Photoassisted Reaction Between Alcohols and Isocyanates

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Summary The action of light enhances the rate of the reaction of alkyl isocyanates and alcohols; the rates of the light-assisted reaction are further enhanced by the addition of certain transition-metal catalysts, such as ferrocene.

The ionic reaction between alcohols and isocyanates has been extensively studied.[1] Catalytic effects have also been explored.[2] We report a novel effect of light which has previously gone unnoticed.

The reaction between cyclohexyl isocyanate (0·0484M) and butan-1-ol (0·0484M) in degassed CCl_4 at 50°, gave a second-order rate constant of $2{\cdot}08 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$. Under constant exposure to light from a tungsten lamp, the measured rate constant was $5{\cdot}42 \times 10^{-3}\,l\,mol^{-1}\,s^{-1}$. With the addition of ferrocene ($1{\cdot}61 \times 10^{-4}$M), the rate constant was 0·219 $l\,mol^{-1}\,s^{-1}$ in the presence of light and $6{\cdot}37 \times 10^{-3}\,l\,mol^{-1}\,s^{-1}$ without light. In all cases, purified starting materials were used and the urethane was formed essentially quantitatively along with traces of coloured materials presumed to be isocyanate polymers.[3]

The synthetic utility of the reaction was demonstrated with t-butyl alcohol, which is known to react slowly by the thermal reaction and gives a large amount of elimination product.[1] We have obtained a 92% yield of t-butyl cyclohexylcarbamate by exposing a 0·05M-CCl_4 solution of the respective alcohol and isocyanate to light for 12 h. Without light no reaction was observed with these reactants under the same conditions.

We note the possible similarity of our results to the recent report of the ferrocene-sensitized photoalkoxycarbonylation of azulene.[4] There seems to be differences: (i) while other ferrocene derivatives and butadiene(tricarbonyl)iron photo-catalyse our reaction, tris(acetylacetonato)iron does not; and (ii) oxygen was found to slow our rates. The photoreaction occurs in other chlorinated solvents but not in benzene or heptane. This suggests to us a complex between the isocyanate and CCl_4. Ferrocene may participate in this complex or it may complex with CCl_4[5] to give a species which may react to form the activated isocyanate intermediate.

Support from the U.S. Army Missile Command is gratefully acknowledged.

(*Received*, 14*th January* 1974; *Com.* 043.)

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[1] For a review, see J. H. Saunders and K. C. Frisch, 'Polyurethanes, Chemistry and Technology,' Part 1, Interscience, New York, 1962, pp. 134—173.

[2] K. C. Frisch and L. P. Rumao, *Rev. Macromolecular Chem.*, 1971, **6**, 103.

[3] V. V. Korshak and L. A. Datskevich, *Plast. Massy*, 1971, **11**; G. S. Kolesnikev, L. A. Datskevich, T. T. Pham, and L. S. Ustinova, Russ. P. 317,682, Oct. 19, 1971 (*Chem. Abs.*, 1972, **76**, 141,527).

[4] T. Ishigami, T. Akiyama, H. Watanabe, T. Kato, and A. Sugimore, *J.C.S. Chem. Comm.*, 1973, 871.

[5] R. E. Bozak, *Adv. Photochem.*, 1971, **8**, 227.