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REACTION BETWEEN ALCOHOLS AND ALKYL ISOCYANATES CATALYZED BY THE LIGHT-SENSITIVE FERROCENE-FERRIC CHLORIDE SYSTEM.

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Kinetic, spectroscopic and quantum yield measurements allow insight into the mechanism of the reaction between t-butyl isocyanate and methanol photocatalyzed by ferrocene and ferric chloride.

S.P. McManus and coll.(1) reported an interesting photoassisted reaction between alcohols and alkyl isocyanates catalyzed by ferrocene (Fn) 10^{-4}M in CCl_4 as solvent. They suggested the involvement of the $Fn \rightarrow CCl_4$ charge-transfer (CT) absorption band(2) in the photocatalysis, the resulting ferricenium cation being subsequently reduced by RNCO so that following scheme could account for a chain process :

$$RNCO^{+} + R'OH \longrightarrow R\text{-}\overset{+}{N}H\text{-}CO\text{-}OR' \xrightarrow{RNCO} R\text{-}NH\text{-}CO\text{-}OR' + RNCO^{+} \qquad (A)$$

Our attention was drawn by several puzzling facts. First, the authors reported a second order rate constant for the photocatalyzed reaction and secondly, since it is known(3)(4) that $Fn^{+}FeCl_4^{-}$ is formed by irradiation of Fn in the presence of CCl_4, the proposed mechanism of photoinitiation looked rather unlikely on account of the much greater extinction coefficient of Fe^{3+} at the wavelengths where the $Fn \rightarrow CCl_4$ CT absorption occurs(4). We report here the conditions and results of our investigations.

The reaction mixtures (5.10^{-3}M t-butyl isocyanate, 5.10^{-3}M methanol, 4.10^{-4}M Fn) were degassed by three successive freezing-thawing cycles (10^{-3}Torr) prior to the measurements. The solvent was a 1/1 mixture of CCl_4 and CH_2Cl_2 in order to be sure of the homogeneity even after formation of the ionic species. Monochromatic 365 nm incident light was used for all kinetic and quantum yield measurements. The degassed reaction assembling consisted of a 5cm path-length cell for irradiation, a 1cm cell for U.V. spectra and 1 mm CaF_2 cell for I.R.

spectra. The thermal reactions were run at 25.0°C. The disappearance of RNCO was monitored at 2250 cm^{-1} and the carbamate formation was observed at 1720 cm^{-1} and 3440 cm^{-1}. Evolution of the light-absorbing catalytic species was monitored by U.V. visible spectroscopy : broad absorption about 320 nm for $Fn \longrightarrow CCl_4$ CT, max. at 365 nm for $FeCl_4^-$, max. at 625 nm for Fn^+.

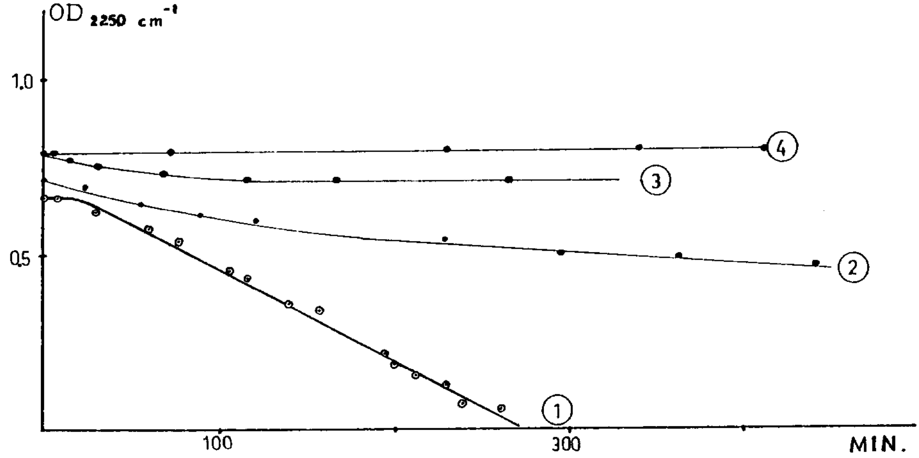

Fig. Optical density due to t-butyl isocyanate as a function of time (1) under irradiation in the presence of ferrocene $4.10^{-4}M$; (2) at 25.0°C in the presence of $FeCl_3$ $10^{-4}M$; (3) at 25.0°C after short irradiation in the presence of ferrocene $4.10^{-4}M$; (4) at 25.0°C in the presence of ferrocene $4.10^{-4}M$.

In the figure, curve 1 shows that the reaction is pretty near zero-order after a short induction period for a typical photoassisted run in the presence of Fn as precatalyst. During this run, 50% of the light only is absorbed at the beginning, but after 30 minutes the amount $FeCl_4^-$ is already high enough to absorb more than 99% of the light leading, from then on, to a zero-order reaction. Although the formation of $FeCl_4^-$ is involved in the existence of an induction period, the inhibiting effect of residual traces of O_2 is also obvious from various runs performed with solutions degassed by only one freezing-thawing cycle. Curve 2 shows the rate of thermal reaction (25.0°C) in the presence of $FeCl_3$ $10^{-4}M$ (5) which is approximately the amount Fe^{3+} formed at the end of the photoassisted runs in the presence of Fn. Curves 3 and 4 show the evolution of the thermal reaction in the presence of ferrocene, respectively after a short irradiation (15 minutes : not represented in the figure) and without irradiation. The shape of curve 3 is consistent with a short-chain mechanism initiated by the light. The quantum yield ϕ of the zero-order reaction (curve 1) was found about 0.3, the intensity of the incident light in the cell being 9.10^{-7} einstein/min. On account of a rather slow thermal chain process, the value of ϕ decreases obviously when the light intensity increases and should in fact be measured after extinction of the thermal reaction promoted by a short flash of light. However, attempts in this way lacked accuracy. We have measured the quantum yield of photoreduction of $FeCl_4^-$ in the following media : (a) CH_2Cl_2-CCl_4 1/1 ; (b) MeOH 5.10^{-3}M in (a) ; (c) t-BuNCO 5.10^{-3}M in (a) ; (d) t-BuNCO 5.10^{-3}M and MeOH 5.10^{-3}M in (a). In all four cases, the quantum yield is about 0.05. If we assume that irradiation promotes the oxidation of RNCO according to :

$$Fe^{3+} - Cl^- \xrightarrow{h\nu} Fe^{2+} + .Cl \quad (B)$$

$$.Cl + RNCO \longrightarrow RNCO^+ + Cl^- \quad (C)$$

comparison of the quantum yields leads to the conclusion that equation (A) should occur at least* 6 times before chain breaking (for example : $RNCO^+ + Fe^{2+} \longrightarrow RNCO + Fe^{3+}$, but this must be checked).

Evidence supporting the main involvement of equations (B) and (C) in the photoinitiation, is further given by the fact that no reaction is observed when irradiation is realized in the presence of Fn 4.10^{-4}M and acrylonitrile 10^{-1}M ; indeed, $FeCl_4^-$ is not formed from Fn when a vinyl monomer is added(6). We have checked that Fn^+ does not oxidize t-BuNCO, which makes again the mechanism proposed by S.P. Mc Manus rather unconvincing.

Thus, the sole role in which Fn is acting, involves the equilibrium(4) (7) : $Fn + Fe^{3+} \longrightarrow Fn^+ + Fe^{2+}$ which regenerates continuously the active Fe^{3+}

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* One must not forget that equation (C) enters in competition with $.Cl + MeOH \longrightarrow Cl^- + \dot{C}H_2OH + H^+$.

catalyst. Indeed, when $FeCl_3$ is used as sole photocatalyst, its photoreduction is complete when only a small amount of RNCO has been transformed. Slower uncatalyzed photoreaction occurs afterwards(1).

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