acid but not the ester substrate, whereas the ligand based on α-D-galactose has the opposite selectivity. It will be noted that the readily available D-sugars give the naturally-occurring L-amino acids in all cases.

Obviously a large number of chiral diphosphinites [illegible] synthesised by this approach and a further one of interest is based on D-xylose (V). This ligand when used with $[Rh(1,5\text{-}COD)Cl]_2$ is not only a more active catalyst than the other diphosphinite catalysts, complete reduction taking about 1 h compared with 8 h for the ligands I—IV, but also gives good optical yields for both the acid and methyl ester. In this case the more abundant D-xylose gives excess of the unnatural D-amino acid.

Further work is in progress on designing related catalysts and studying their reactivity and selectivity.

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Preliminary communication

PHOTOLYSIS OF DI-η^5-CYCLOPENTADIENYLDIMETHYLTITANIUM(IV): APPLICATION OF FREE-RADICAL POLYMERIZATION IN A STUDY OF THE MECHANISM

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Summary

Photolysis of di-η^5-cyclopentadienyldimethyltitanium(IV) (λ 435.8 nm) leads to the initiation of free-radical polymerization. Labelling studies reveal that no free methyl is formed on photolysis and it is suggested that initiation occurs through interaction with monomer of a labile photolysis product containing titanium.

It has been suggested that the photolysis of $(\eta^5\text{-}C_5H_5)_2TiMe_2$ (I) occurs by homolysis of the methyltitanium bonds (eq. 1) [1].

$$\underset{\text{(I)}}{(\eta^5\text{-}C_5H_5)_2TiMe_2} \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)_2Ti + 2Me\cdot \qquad (1)$$

Such a reaction should be effective in initiating free-radical polymerization. We have confirmed that photolysis of I in methyl methacrylate (MMA) does initiate polymerization, but the results indicate that free methyl radicals are not formed. Photolyses were conducted in rigorously degassed solutions using the 435.8 nm line of a mercury lamp. Some principal results are:

1. Photolysis of I in toluene gave essentially 2 mol of methane (90% yield of the total based on methyl groups) whereas photolysis in MMA or styrene gave only 1 mol of methane (54 and 45% yield, respectively) and polymerization of the monomer occurred.

2. Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CD_3)_2$ in toluene-d_8 gave only CD_3H with no detectable CD_4 as gaseous product. Hence exclusive abstraction of hydrogen from the $\eta^5\text{-}C_5H_5$ groups occurs in formation of methane in our experiments. If free $CD_3\cdot$ radicals were formed, CD_4 would be expected to arise by facile abstraction from toluene-d_8. The absence of CD_4 conflicts with the interpretation of Rausch et al. [2]; however, the latter workers seem to have used different photolysing wavelengths.

3. The polymer formed by photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(Me\text{-}^{14}C)_2$ in MMA contained approximately one ^{14}C atom per polymer chain (0.8—1.1 ^{14}C/chain depending on conditions), but contained no titanium.

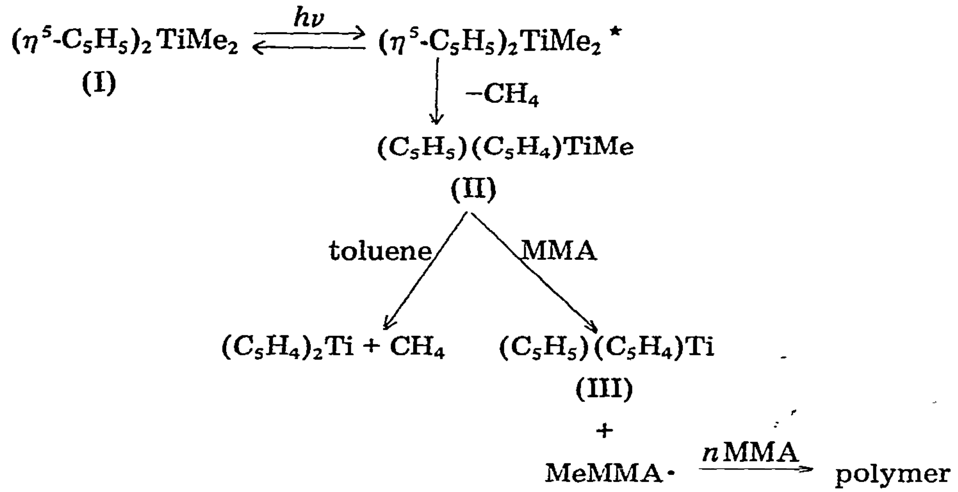
4. The polymer formed by photolysis of $(\eta^5\text{-}C_5H_5\text{-}t)_2TiMe_2$ in MMA contained insignificant amounts of tritium (corresponding to <0.01 cyclopentadienyl hydrogens per average chain).

5. There was a short but reproducible induction period (ca. 1 min) before polymerization of MMA started. On interrupting the irradiation, polymerization ceased after a short time, of the order of 0.5 min; when illumination was resumed the onset of polymerization was again preceded by an induction period.

6. In the early stages of reaction (after the induction period) the kinetics of polymerization and the molecular weights of the polymers formed were consistent with an uncomplicated free-radical polymerization. Thus, the rate of polymerization ω was proportional to $I_0^{1/2}$ (I_0 being the incident light intensity) and the product $\omega\bar{P}_n$ for MMA had values close to 0.3 mol $l^{-1}s^{-1}$ ($\bar{P}_n$ being the number-average degree of polymerization). For the polymerization of MMA under "conventional" conditions at 25°C, $\omega\bar{P}_n = 0.32$ mol $l^{-1}s^{-1}$.

7. In the later stages of reaction, both ω and $\bar{P}_n$ fell below the values expected for an uncomplicated polymerization, indicating the occurrence of retardation processes.

We interpret these findings in terms of the mechanism of initiation shown in Scheme 1.



SCHEME 1

On this view, the induction period is the time required to build up a stationary concentration of II, which is the active initiator. II has been proposed previously as an intermediate in the thermal decomposition of I [3]. The formation of II may occur through a tight radical pair mechanism or through preliminary hydride transfer to titanium giving an intermediate $(C_5H_5)(C_5H_4)TiHMe_2$ which then eliminates methane, but it cannot involve free methyl radicals. Species III, or products arising from its reaction with MMA, must be very active in retarding polymerization, perhaps by reactions with propagating chains according to eq. 2.

$$\sim\sim\sim CH_2\dot{C}Me(CO_2Me) + (C_5H_5)(C_5H_4)Ti \rightarrow$$

$$\sim\sim\sim CH{=}CMe(CO_2Me) + (C_5H_5)_2Ti \quad \text{or} \quad (C_5H_5)(C_5H_4)TiH \qquad (2)$$

Numerical solution of the kinetic equations confirms that the mechanism described is consistent with the experimental data.

Although the precise nature of the intermediate titanium species is uncertain, the work shows that the methyl groups in I are cleaved on photolysis in two distinct steps, neither of which involves formation of free methyl radicals.

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