# Kinetics of the Reaction of $N_2$ with Titanium Cyclopentadienyl Complexes

By R. MASKILL and J. M. PRATT*
*(Inorganic Chemistry Laboratory, Oxford University)*

SEVERAL reactions have recently been discovered in which $N_2$ is reduced homogeneously at room temperature and under a pressure of 1 atm. The most active system appears to be a mixture of $Ticp_2Cl_2$ (cp = $C_5H_5$) and a Grignard reagent in a solvent such as ether.[1] Knowledge of the mechanism of this reaction would clearly help our understanding of "fixation" reactions. This reaction has been studied using isotopic labelling and gas analysis[2] and e.s.r. spectroscopy.[3] We have studied the kinetics of the reaction of $N_2$ with a mixture of $Ticp_2Cl_2$ and EtMgBr in diethyl ether. Except where otherwise stated, the experimental conditions were: 0·04M-Ti, 0·66M-EtMgBr, 1 atm. $N_2$, room temp. The amount of fixed nitrogen was determined as $NH_3$ after decomposition of the reaction mixture and is given as a percentage of the expected stoicheiometric yield (100 × $[NH_3]/[Ti]$). In all the experiments reported here a stream of $N_2$ (or argon) was passed continuously through the reaction vessel; additional experiments under "static" conditions showed no significant difference.

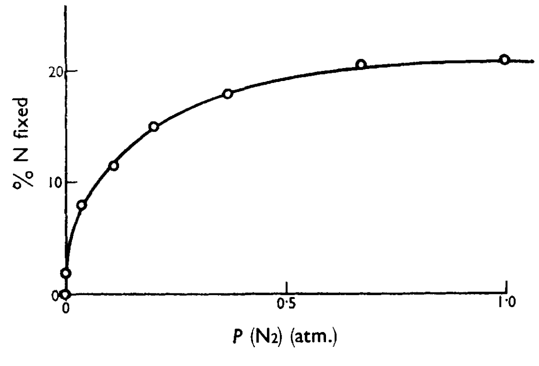
$Ticp_2Cl_2$ and EtMgBr react rapidly with similar colour changes and effervescence under both $N_2$ and Ar; these reactions clearly precede fixation. Preliminary experiments on the course of fixation with time showed that the amount fixed increased for about 2 hr., after which it levelled off (0·5 hr. 16%; 1 hr. 30%; 2 hr. 48%; 6 hr. 55%); a similar curve was obtained by Vol'pin and Shur.[4] The amount fixed after 1 hr. was used to test the effect of different variables on the rate of fixation with the following results:

(1) [EtMgBr]. The rate increases rapidly up to about 0·66M, above which the rate is independent of concentration of EtMgBr. Judging from the colour changes, this reflects the rate of the initial, usually rapid, reaction between $Ticp_2Cl_2$ and EtMgBr and is not related to the fixation reaction.

(2) Allowing $Ticp_2Cl_2$ and EtMgBr to react under argon before admitting $N_2$ has no significant effect (0 hr. argon, 21%; 1 hr. 19%; 2 hr. 18%; 6 hr. 15%).

(3) Partial pressure of $N_2$ (in $N_2$–Ar mixtures). This has a very marked effect (see Figure).

FIGURE



(4) [$Ticp_2Cl_2$]. The amount fixed depends approximately on the square of the titanium concentration (0·016M-Ti, 4·5%, $[NH_3]/[Ti]^2 =$ 140; 0·024M, 9·0%, 156; 0·032M, 16·3%, 159; 0·040M, 28·0%, 175).

The most interesting result is (3), which clearly shows a change from a rate-determining step which involves $N_2$ at low $P(N_2)$ to one which does not at high $P(N_2)$. The apparent second-order dependence on titanium concentration may possibly be spurious (*e.g.*, due to a salt effect), but it probably represents the rate-determining step at high $P(N_2)$. Result (2) shows that after the initial rapid reaction there is no significant change with time in the composition of the bulk of the solution (complexes represented by $Ti^X$ below). The simplest scheme to explain the results of the fixation reaction is therefore

$$2\,Ti^X \xrightarrow[A]{} Ti_2^X \xrightarrow[B]{N_2} \text{Products}$$

where A is the rate-determining step at high $P(N_2)$ and B at low $P(N_2)$. The identity of $Ti^X$ has not been established. The i.r. spectra of the reduced solutions apparently "indicate deep-seated changes; the distinctive structure of the titanium derivative is lost", while decomposition liberates $H_2$ in the ratio $H_2/Ti \sim 2$.[2] Complexes such as $Ti^0(C_5H_6)_2$, perhaps in equilibrium with $Ti^{IV}(C_5H_6)_2H_2$, could explain the observations. Brintzinger[3] has obtained e.s.r. evidence for the presence of a paramagnetic compound with two equivalent hydrides, to which he assigns the dimeric structure $Ti^{III}{}_2cp_4H_2$ and which he suggests is the complex which reacts with $N_2$. He has not, however, shown whether this compound is present as a major or minor constituent of the solution; if present as the major constituent, it would not explain our results (3) and (4). Labelling experiments showed that no hydrogen atoms are bound to nitrogen in the product(s).[2]

In view of the very exothermic reaction of $N_2$ with titanium metal (enthalpy of formation of TiN $= -80$ kcal./mole)[5] it is tempting to postulate a mechanism of fixation involving a complex of zerovalent titanium such as

$$2[Ti^0(C_5H_6)_2] \rightleftharpoons [Ti_2{}^0(C_5H_6)_4] \xrightarrow{N_2} [(C_5H_6)_2TiN]_{1\text{ or }2}$$

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