion and for the first 20% of reaction at lower thiocyanate concentration (using a theoretically calculated infinity time absorbance). (3) *$(C_6H_5)_2Ti(SCN)_2$*. This complex reacted with $(C_6H_5)_4AsCl$ to give $(C_6H_5)_2TiCl_2$ in a reaction kinetically first order in complex.

TABLE 1

KINETICS OF THE REACTION $(C_5H_5)_2TiX_2 + 2MY \rightarrow (C_5H_5)_2TiY_2 + 2MX$ IN "DRY" ACETONE AT 25.0°

$(C_5H_5)_2TiX_2$	*MY*	k_1 (*min^{-1}*)	k_2 (*$M^{-1} min^{-1}$*)
$(C_5H_5)_2TiBr_2$	LiCl	3.4 × 10^{-2}	2.66
	$(C_6H_5)_4AsCl$	6 × 10^{-2}	289
	$(C_6H_5)_4AsSCN$	4 × 10^{-2}	176
	$(n\text{-}C_4H_9)_4NSCN$	3 × 10^{-2}	167
	$(C_6H_5)_4AsN_3$	—	> 4000
$(C_5H_5)_2TiCl_2$	$(C_6H_5)_4AsSCN$	small	85.7[a]
	$(C_6H_5)_4AsN_3$	—	> 4000
$(C_5H_5)_2Ti(SCN)_2$	$(C_6H_5)_4AsCl$	2 × 10^{-2}	80.9

[a] This constant obtained from data taken at 29°.

In Table 1, the values of k_1 and k_2 [see eqn. (2)] obtained in the "dry" acetone studies are listed. A "nucleophilicity" order for tetraphenylarsonium salts attacking dicyclopentadienyltitanium(IV) centers emerges from the k_2 values as $N_3^- > Cl^- \sim SCN^-$ ($> Br^-$?) where the sign, >, signifies a rate difference of a factor of 10 or more. It is more difficult to see a pattern in the changes in k_2 that follow changes in the leaving (X) group. Apparently, k_2 is *less sensitive* to the nature of the leaving group. The variations in k_1 are probably not significant. The values are determined from small and uncertain intercepts. Note that k_2 is much smaller for LiCl than for $(C_6H_5)_4AsCl$. In acetone, both species are probably extensively associated and are, therefore, quite different reactants, not merely different sources of chloride.

The role of water

Experiments on the reaction of $(C_6H_5)_2TiBr_2$ with LiCl and $(C_6H_5)_4AsCl$ were carried out in "wet" acetone up to 2 % by volume H_2O. Fig. 1 shows plots of pseudo first order rate constant *vs.* $(C_6H_5)_4AsCl$ concentration at the various water concentrations. Fig. 2 shows analogous curves for the LiCl system. There is marked curvature in some of the LiCl dependence plots. The system LiCl–water–acetone probably has quite complicated aggregation equilibria. Despite the complications revealed in Fig. 2, the intercepts obtained with the two different chloride salts agree reasonably well* and are also found to be in agreement (at 0.25 % H_2O) with an intercept obtained from the $(C_6H_5)_4AsSCN$ dependence of thiocyanate entry into $(C_5H_5)_2TiBr_2$. *Thus,* k_1

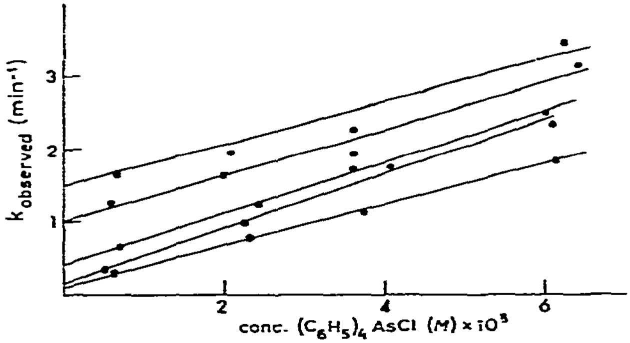

Fig. 1. Pseudo first-order rate constants for the reaction $(C_5H_5)_2TiBr_2 + 2(C_6H_5)_4AsCl \longrightarrow (C_5H_5)_2TiCl_2 + 2(C_6H_5)_4AsBr$ at various water concentrations. Water concentrations are: (from the lowest line) 0.25 %, 0.50 %, 1.0 %, 2.0 %, and 3.0 %.

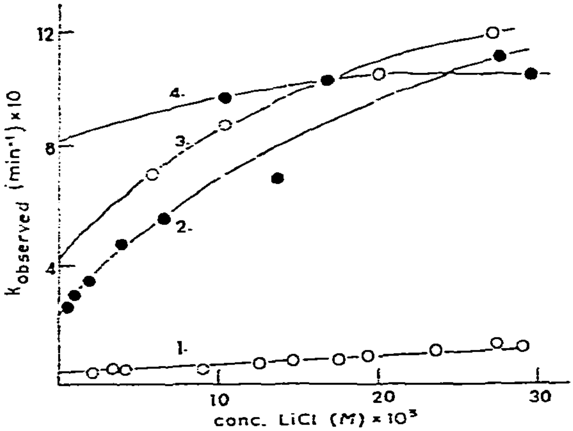

Fig. 2. Pseudo first-order rate constants for the reaction $(C_5H_5)_2TiBr_2 + 2LiCl \longrightarrow (C_5H_5)_2TiCl_2 + 2LiBr$ at water concentrations: 1. "dry", 2. 0.5 %, 3. 0.75 %, and 4. 1.0 %.

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* These results indicate that rate constants (k_1) obtained by Jensen correspond to ~ 0.2 % aqueous acetone.

appears to characterize a well-defined entering anion-independent path of substitution.

Using the intercepts in Fig. 1, the dependence of k_1 on the concentration of water is shown in Fig. 3. A reasonable straight line can be drawn passing through the origin. Without specifying its significance, the second order rate constant for the "water dependent" path is 8.2×10^{-1} min^{-1} M^{-1}. Jensen and Basolo[2] showed that methanol accelerates ligand exchange very much as water does, but that phenol does not. Our experiments indicate that small concentrations of pyridine and thiourea have no effect on the rate of ligand exchange. (See experimental section.)

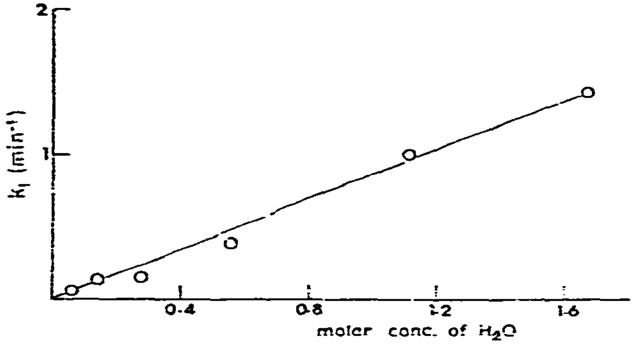

Fig. 3. The anion-independent constant k_1 for the reaction $(C_5H_5)_2TiBr_2 + 2Cl^- \longrightarrow (C_5H_5)_2TiCl_2 + 2Br^-$ as a function of the molecular concentration of water. The lowest point represents the estimated water concentration of the "dry" acetone.

DISCUSSION

Structure of $(C_5H_5)_2TiX_2$

At the outset, the probability must be admitted that detailed examination of this system by the kineticist is premature. The subject was opened because the Ti(IV) complexes seemed to offer a case of tetrahedral substitution to the inorganic kineticist. The subsequent work has mooted the basic structural question. Jensen[2] reports spectrophotometric studies of the equilibrium position of some of the reactions discussed in this paper that require "too many" intermediates for the simple tetrahedral structures. He proposes that $(C_6H_5)_2TiX_2$ compounds are *dimeric*. This conclusion follows from attempts to find successive formation constants using the procedure of Newman and Hume[4]. According to Jensen, the excess species that lead to the dimer assumption are found *despite* "apparent" isosbestic points[2,3] which are consistent with the monomeric structure. The dimer assumption lead to writing the substitution reactions in four steps and considering the rates to represent successive processes of comparable rate *despite* the fact that good first-order plots are obtained at ten different wavelengths[3]. Since species found by spectroscopic analysis of multiple equilibria are somewhat uncertain, we shall discuss our results on the assumption of a monomeric structure. This choice is made for the following additional reasons. (1) Attempts to determine molecular weight in benzene and tetramethylene sulfone solutions gave values less than monomeric[5]. (2) Dipole-moment measurements in benzene are in good agreement with a nearly tetrahedral monomer[6] but would be difficult to reconcile with any reasonable dimer structure. (3) The visible spectra are very similar in benzene, acetone and aqueous hydrochloric aeid.

The assumed monomer structure has been discussed theoretically by Ballhausen and Dahl[7]. They account for the bonding by hybridizing metal $3d$, $4s$, and $4p$ levels for maximum overlap with the $C_5H_5^-$ ring π orbitals. This leads to three orbitals left over centered in the plane between the rings. Two are used to bond halides and the third is *empty*. This suggests a very simple account of the kinetic results. The process involves nucleophilic attack using the empty orbital. But, whatever the structure, the results at least indicate an associative pathway, characterized by k_2, along which the activation parameters are significantly dependent upon the nature of the entering ligand.

Nucleophilicity order

Our interest in this problem originated in the observations of Weinstein *et al.*[8] and Parker[9] that halide nucleophilicity in acetone solution is in the reverse order of nucleophilicity in water. That is the aqueous order $I^- > Br^- > Cl^-$ becomes $Cl^- > Br^- > I^-$ in acetone. Weinstein and Parker both suggested that this inversion signified that the nucleophilicity order was determined primarily by the ground state energy of the nucleophile (as opposed to its bonding in the transition state) and that the ground state energy was determined by *solvation*. Thus there is a leveling effect in acetone solutions where all anions are poorly solvated. These nucleophilicity orders all applied to attack at carbon centers where there are no available low energy orbitals. It was of interest to examine nucleophilicity in a system where such orbitals are available, and the ability of the nucleophile to bond to the substrate might become more nearly a determinant of nucleophilicity order. If the structural ambiguity is resolved in favor of the monomer, then it is reasonable to interpret the nucleophilicity order $N_3^- > Cl^- \sim SCN^- > Br^-$ covering a rate range minimally varying over a factor of 10^2 as confirmation of the anticipated mitigation of the leveling effect.

The water-dependent reaction

It is tempting to account for the water-dependent reaction as simply a nucleophilic attack by water on the complex. The second order rate law is consistent with this view. But, the absence of a thiourea or pyridine effect undermines the argument. Conversely, as Basolo and Jensen noted, phenol has no effect on the rate. It does not seem probable that H-bonding to the leaving halide is the key effect of water.

EXPERIMENTAL

Diacidodicyclopentadienyltitanium(IV) compounds

$(C_5H_5)_2TiCl_2$ was obtained as an Eastman White Label product. $(C_5H_5)_2TiBr_2$ was prepared from this according to the procedure of Jensen and Basolo[2] and was spectroscopically equivalent to their compound.

Dicyclopentadienyltitanium(IV) dithiocyanate was prepared by refluxing 1.25 g of $(C_5H_5)_2TiCl_2$ with 10.0 g of NaCNS in 150 ml of reagent-grade acetone for 45 min. The acetone was evaporated under vacuum; the product extracted from the residue with hot toluene, recrystallized from toluene, and dried under vacuum over P_2O_5. (Found: C, 48.70; H, 3.68. $C_{12}H_{10}N_2S_2Ti$ calcd.: C, 48.96; H, 3.43 %.)

Dicyclopentadienyltitanium(IV) diazide was prepared by refluxing 1.25 g of $(C_5H_5)_2TiCl_2$ and 8.2 g of NaN_3 in 150 ml of reagent-grade acetone for 45 min. The product was isolated following the procedure described for the thiocyanate. Yield: 0.5 g of orange-red crystals. This compound decomposes in dilute acetone solution. The decomposition is significant within 5 min. (Found: C, 45.84; H, 4.05. $C_{10}H_{10}N_6Ti$ calcd.: C, 45.82; H, 3.85 %.)

The most important features of the spectra of these compounds in the visible region are summarized in Table 2.

TABLE 2

SPECTRAL PROPERTIES OF $(C_5H_5)_2TiX_2$ COMPOUNDS IN ACETONE

Complex	λ_{max} (μ)	*Molar extinction coefficient*
$(C_5H_5)_2TiCl_2$	391	2,290
$(C_5H_5)_2TiBr_2$	425	2,400
$(C_5H_5)_2Ti(SCN)_2$	438	12,400
$(C_5H_5)_2Ti(N_3)_2$	410	

Tetraphenylarsonium salts were prepared from G. F. Smith reagent-grade tetraphenylarsonium chloride by ion exchange using amberlites IRA 400 anion-exchange resin. They were recrystallized from aqueous acetone. Tetrabutylammonium thiocyanate was obtained similarly and recrystallized from acetone. Lithium chloride was obtained as a reagent-grade material and dried.

Solvent preparation and solution handling

To obtain acetone that was 99.99 % or better water free, reagent-grade acetone was fractionally distilled from P_2O_5[10]. A middle fraction (about 50 %) boiling at 56° was collected and stored in a dry box. Solutions were prepared and stored in the dry box as well. For convenience, pipetting of the solution added at the start of a reaction run was done at the spectrophotometer and not in the dry box.

Kinetic measurements

Spectra of reactants and products were obtained on a Bausch and Lomb Spectronic 505 recording spectrophotometer and "crude" kinetic analysis of several systems was performed on this instrument to determine in detail the nature of the changes taking place during a reaction and to check rate constants using data at several wavelengths. Precise rate measurements were made with a thermostated chamber Beckman DU spectrophotometer at appropriate product wavelength maxima. This instrument was thermostated at 25.0 ± 0.05°. "Dry" acetone reaction solutions were made up with nucleophile concentrations at least 20 times substrate concentration to ensure pseudo first-order kinetics; the reactions were followed for two to three half-lives and infinity absorbance recorded after seven half-lives. Substrate concentrations were varied in the range $1-4 \times 10^{-4}$ *M* except in the case of thiocyanate reactions where the high extinction coefficient of $(C_5H_5)_2Ti(SCN)_2$ required concentrations of about 1/5 of these. Plots of log $(A_\infty - A)$ *vs.* t were accurately linear and first order rate constants were calculated from the slopes.

The experiments in "dry" acetone solutions were repeated for the reactions of $(C_5H_5)_2TiBr_2$ with LiCl and $(C_6H_5)_4AsCl$ in solvents made 0.25 to 2.0 % by volume aqueous. The reaction of $(C_5H_5)_2TiBr_2$ with $(C_6H_5)_4AsSCN$ was run at several salt concentrations in 0.25 % aqueous acetone, and the reaction of $(C_5H_5)_2TiBr_2$ with $(C_6H_5)_4AsCl$ was run in acetone solutions 1.0 *M* in pyridine or 1.0 *M* in thiourea. In all cases the rates conformed to a first process of conversion of $(C_5H_5)_2TiBr_2$ into its dichloro or dithiocyanate derivative.

SUMMARY

The kinetics of substitution of acido ligands in diacidodicyclopentadienyltitanium(IV) compounds have been investigated in acetone solutions. The observed pseudo first-order rate constants conform to the expression

$$k_{observed} = k_1 + k_2[X]$$

where [X] is the concentration of the entering ligand. k_2 varies significantly from one anion to another suggesting a rate process involving a nucleophilic attack. k_1 is a sensitive function of the water content of the medium, apparently approaching zero at zero water content.

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