Studies of the Catalyzed Reaction between Alcohols and Alkyl Isocyanates. Evidence for a Light-Assisted Reaction[1]

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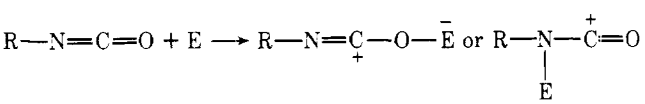
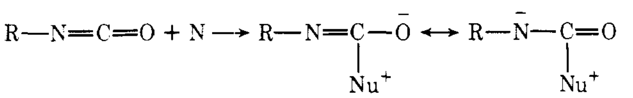
The thermal reaction between cyclohexyl isocyanate and 1-butanol to produce the expected carbamate occurs spontaneously in degassed CCl_4 at 50 °C with a measured second-order rate constant of 4.67×10^{-5} L mol^{-1} s^{-1}. By maintaining the identical conditions but exposing the reaction to light from a tungsten lamp, we have observed a 125-fold rate increase. The light-assisted reaction is greatly enhanced upon the addition of certain transition metal catalysts, such as ferrocene. By studying the effect of electronic and steric factors and the influence of light and solvent, we propose that the enhanced reactions occur by excited state charge-transfer complexes involving the isocyanate and solvent or ferrocene and solvent. A set of mechanistic reactions and the experiments supporting them are discussed. The steric influence of the alkyl group on the reactivity of alkyl isocyanates is also reported under a variety of conditions.

Catalysis of alcohol–isocyanate reactions is a topic which has received a considerable amount of study. Tarbell et al.[3] observed that these reactions are subject to either electrophilic or nucleophilic catalysis. This may be rationalized in terms of the electrophile (E, a Lewis acid) or nucleophile (Nu, a Lewis base) activating the isocyanate group for attack as shown in eq 1 and 2. The alcohol itself may be assumed to react as in eq 2.

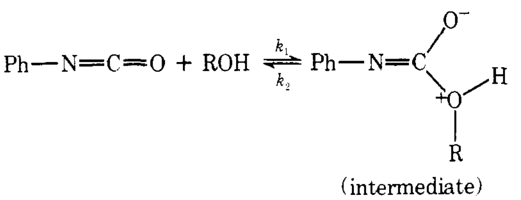


$$R{-}N{=}C{=}O + E \longrightarrow R{-}N{=}\underset{+}{C}{-}O{-}\overset{-}{E} \text{ or } R{-}\underset{\displaystyle E}{\underset{|}{N}}{-}\overset{+}{C}{=}O \qquad (1)$$



$$R{-}N{=}C{=}O + N \longrightarrow R{-}N{=}\underset{\displaystyle Nu^+}{\underset{|}{C}}{-}\overset{-}{O} \longleftrightarrow R{-}\overset{-}{N}{-}\underset{\displaystyle Nu^+}{\underset{|}{C}}{=}O \qquad (2)$$

Baker and Gaunt[4] have extensively studied the thermal reaction and have postulated a mechanism that generally accounts for their observations. The reaction sequence was written as a two-step process where the alcohol was catalytically involved in the second step; see eq 3 and 4. Owing to a



$$Ph{-}N{=}C{=}O + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ph{-}N{=}C(O^-)(\overset{+}{O}(H)R) \qquad (3)$$

(intermediate)

$$\text{(intermediate)} + ROH \xrightarrow{k_3} PhNHCO_2R + ROH \qquad (4)$$

mild catalysis by the product, the reaction kinetics are not completely linear throughout the reaction.[4,5]

Several groups[4-12] have studied the kinetics of the nucleophilically catalyzed reaction. 1,4-Diazobicyclo[2.2.2]octane (Dabco) is found to be one of the best nucleophilic catalysts owing to the availability of its electron pairs. The mechanism for the action of nucleophilic catalysts generally follows that pictured in eq 3 and 4 with the nucleophilic catalysts replacing the alcohol in the formation of the complex.[13-15]

Studies of catalysis by electrophilic or acidic agents have essentially been confined to organometallic compounds owing to the interest in the great rate enhancement seen with many of these materials. Organometallic compounds offer room for additional mechanistic complications since they may offer sites for coordination for both the isocyanate and the alcohol.[13-15] Kinetic surveys on various organometallic compounds,[16] organotin catalysts,[17] and metal carboxylates[18] have appeared, and mechanistic papers on the action of metal chelates,[19] organotin compounds,[19] and ferric acetylacetonate[20] have been published.

Since the practical interest in catalysts is their effect on rate, steric effects must also be considered. Because of the mechanistic complexities, it is difficult to predict how catalysts will affect the rates when steric factors in the reactants are operative. Davis and Farnum[21] observed that among aliphatic alcohols, the relative rates of reaction of primary, secondary, and tertiary alcohols are approximately 1.0, 0.3, and 0.003–0.007, respectively. These results, while in agreement with the general order expected from steric hindrance due to branching, are not entirely accurate for the tertiary system owing to the elimination process that becomes preponderant in tertiary aliphatic alcohols (Scheme I).

Scheme I

$$(CH_3)_3COH + C_6H_5NCO \rightarrow (CH_3)_2C{=}CH_2 + C_6H_5NHCO_2H$$

$$C_6H_5NHCO_2H \xrightarrow{-CO_2} C_6H_5NH_2 \xrightarrow{C_6H_5NCO} C_6H_5NHCONHC_6H_5$$

Although a few generalizations have been drawn from studies on aromatic isocyanates,[15] not too much is known about the steric influence on rate upon changing the substituent R in RNCO.[22] One would predict a less important effect in the isocyanate substrate than in the alcohol moiety since the reacting site is further removed in the former. Since, in many polymer applications, diisocyanates are added to extend or cure polyesters or other hydroxy-terminated prepolymers, we were interested in observing the effects of branching on rate in alkyl isocyanates with and without typical added catalysts.

In the course of our studies on the catalytic effects of organometallic agents on the alcohol–isocyanate reaction, we observed a remarkable light-assisted process[23] which we now wish to discuss. We also discuss here our studies of the steric consequences of branching in alkyl isocyanates on the rate of catalyzed alcohol–isocyanate reactions.

Results

In the course of characterizing the catalytic effect of ferrocene and its derivatives on alcohol–isocyanate reactions we serendipitously discovered that the near-infrared Cary 14 light source was responsible for a light-assisted reaction. The uncatalyzed thermal reaction[24] between a degassed solution of cyclohexyl isocyanate and *n*-butyl alcohol in carbon tetrachloride occurs at a moderate rate at 50 °C (see Table I, entry 1). However, if the solution is subjected to constant exposure to the near-infrared light source of the Cary 14 spectropho-

Table I. Second-Order Rate Constants for the Reaction of Cyclohexyl Isocyanate and n-Butyl Alcohol in Carbon Tetrachloride at 50.5 ± 0.5 °C

Entry no.	Conditions	[n-BuOH] = [$C_6H_{11}NCO$], M	[Ferrocene], M	k_2, L mol^{-1} s^{-1} [a]
1	Thermal[b]	1.00×10^{-1}	0.00	$(4.67 \pm 0.91) \times 10^{-5}$
2	Photoassisted[c]	5.00×10^{-2}	0.00	$(5.85 \pm 0.40) \times 10^{-3}$
3	Thermal[b]	1.00×10^{-1}	3.39×10^{-3}	$(4.61 \pm 1.34) \times 10^{-3}$
4	Photoassisted[c]	4.29×10^{-2}	1.43×10^{-5}	$(2.19)^{d} \times 10^{-1}$
5	Photoassisted[c]	4.84×10^{-2}	3.23×10^{-6}	$(5.40)^{d} \times 10^{-2}$

[a] Determined by observing the disappearance of n-BuOH in the near infrared; see Experimental Section. Values are average of several runs unless otherwise indicated. [b] Reactions were run on a 200-mL scale in the dark in a thermostated oil bath; small aliquots were removed at intervals for near-IR analysis in a 1.0-cm cell. [c] Reactions were run in a thermostated 10-cm quartz cell with constant light exposure from the Cary 14 near-IR source; see Experimental Section. [d] Represents only one run under these conditions, but similar rates under similar conditions were observed.

tometer, under otherwise similar conditions, the second-order rate constant for the reaction was found to increase by a factor of 125 (compare entries 1 and 2, Table I). The product is the carbamate under both sets of conditions.

The enhancement of the rate of the thermal reaction between cyclohexyl isocyanate and n-butyl alcohol by ferrocene has been determined. At a 3.39% molar concentration, ferrocene increases the second-order rate constant of the thermal reaction by a factor of nearly 100; compare entries 1 and 3, Table I. Under conditions nearly identical with those where the light-assisted reaction discussed above was observed but now with 0.033 mol % added ferrocene, an enhancement in rate constant by a factor of approximately 4700 over the uncatalyzed thermal reaction and by a factor of 47.5 over the already efficient ferrocene-catalyzed thermal reaction is observed; compare entry 4 with entries 1 and 3. The ferrocene-catalyzed light-assisted reaction is somewhat sensitive to the amount of added ferrocene as seen by a comparison of entries 4 and 5 of Table I.

The light-assisted reactions with added ferrocene were found to be very sensitive to the presence of oxygen and to known quenchers, e.g., methyl violet. After short exposure times to light in the presence of air, the solution took on a greenish color from ferrocinium ion formation.[25] Hence, at least in the presence of ferrocene, the role of oxygen could be simply to destroy the ferrocene catalyst. Methyl violet would probably act differently. Nevertheless, to protect against oxygen inhibition, all reactions with and without added ferrocene were degassed and dry nitrogen was introduced to the flasks or reaction cells.

There is possible evidence for a chain process. For example, all light-assisted reactions were characterized by an induction period where the reaction began slowly yielding a curve when a second-order kinetic plot was constructed; see Figure 1. After a period of time, the plot became linear. Azobisisobutyronitrile (AIBN), a common free-radical initiator, did not accelerate the thermal reaction when a CCl_4 solution of the reactants with added AIBN was heated at 80–100 °C.

Since the Cary 14 lamp is a broad wavelength source it was of interest to determine what wavelength of light caused the reaction to occur. We found that the photoreaction also occurred readily in a Rayonet reactor.[26] Additionally, we could measure the rates of the thermal reactions by inserting a 650-nm Corning filter[27] between the Cary 14 source and the sample. Using this filter, a rate constant of 5.37×10^{-5} L mol^{-1} s^{-1} was measured for a reaction comparable to that shown as entry 1 of Table I. Further definition of the effective wavelength was not achieved.

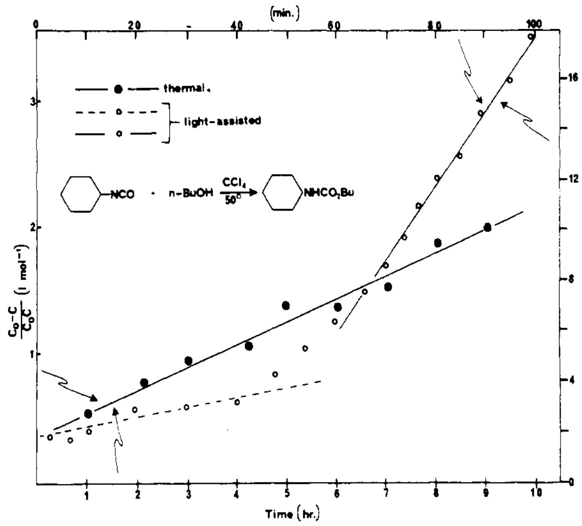


Figure 1. Second-order plots for the thermal and light-assisted reactions of cyclohexyl isocyanate with n-butyl alcohol.

The light-assisted reaction was also sensitive to a change in solvent. On changing to either benzene or hexane, a rate effect occurred. A 30-mL benzene solution 0.05 M in cyclohexyl isocyanate and 0.05 M in n-butyl alcohol proceeded only to about 5% completion when held either in UV light or in the dark for 4 h. Under the same conditions the reactants in carbon tetrachloride were 95% consumed when exposed to light. A similar result was obtained with hexane as with benzene. When an o-dichlorobenzene solution of the reactants was exposed to UV light in a Rayonet reactor, carbamate formation was complete after 12 h. A control run under the same conditions but in the dark gave <5% reaction.

Each light-assisted reaction contained a stable yellowish color after reaction, yet the purified carbamate was colorless in each case. An attempt to isolate or identify the yellow impurity proved to be quite difficult as it was shown to be well less than 1% of the reaction product and no distinctive NMR absorptions in presence of the carbamate were observed. Duplicate kinetic measurements of the light-assisted reaction with an added concentrate of the yellow component proceeded at a rate similar to that measured without the added impurity. The induction period was also still present and of a similar magnitude. Hence buildup of the yellow impurity as a reactive intermediate or catalyst was not considered to be the source of the induction period.[28,29]

The effect of varying the steric environment of the isocyanate on the rate constant of the isocyanate–alcohol reaction under various kinds of catalysis was measured; see Table II. Also, with cyclohexyl isocyanate as the isocyanate reactant, the sensitivity of the light-assisted ferrocene-catalyzed reaction to a change in steric bulk in the alcohol was determined; see Table III. Finally, rate studies were run to measure the effects of varying electronic and steric factors in the ferrocene catalyst; see Table IV.

Table II. Second-Order Rate Constants and Relative Rates for the Catalyzed Reaction of Alkyl Isocyanates with *n*-Butyl Alcohol in Carbon Tetrachloride at 50.5 ± 0.5 °C

$$\mathrm{RNCO} + \mathrm{CH_3(CH_2)_3OH} \rightarrow \mathrm{RNHCO_2(CH_2)_3CH_3}$$

	Light-assisted[a] (no ferrocene present)		Light-assisted[b] ferrocene catalyzed		Dabco[c] catalyzed		Fe(acac)$_3$[b] catalyzed	
R	k_{obsd},[d] L mol^{-1} s^{-1}	k_{rel}	k_{obsd},[d] L mol^{-1} s^{-1}	k_{rel}	k_{obsd},[d] L mol^{-1} s^{-1}	k_{rel}	k_{obsd},[d] L mol^{-1} s^{-1}	k_{rel}
Methyl	$(3.52 \pm 0.09) \times 10^{-5}$	1.00	$(3.93 \pm 0.78) \times 10^{-2}$	1.00	$(1.29 \pm 0.14) \times 10^{-2}$	1.00	$(8.18 \pm 0.52) \times 10^{-2}$	1.00
Ethyl	$(3.28 \pm 0.11) \times 10^{-5}$	0.93	$(3.40 \pm 0.07) \times 10^{-2}$	0.87	$(7.40 \pm 0.60) \times 10^{-3}$	0.57	$(9.30 \pm 0.50) \times 10^{-2}$	1.14
Isopropyl	$(3.74 \pm 0.82) \times 10^{-5}$	1.06	$(2.18 \pm 0.40) \times 10^{-2}$	0.55	$(4.60 \pm 0.40) \times 10^{-3}$	0.36	$(6.80 \pm 0.20) \times 10^{-2}$	0.83
tert-Butyl	$(2.65 \pm 0.04) \times 10^{-5}$	0.75	$(4.21 \pm 0.90) \times 10^{-3}$	0.11	$(7.00 \pm 0.60) \times 10^{-4}$	0.054	$(2.43 \pm 0.08) \times 10^{-2}$	0.30

[a] [RNCO] = [n-C$_4$H$_9$OH] = 0.125 M. [b] [RNCO] = [n-C$_4$H$_9$OH] = 0.0484; [catalyst] = 3.22×10^{-4} M. [c] [RNCO] = 0.25 M; [n-C$_4$H$_9$OH] = 0.125 M; [Dabco] = 1.0×10^{-2} M. [d] Average second-order rate constant from two or more runs.

Table III. Rate Data for the Light-Assisted Reaction of Cyclohexyl Isocyanate with Various Alcohols in Carbon Tetrachloride at 50.5 ± 0.5 °C with Ferrocene as Catalyst[a]

Alcohol	k, L mol^{-1} s^{-1} [b]	k_{rel}
Methyl alcohol	$(8.80 \pm 0.63) \times 10^{-2}$	1
Ethyl alcohol	$(3.84 \pm 2.87) \times 10^{-2}$	0.44
n-Butyl alcohol	$(3.58 \pm 0.30) \times 10^{-2}$	0.41
Isopropyl alcohol	$(1.43 \pm 0.01) \times 10^{-2}$	0.16
tert-Butyl alcohol	$(4.25 \pm 1.24) \times 10^{-4}$	0.0048

[a] [C$_6$H$_{11}$NCO] = [ROH] = 0.0484 M; [ferrocene] = 3.23×10^{-4} M. [b] Average second-order rate constant from two or more runs.

To assess the potential synthetic utility of the reaction, two tertiary alcohols were selected for reaction with cyclohexyl isocyanate under photochemical conditions. In a Rayonet photochemical reactor, a carbon tetrachloride solution of *tert*-butyl alcohol reacted smoothly with cyclohexyl isocyanate giving nearly a quantitative yield of carbamate based on conversion. Under the same conditions, triphenylmethanol was not converted to a carbamate and was recovered unchanged.

Discussion

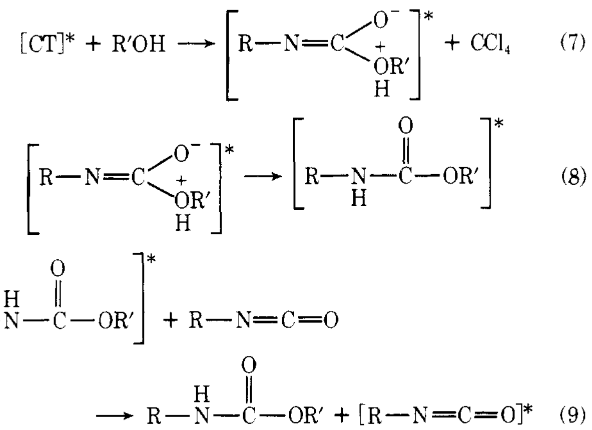
The finding of a light-assisted alcohol–isocyanate reaction is interesting and without a close precedent; many of our observations, however, do have precedent. We will now treat various possible mechanisms which are suggested based on the data available.

Ferrocene and carbon tetrachloride are both known for their ability to form charge transfer complexes[30] (CT) and, in fact, they form a charge transfer complex with each other.[31] Thus the possible involvement of charge transfer complexes in these processes is suggested. With ferrocene absent, one could envision charge transfer formation between the isocyanate and carbon tetrachloride. The absorption of light by the complex could lead to an excited state complex; see eq 5. Alternatively, exciplex formation, as shown in eq 6, could occur.

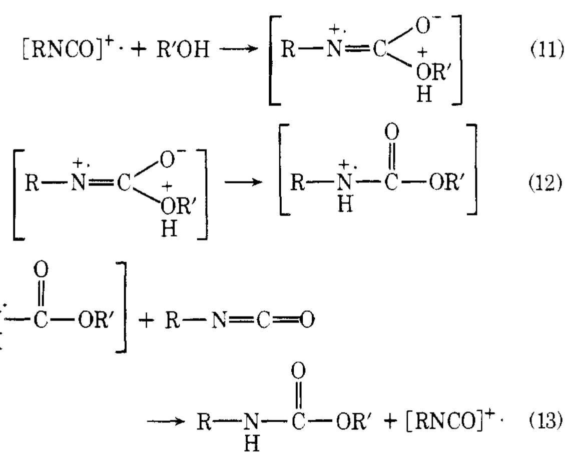
$$\mathrm{RN{=}C{=}O} + \mathrm{CCl_4} \rightarrow [\mathrm{CT}] \xrightarrow{h\nu} [\mathrm{CT}]^* \qquad (5)$$

$$\mathrm{RN{=}C{=}O} \xrightarrow{h\nu} [\mathrm{RN{=}C{=}O}]^* \xrightarrow{\mathrm{CCl_4}} [\mathrm{CT}]^* \qquad (6)$$

Two modes of reaction are conceivable for the [CT]* species. There may be sufficient charge transfer in the complexed species to cause it to react faster with an alcohol, e.g., by eq 7–9, in comparison with an unactivated isocyanate. This sequence of reactions is written as a chain process. Alternatively, complete electron transfer may occur yielding the isocyanate cation radical; see eq 10. This species would certainly be activated toward reaction with alcohols. Thus, eq 11–13 form a chain process that could account for the observed product.


(7)
(8)
(9)

$$[\mathrm{CT}]^* \longrightarrow [\mathrm{RNCO}]^{+\cdot} + [\mathrm{CCl_4}]^{-\cdot} \qquad (10)$$


(11)
(12)
(13)

A cursory search for evidence supporting the reactions shown in eq 5 revealed nothing favorable as no CT absorption band was found in the electronic spectrum[32,33] of cyclohexyl isocyanate in carbon tetrachloride or in solutions of cyclohexyl isocyanate and carbon tetrachloride in cyclohexane or in heptane;[34] alkyl isocyanates show a $\lambda_{\max}$ at ca. 260 nm. However, the reaction of electronically excited isocyanate with carbon tetrachloride to give the excited state CT complex, e.g., eq 5, is not inconsistent with the absence of a CT absorption band.

Although there is some evidence which might favor a chain process, a chain mechanism is not required by the available

Table IV. Rate Data for the Light-Assisted Reaction of Cyclohexyl Isocyanate with *n*-Butyl or *tert*-Butyl Alcohol in Carbon Tetrachloride at 50.5 ± 0.5 °C with Various Ferrocene Derivatives as Catalyst[a]

Alcohol	Catalyst	k, L mol^{-1} s^{-1} [b]	k_{rel}
n-Butyl alcohol	*n*-Butylferrocene	$(1.20 \pm 0.21) \times 10^{-1}$	3.35
n-Butyl alcohol	Acetyl-1,1′-dimethylferrocene	$(9.14 \pm 0.74) \times 10^{-2}$	2.55
n-Butyl alcohol	Ferrocene	$(3.58 \pm 0.30) \times 10^{-2}$	1.00
n-Butyl alcohol	Acetylferrocene	$(2.32 \pm 0.49) \times 10^{-2}$	0.65
n-Butyl alcohol	1,1′-Diacetylferrocene	$(5.88 \pm 1.01) \times 10^{-2}$	0.16
tert-Butyl alcohol	Ferrocene	$(4.28 \pm 1.24) \times 10^{-4}$	1
tert-Butyl alcohol	1,1′-Diacetylferrocene	(9.23)[c] $\times 10^{-4}$	0.22

[a] $[C_6H_{11}NCO] = [ROH] = 0.0484$ M; [cat.] $= 3.23 \times 10^{-4}$ M. [b] Average second-order rate constant from two or more runs. [c] Represents only one kinetic run.

evidence. For example, as evidence for a chain process, the induction period in the light-assisted reaction in the absence of ferrocene, see Figure 1, could be the result of a preequilibrium step to form a species which is kinetically important; alternatively, it may be the result of the destruction of some species which acts as an inhibitor. Thus, while the reaction sequences represented by eq 5 or 6–9 and 5 or 6, 10–13 offer possible explanations for some of our observations, the chain propagating steps, especially the sequence in eq 7–9, are highly unusual. In fact, the sequence of reactions 7–9 is very unlikely.

The ferrocene-catalyzed reaction[35] is all the more interesting. From the data in Table I it can be seen that the process is complicated by the occurrence of three reactions simultaneously. At the concentration tested, ferrocene increases the second-order rate constant of the thermal reaction by a factor of nearly 100. Furthermore, in the presence of light, ferrocene further enhances the rate constant of the ferrocene-catalyzed thermal reaction by a factor of 47.5. Thus, the observed second-order rate constant is a sum of the three individual rate constants, eq 14, but only ferrocene-catalyzed reactions would appear to be kinetically important.

$$k_{obsd} = k_{FcH,light} + k_{FcH,thermal} + k_{thermal} \qquad (14)$$

The intensity of the CT absorption band for the ferrocene and carbon tetrachloride[31] suggests its involvement here; see eq 15 and 16. In the mechanistic schemes discussed earlier, eq 14 and 15 fit nicely in an overall scheme with eq 10–13.

$$FcH + CCl_4 \rightarrow [CT] \xrightarrow{h\nu} [CT]^* \xrightarrow{h\nu} FcH^+\cdot + CCl_4^-\cdot \qquad (15)$$

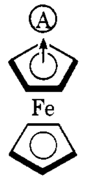
(FcH = ferrocene)

$$FcH^+\cdot + R\text{-}N{=}C{=}O \rightarrow FcH + [R\text{-}NCO]^+\cdot \qquad (16)$$

The observation that the light-assisted reaction occurs in some solvents but not in others confirms the postulated involvement of solvent. Since *o*-dichlorobenzene, a charge transfer acceptor, is an acceptable solvent for the light-assisted reaction, it apparently is acting in the same role as carbon tetrachloride. Although we have not evaluated an extensive list of acceptors (solvents or solutes), one would assume that a host of acceptors would suffice in the light-assisted process. Indeed it would be interesting to see if there is a correlation of rate with acceptor effectiveness and reduction potential since such would be expected if eq 6 is important in determining the overall rate.

Varying the steric environment of the isocyanate is shown to hardly affect the measured second-order rate constant in the light-assisted reaction (Table II). This result differs from that obtained from the other catalyzed reactions studied. This result can be interpreted to confirm that, if an isocyanate species is involved in the rate-determining step, a very reactive isocyanate derivative is involved. This, of course, is not inconsistent with eq 7 or 11.

In the light-assisted reaction with ferrocene present, the observed trend (Table II) would tend to be evidence of a reaction between a ferrocene species and isocyanate in the rate-limiting step. Consistent with the required transfer of an electron from the ferrocenium ion to the isocyanate species, e.g., eq 16, one might expect steric factors to be important depending on the geometry required. It has been demonstrated[36] that ferrocene and its derivatives interact with acceptors (A) as shown in structure 1 and not as 2. However, electron transfer may occur by approach of the isocyanate as pictured in 3. Accordingly, the transfer would be much slower for isocyanates with large alkyl groups.



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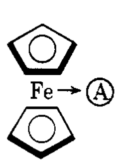

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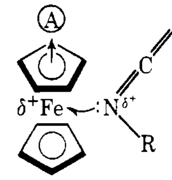

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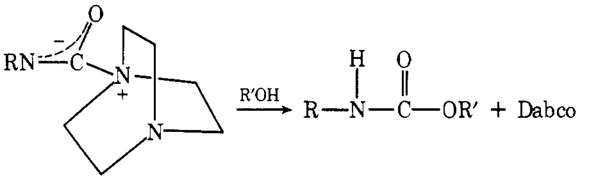
The effect on rate of varying the R group in alkyl isocyanates in alcohol–isocyanate reactions catalyzed by the common catalysts 1,4-diazabicyclo[2.2.2]octane (Dabco) and ferric acetylacetonate [Fe(acac)$_3$] (Table II) serves as a basis for comparison. The Dabco-catalyzed process is thought to involve rate-limiting reaction of 4 with the alcohol, eq 17.[13–15]



(17)

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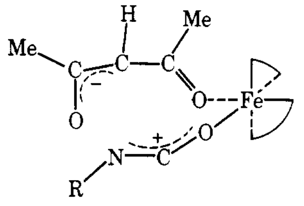
Obviously, the bulk of the Dabco–isocyanate complex should render the reaction more sensitive to steric factors and this is observed.

The catalytically active complex in the Fe(acac)$_3$-catalyzed reaction of isocyanates with alcohols is a 1:1 complex of the isocyanate and Fe(acac)$_3$.[37] This species most likely involves oxygen coordination to the metal as in 5. If the alcohol also becomes coordinated to iron, e.g., as shown in 6,[13,37] then the



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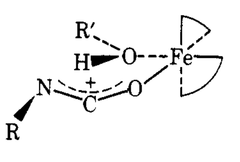

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alkyl group in RNCO is not in the pathway for an approaching reactant. The data in Table II show that the Fe(acac)$_3$-catalyzed reactions are not unusually sensitive to a change of R in RNCO.

With cyclohexyl isocyanate as the isocyanate reactant, we have investigated the sensitivity of the ferrocene-catalyzed light-assisted reaction to a change in steric bulk of the alcohol (Table III). The trend is quite impressive and reminiscent of the data obtained from similar studies of the thermal reaction of alcohols with phenyl isocyanate.[38] Interestingly, the fact that a trend is present conflicts with the conclusion suggested above that a ferrocenium species and isocyanate are involved in the rate-limiting step.

The effects on rate of varying the electronic and steric factors of the catalyst (Table IV) are significant. The mechanism involving eq 15 and 16 would be supported by electron-donating groups enhancing the rates (ferrocenium ion stabilizing)[39] and this is the case as alkyl substitution on the ferrocene ring provides a modest rate acceleration. Interestingly, acetyl 1,1′-dimethylferrocene is not effective in slowing the rate in agreement with complex formation with the electron-rich ring of the type depicted by structure **1** but somewhat contradictory to the involvement of structure **3**.

While there is some evidence supporting the mechanistic equations presented above, the weight of the evidence is weak and unconvincing. For example, the nature of the induction period is puzzling and its origin is speculative. Although it could be used as evidence for a radical chain reaction, the requirement of ca. 30 min to build up steady-state concentrations of apparently reactive intermediates, e.g., (CT)* and RNCO$^{+\cdot}$, seems odd.

There are other observations that lead us to believe that the reaction is not a simple radical chain process as we have shown in our mechanistic equations above. Since the light-assisted reaction is first order both in alcohol and in isocyanate[40] one would assume that there is a rate-determining step involving these species in some form. Nevertheless, we have shown that the rate constant of the catalyzed reaction is sensitive to ferrocene concentration (Table I), to substituents on the ferrocene rings (Table IV), and to alcohol structure (Table III). Furthermore, the catalyzed light-assisted reaction and the light-assisted reaction show a difference in their sensitivity to changes in the steric environment of the isocyanate (Table II). Therefore, we cannot reconcile all of these facts with the radical chain mechanism discussed above or any other simple mechanism.

Mechanistic considerations aside, it seemed appropriate to consider the synthetic utility of the light-assisted reaction. Although many catalysts are known which accelerate alcohol–isocyanate reactions, light is unique among them. It has advantages since it leaves no catalyst residue. Its use also has disadvantages since the reactor must be of a design which allows the input of light. We have explored the use of this process for causing otherwise difficult reactions to occur with mixed results. Under thermal conditions, tertiary alcohols react very slowly with isocyanates and often give large quantities of elimination products.[21] However, we have found that *tert*-butyl alcohol reacts smoothly with cyclohexyl isocyanate in carbon tetrachloride in a Rayonet photochemical reactor. The yield of carbamate is nearly quantitative based on conversion. On the other hand, we were not able to convert triphenylmethanol to a carbamate by this procedure.

Experimental Section[41]

Materials. The isocyanates were purchased from Aldrich and were distilled and stored in a desiccator prior to use. Alcohols, except ethanol, were Fisher certified reagent grade and were distilled prior to use. Absolute ethanol was used as obtained from USI. Ferrocene, obtained from Ventron, was doubly sublimed, acetylferrocene[42] was sublimed, 1,1′-diacetylferrocene, obtained from Arapahoe, was recrystallized from petroleum ether (bp 60–90 °C), *n*-butylferrocene, obtained from Arapahoe, was distilled prior to use, and acetyl-1,1′-dimethylferrocene, obtained as a mixture of isomers from the Ethyl Corp., was used without further purification. Ferric acetylacetonate, obtained from Ventron, was recrystallized from a mixture of benzene and petroleum ether, and diazobicyclo[2.2.2]octane (Dabco) was used as obtained from Aldrich. Solvents were spectrograde and were used without further purification.

Kinetic Method. All reactions, except those specified, were run in a water-jacketed 10-cm quartz cell with the water temperature controlled to ±0.5 °C by circulating the water from a thermostated (Haake Model FJ) bath maintained at 50.0 ± 0.1 °C. The kinetics of the reactions were followed by observing the decrease in alcohol concentration in the near infrared (1.406 μ for 1-butanol) with a Cary 14 spectrophotometer.[43] A product peak also appeared in each case at about 1.480 μ and was recorded only as a measure of product formation. Measurements were made at convenient time intervals and the reactions were treated as second order for the purpose of calculating the rate constant. The reported rate constants were generally derived from treatment of all the data obtained for thermal reactions and the data for light-assisted reaction obtained after an initial induction period. Generally, data were obtained through the first reaction half-life.

The near-infrared light source in the Cary 14 spectrophotometer is a GE CPR tungsten filament projector lamp operating at 18 A and 6 V. The light passes through the sample prior to going through the monochromator. The wavelength of light passing through the sample was limited in certain cases by the use of Corning filters.

The lamp was turned on only for obtaining datum points for slow reactions unless otherwise stated. For fast reactions, the light remained on constantly. With the lamp constantly on, the sample temperature increases by 1–2 °C in some cases (i.e., $t_{1/2} \gtrsim$ 20–30 min). Thus, the k values for the reactions run with the lamp constantly on are more appropriately at 51 ± 1 °C.

The standard solutions of alcohol and of isocyanate in the designated solvent were separately preheated to 50 °C in a thermostated bath prior to mixing in the reaction cell. After mixing, the solutions were degassed and the cells were back-filled with dry nitrogen since the rates of the photoreactions were found to be affected by the presence of oxygen.

Product Studies. In addition to verifying the appearance of a product band in the near infrared as mentioned above, at least one run with each catalyst system and alcohol–isocyanate combination was checked for product formation by an alternate method. These included the use of GLC to monitor the disappearance of isocyanate and the stripping of solvent to isolate product. Routinely, a trace amount of a yellow side product was observed in the photoassisted reactions. This material was not identified but it may be the result of isocyanate self-photoreactions.[28,29]

Samples of the carbamates were recrystallized for positive (NMR, melting point) identification. Yields were consistent only with nearly quantitative alcohol–isocyanate reaction for the alcohol or isocyanate converted. A preparative scale reaction is detailed below.

***tert*-Butyl *N*-Cyclohexylcarbamate. A. By Irradiation.** Fifty milliliters of 0.10 M cyclohexyl isocyanate in carbon tetrachloride was mixed with 5 mL of 1.0 M *tert*-butyl alcohol in carbon tetrachloride in a 5 × 35 cm single-necked, cylindrical quartz round-bottom flask. The solution was degassed and the flask back-filled with dry nitrogen. The solution was irradiated for 12 h in a Rayonet photochemical reactor equipped with 12 mercury lamps with predominant output at ca. 3120 Å. The solvent was stripped in vacuo to yield a slightly yellow crystalline product, mp 76.5–77.5 °C, 92% yield. Recrystallization from petroleum ether (bp 30–60 °C) gave colorless crystals, mp 78.5–79 °C (lit. 78[44] and 76–78 °C[45]). The IR and NMR were consistent with the assigned structure.

B. Without Irradiation. A vial containing a solution of the reactants in the same proportions as above was degassed, back-filled with nitrogen, and completely covered with black tape to exclude light. The vial was stored in the photochemical reactor during the reaction period of the solution in paragraph A above. After 12 h the vial was opened and the contents were analyzed. No reaction was apparent by GLC analysis.

In another trial, a solution of 30 mL of 0.10 M cyclohexyl isocyanate in carbon tetrachloride and 3 mL of 1.0 M *tert*-butyl alcohol in carbon tetrachloride was prepared in a 100-mL round-bottom flask. The solution was degassed and the flask was back-filled with dry nitrogen. The flask was covered with aluminum foil and heated under nitrogen at 76 °C for 9 days. Analysis for unreacted alcohol after that period revealed 84% conversion. The solvent was stripped off to give a solid, mp <74 °C, which was revealed to be impure carbamate.

Attempted Photoreaction of Triphenylmethanol with Cyclohexyl Isocyanate. A solution of 0.125 g of cyclohexyl isocyanate and 0.260 g of triphenylmethanol in 200 mL of carbon tetrachloride was prepared and irradiated as described in paragraph A of the reaction above. IR, NMR, and GLC analysis revealed negligible conversion of the alcohol or isocyanate.

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Registry No.—*n*-Butyl alcohol, 71-36-3; *tert*-butyl alcohol, 75-65-0; *tert*-butyl *N*-cyclohexylcarbamate, 3712-40-1; cyclohexyl isocyanate, 3173-53-3; methyl isocyanate, 624-83-9; ethyl isocyanate, 109-90-0; isopropyl isocyanate, 1795-48-8; *tert*-butyl isocyanate, 1609-86-5; butyl *N*-methylcarbamate, 5461-30-3; butyl *N*-ethylcarbamate, 16246-07-4; butyl *N*-isopropylcarbamate, 18312-36-2; butyl *N*-*tert*-butylcarbamate, 22815-64-1; butyl *N*-cyclohexylcarbamate, 17671-80-6; methyl alcohol, 67-56-1; ethyl alcohol, 64-17-5; isopropyl alcohol, 67-63-0.

References and Notes

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(25) This is assumed to be a photooxidation. From the intensity of the green color, it was assumed that the oxidation was facile. Accordingly, a rate decrease was evident and reproducible rate constants were not obtained.

(26) This reactor and the Hg lamps are available from Southern New England Ultraviolet Co.

(27) This filter allows only wavelengths longer than 650 nm to pass through the sample.

(28) The yellow color may be from isocyanate trimer or polymer; it is known, for example, that ferrocene catalyzes the polymerization of isocyanates in the presence of light, cf. Japanese Patent 049 221 (Feb 28, 1973); V. V. Korshak and L. A. Datskevich, *Plast. Massy*, 11 (1971).

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(40) The kinetic dependence of rate on isocyanate concentration in the light-assisted reaction was shown by experiment.

(41) All melting points are uncorrected. NMR were recorded in $CDCl_3$ or CCl_4 with a Me_4Si internal standard on a Bruker HFX-10 90-MHz spectrometer. IR were recorded as KBr disks or as Nujol mulls on a Beckman IR-10 spectrophotometer. GLC was performed on a Varian A-90P chromatograph equipped with a thermal conductivity detector.

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