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N63-13471
Code 1

Technical Report No. 32-129

**Kinetics of the Reaction Between Alcohols
and Isocyanates Catalyzed by
Ferric Acetylacetonate**

Leroy Schieler

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA


July 1, 1961

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NO. NASW-6

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PREFACE

This Report is an unclassified summary of some work done a few years ago at JPL. Though the proposed mechanism and kinetics of the reactions may be questioned, the data merit publication in this unclassified form.

In particular, the conclusion that K_{eq} of Eq. (16) is small may be questioned. The data indicate that very little isocyanate-catalyst complex might have been formed under the conditions employed to test for its presence (highly polar solvent or aliphatic isocyanate). Thus, the temperature dependence of k (Fig. 5) may well represent a large dependence of K_{eq} on temperature.

Thus the work suggests an interesting extension, to dissect the two components of k , Eq. (18). Moreover, subsequent studies on urethane polymers have shown a marked effect of trace amounts of water and oxygen on physical properties, and it is not clear to what extent these could have influenced the kinetic studies described here.

N63-13471

ABSTRACT

The rate and temperature dependence of reaction for the ferric acetylacetonate catalyzed reaction between α -naphthyl, ortho-tolyl, and para-tolyl isocyanates and *n*-butyl alcohol are investigated. The effect of substituents on the reactivity of isocyanate and hydroxyl group are reported and for substituted isocyanates are correlated by means of the Hammett equation. Several metal chelates were studied and their catalytic activity was compared to that of ferric acetylacetonate. All rate data are interpreted in terms of a mechanism involving simultaneous second-order uncatalyzed and catalyzed reactions between alcohol and isocyanate.

I. INTRODUCTION

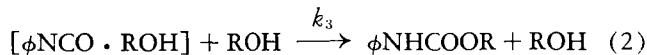
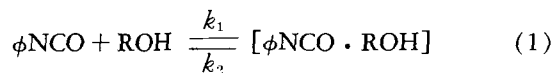
In connection with a study of the relationship between the physical properties of elastomers and their chemical structure, polyurethane synthetic rubbers are being investigated. Since polyurethane resin binders are commonly prepared by the ferric acetylacetonate (cf. Ref. 1) catalyzed reaction of diisocyanates, such as toluene or hexamethylene diisocyanate, with diols, such as polypropylene glycol or polyglycidyl nitrate, it was important to establish kinetics of such reactions. The objectives of this study were to determine the rate of reaction between different alcohols and isocyanates, the temperature dependence of the rate, and the effect of various metal chelates on the rate. Such information is useful in selecting the catalyst and catalyst concentration to control the cure of polyurethane binders.

In order to understand the kinetics of polyurethane formation, it is first desirable to secure information on simple analogs of the polymer. Therefore, kinetic data were obtained on the metal chelate catalyzed reaction of several representative monofunctional isocyanates and alcohols in diethylene glycol diethyl ether solution.

Previous work has indicated that the reaction kinetics for both the spontaneous and tertiary base-catalyzed reactions between alcohols and isocyanates are complex and in some respects incompletely understood.

Dyer et al (cf. Ref. 2) and Baker et al (cf. Ref. 3) have studied the uncatalyzed reaction of phenyl isocyanate.

anate with alcohols and propose the following mechanism which is consistent with their data:



Assuming steady-state conditions, the concentration of the complex is given by the following expression:

$$[\text{complex}] = \frac{k_1 (\phi\text{NCO}) (\text{ROH})}{k_2 + k_3 (\text{ROH})} \quad (3)$$

The second-order rate constant of the reaction, k_0 , may be expressed as a function of the alcohol concentration.

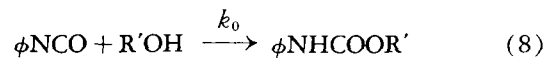
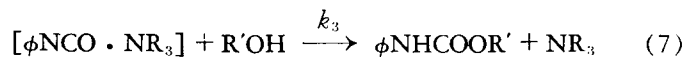
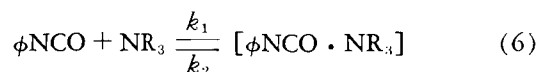
$$\frac{d(\phi\text{NHCOOR})}{dt} = k_0 = \frac{k_1 k_3 (\text{ROH})}{k_2 + k_3 (\text{ROH})} \quad (4)$$

Rearrangement of Eq. (4) yields the following expression:

$$\frac{(\text{ROH})}{k_0} = \frac{k_2}{k_1 k_3} + \frac{(\text{ROH})}{k_1} \quad (5)$$

The straight line obtained by plotting $(\text{ROH})/k_0$ against (ROH) supports the validity of the kinetic treatment. The observation that the second-order rate constant, k_0 , decreased with decreasing alcohol concentration is also consistent with the view that association and solution are important in controlling the kinetics because of their effect on the concentration of free alcohol in solution.

Baker et al (cf. Refs. 3 through 7), who studied the tertiary base-catalyzed reaction between isocyanates and alcohols, propose a somewhat similar mechanism.



Assuming steady-state conditions, the concentration of the complex is given by the following expression:

$$[\text{complex}] = \frac{k_1 (\phi\text{NCO}) (\text{NR}_3)}{k_2 + k_3 (\text{R}'\text{OH})} \quad (9)$$

The rate of formation of the urethane product is given by the following equation:

$$\begin{aligned} \frac{d(\phi\text{NHCOOR}')}{dt} &= k_0 (\text{R}'\text{OH}) (\phi\text{NCO}) \\ &+ \frac{k_1 k_3 (\phi\text{NCO}) (\text{R}'\text{OH}) (\text{NR}_3)}{k_2 + k_3 (\text{R}'\text{OH})} \\ &= k_{bi} (\text{R}'\text{OH}) (\phi\text{NCO}) \end{aligned}$$

where

$$k_{bi} = k_0 + \frac{k_1 k_3 (\text{NR}_3)}{k_2 + k_3 (\text{R}'\text{OH})} \quad (10)$$

Since no kinetic information was available about the ferric acetylacetonate catalyzed reaction between alcohols and isocyanates, a study of the rate and temperature dependence of reaction was made for the ferric acetylacetonate catalyzed reaction of *n*-butyl alcohol with α -naphthyl, ortho-tolyl, and para-tolyl isocyanates. The effect of substituents on the reactivity of the isocyanate and hydroxyl group has been investigated and these data have been correlated for substituted isocyanates by means of the Hammett equation. Several metal chelates were studied and their catalytic activity was compared to that of ferric acetylacetonate.

II. KINETICS OF FERRIC ACETYLACETONATE CATALYZED URETHANE FORMATION

A. Experimental Methods

Reagent grade α -naphthyl, ortho-tolyl, and para-tolyl isocyanates¹ were distilled prior to use and their purity verified by means of refractive index measurements and amine equivalent titration. Reagent-grade *n*-butyl alcohol² was dried over Drierite and distilled before being used. Reagent-grade diethylene glycol diethyl ether² was distilled, and verified to be free of hydroxyl contaminants by Karl-Fischer titration before use. Ferric acetylacetonate³ was recrystallized from benzene, and its purity checked by means of its melting point (M.P. 183-44°C corr., 184°C, cf. Ref. 8).

All rates of reaction were measured in dilatometers constructed from 1-mm capillary tubing sealed to a 25-ml bulb, with a buret scale for recording volume changes. The dilatometers were calibrated by thermal expansion of mercury in order to make certain that the capillaries were uniform.

In all experiments the reactants and solvents were brought approximately to temperature, the solutions prepared and then rapidly introduced into the dilatometer in a constant-temperature bath. The temperature control was $\pm 0.1^\circ\text{C}$ for all measurements. Readings were taken at approximately 5-min. intervals until no further volume contraction occurred. Second-order rate constants were calculated by the method presented in detail by Dyer et al (cf. Ref. 2) in which the customary second-order expressions (Eqs. 11 and 13) were used in the form of Eqs. (12) and (14) for equal and unequal reactant concentrations, respectively.

$$k = \frac{1}{t} \frac{x}{a(a-x)} \quad (11)$$

$$k = \frac{1}{t} \frac{R_0 - R_t}{a(R_t - R_\infty)} \quad (12)$$

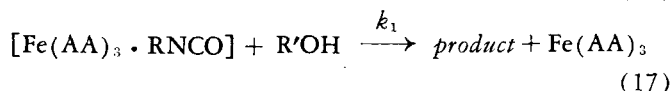
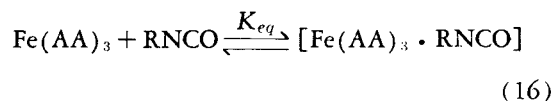
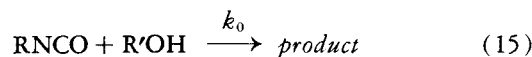
$$k = \frac{1}{t} \frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)} \quad (13)$$

$$k = \frac{1}{t} \frac{2.303}{a-b} \log \frac{a(R_0 - R_\infty) - b(R_0 - R_t)}{a(R_t - R_\infty)} \quad (14)$$

where R_0 , R_t , and R_∞ are the dilatometer readings at the times indicated. The value of R_0 for Eq. (12) was found by extrapolating to zero time a plot of $1/(R_t - R_\infty)$ against time, and for Eq. (14) by extrapolating to zero time the plot of $\log (R_t - R_\infty)$ against time.

B. Kinetic Investigations

It has been found that the kinetics observed for the ferric acetylacetonate catalyzed reaction between isocyanates and alcohols can be treated as a simultaneous uncatalyzed and catalyzed reaction. The most likely mechanism for the reaction is the following, where for simplicity of notations $\text{Fe}(\text{AA})_3$ is used to represent the ferric acetylacetonate catalyst: Here $[\text{Fe}(\text{AA})_3 \cdot \text{RNCO}]$ represents the reactive intermediate formed between catalyst and isocyanate. The term *product* is used to represent the urethane product formed by reaction of an alcohol and an isocyanate.



From this mechanism the following differential equation was derived, representing the rate of formation of urethane product on the assumption that K_{eq} is very small. This is in fact true and experimental evidence supporting this view is presented in a following section.

$$\frac{d(\text{product})}{dt} = k_0 [\text{RNCO}] [\text{R}'\text{OH}] + k_c [\text{Fe}(\text{AA})_3] [\text{RNCO}] [\text{ROH}] \quad (18)$$

where $k_c = k_1 K_{eq}$. Typical second-order, integrated rate curves obtained in this manner are shown in Figs. 1

¹Obtained from Eastman Organic Chemicals, Rochester, New York.

²Obtained from Matheson, Coleman and Bell, Inc., East Rutherford, N. J.

³Obtained from MacKenzie Chemical Works, Inc., Central Islip, L. I., N. Y.

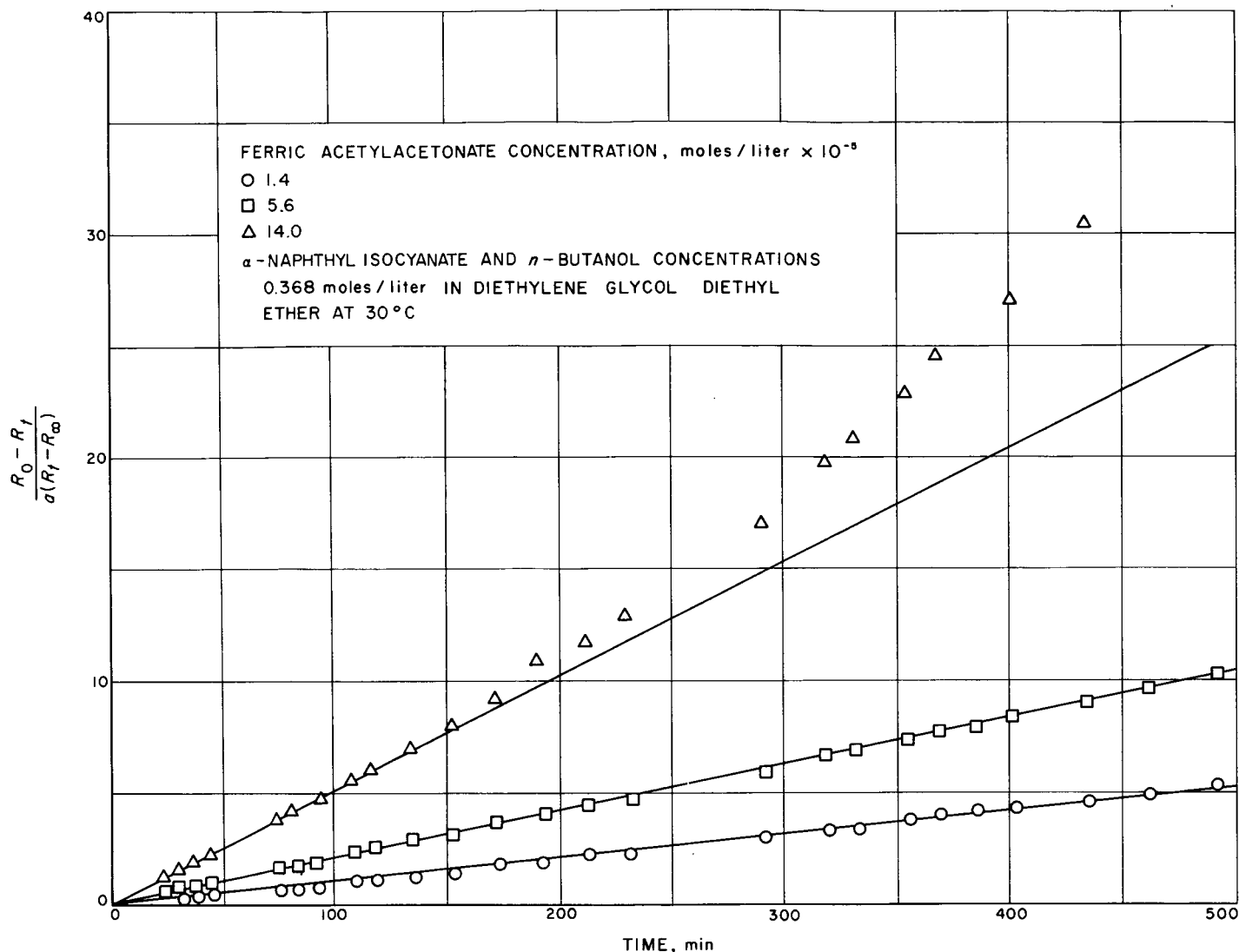


Fig. 1. Second-Order Integrated Rate Curves for the Reaction of α -Naphthyl Isocyanate and *n*-Butyl Alcohol at Several Catalyst Concentrations

through 3. From Fig. 1 it is seen that the integrated rate curves show no significant deviation from linearity except at high extent of reaction. The integrated rate curves obtained at three alcohol concentrations (Fig. 2) all yield linear plots. Serious deviations from linearity in the second-order rate curves were encountered only when excess isocyanate was used. It is probable that secondary reactions such as dimerization and reaction with the urethane hydrogen are the source of this difficulty.

The reaction was also confirmed to be second-order from a Powell plot. A typical plot for the ferric acetylacetonate catalyzed reaction between α -naphthyl isocyanate and *n*-butyl alcohol is shown in Fig. 4.

The system most exhaustively studied was the reaction of α -naphthyl isocyanate with *n*-butyl alcohol using ferric acetylacetonate as catalyst, and diethylene glycol diethyl ether as solvent. Initial slopes for the reaction at several concentrations of catalyst, isocyanate, and alcohol over the temperature range 20 to 69.5°C were used for the determination of the order of each reactant. Holding the concentration of two of the reactants constant and plotting log concentration of the third reactant vs log of the initial slope gives a straight line, the slope of which is the order of reactant. This procedure was carried out for each reactant over the temperature range 20 to 69.5°C using the data presented in Table 1.

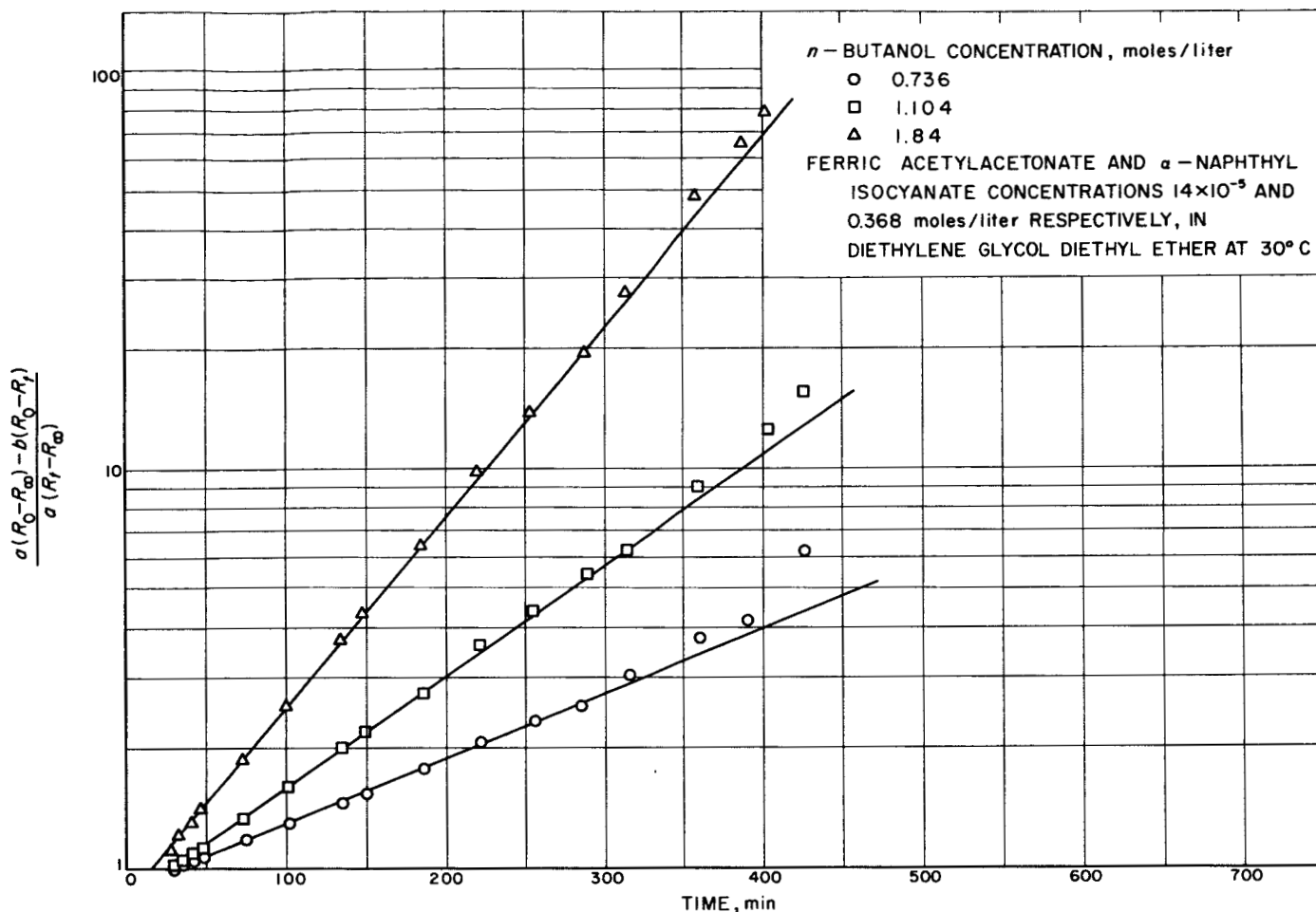


Fig. 2. Second-Order Integrated Rate Curves for the Reaction of α -Naphthyl Isocyanate with Several Concentrations of *n*-Butyl Alcohol

The results of a similar set of experiments carried out with ortho- and para-tolyl isocyanate are given in Tables 2 and 3. From Table 4 it is clear that the reactions are first order for isocyanate and alcohol and fractional order for ferric acetylacetonate. The power of the catalyst was fractional in all cases, but the numerical value is found to vary slightly with the nature of the isocyanate. For α -naphthyl, para-tolyl, and ortho-tolyl isocyanates, the average value of the catalyst exponent is 0.61, 0.56, and 0.77, respectively.

The fractional-catalyst exponents found for the catalyzed reaction are in harmony with a mechanism involving simultaneous second-order reactions such as that proposed in Eqs. (15) through (17). Fractional-catalyst exponents would be anticipated if the rate of the uncatalyzed reaction were rapid enough to contribute to the observed rate of the catalyzed reaction.

If Eq. (18) is rewritten in the form

$$\frac{d(\text{product})}{dt} = \left\{ k_0 + k_c [\text{Fe}(\text{AA})_3] \right\} [\text{RNCO}] [\text{ROH}] \quad (19)$$

it is evident that $k = k_0 + k_c [\text{Fe}(\text{AA})_3]$, where k is the over-all rate constant determined for the catalyzed reaction from an integrated second-order rate equation. Hence, a plot of k vs $[\text{Fe}(\text{AA})_3]$ should yield a straight line with an intercept of k_0 and a slope of k_c .

The plots of k vs catalyst concentration from which k_c is evaluated for the reaction of α -naphthyl isocyanate and *n*-butyl alcohol at several temperatures are shown in Fig. 5. The linearity of these plots furnishes rather convincing evidence that the reaction is in reality a simultaneous

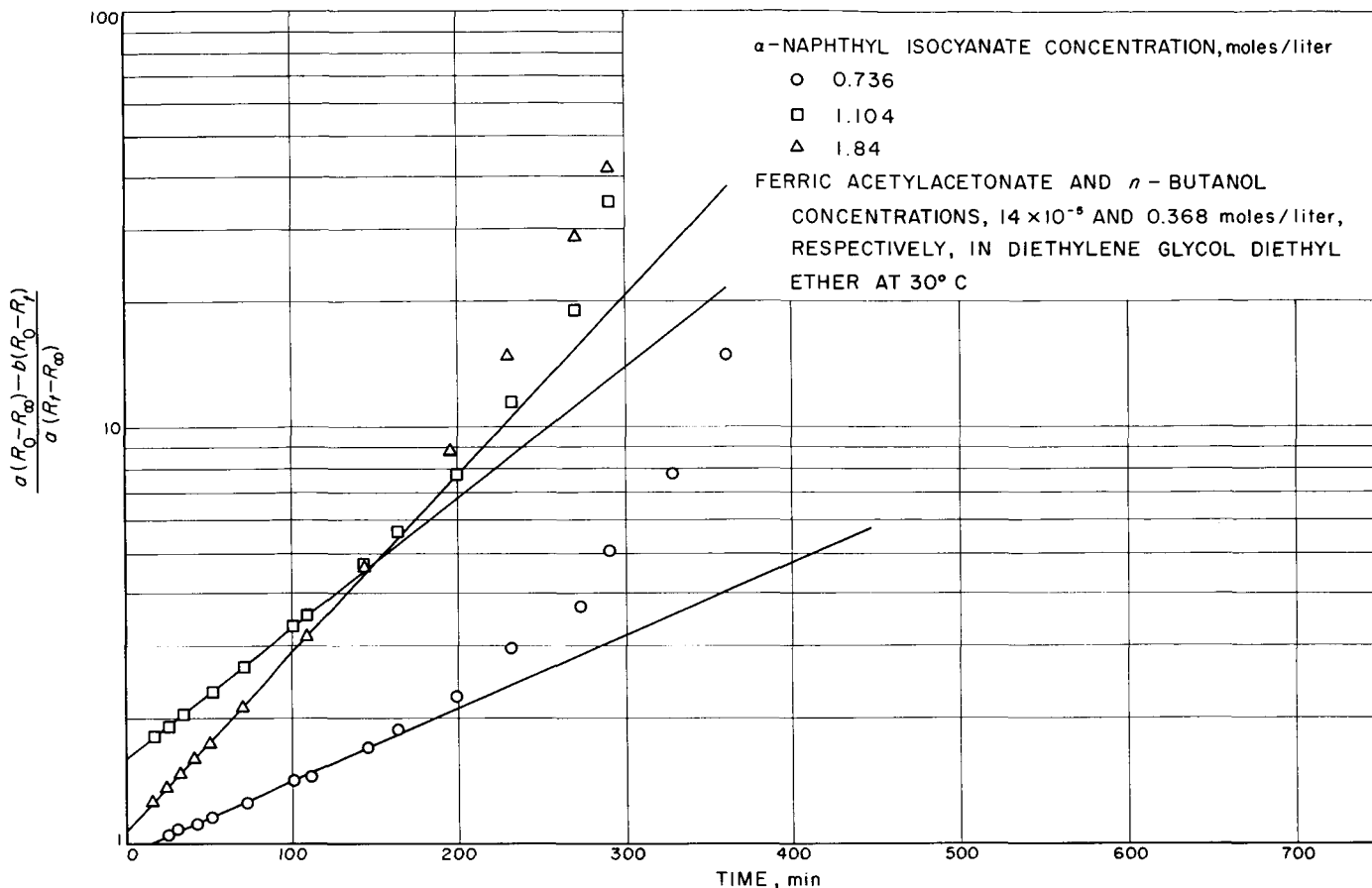


Fig. 3. Second-Order Integrated Rate Curves for the Reaction of *n*-Butyl Alcohol with Several Concentrations of α -Naphthyl Isocyanate

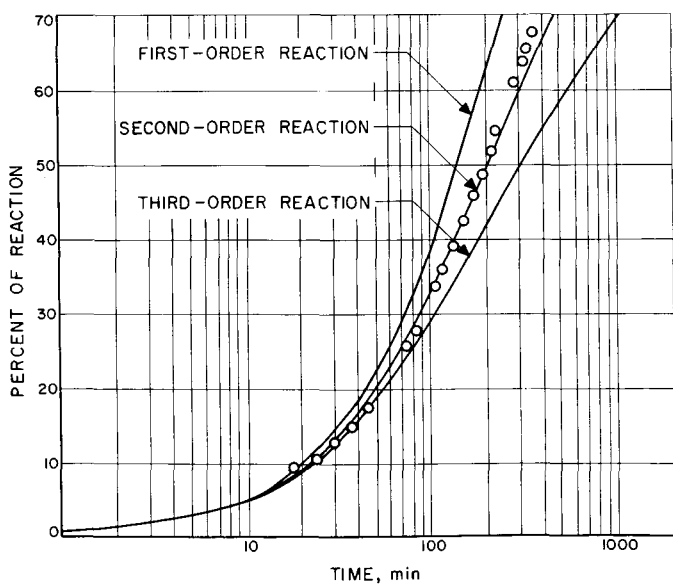


Fig. 4. Powell Plot for Ferric Acetylacetonate Catalyzed Reaction of α -Naphthyl Alcohol with *n*-Butyl Alcohol

second-order reaction as expressed by Eq. (18). Except at low catalyst concentrations, the intercept cannot be used to accurately evaluate k_0 , presumably because the spontaneous reaction is swamped by the much faster catalyzed reaction. It is important to note at this point that the integrated second-order curves were linear for at least 30% reaction for all data reported.

Similar data obtained for ortho- and para-tolyl isocyanates, although less extensive, behaved in the same manner. Values of k_c for all reactions investigated are tabulated in Tables 1 through 3.

From the plot of $\log k_c$ against $1/T$ (Fig. 6) an activation energy of 7.05 kcal/mole is obtained for the catalyzed reaction of α -naphthyl isocyanate and *n*-butyl alcohol.

The possibility that the catalytic activity of ferric acetylacetonate might arise by interaction of alcohol or isocyanate with the catalyst was investigated by means of distribution studies in which isocyanate and alcohol were

Table 1. Ferric Acetylacetonate Catalyzed Reaction of α -Naphthyl Isocyanate with *n*-Butyl Alcohol

Catalyst moles/liter $\times 10^5$	Alcohol moles/liter	Isocyanate moles/liter	Temperature $^{\circ}\text{C}$	$k \times 10^4$ liter mole $^{-1}$ sec $^{-1}$	k_c liter 2 mole $^{-2}$ sec $^{-1}$
2.8	0.368	0.368	20.0	0.24	
14.0	0.368	0.368	20.0	0.54	0.25
28.0	0.368	0.368	20.0	0.84	
1.4	0.368	0.368	30.0	1.61	
2.8	0.368	0.368	30.0	1.88	2.41
5.6	0.368	0.368	30.0	2.89	
14.0	0.368	0.368	30.0	4.67	
1.4	0.368	0.368	40.0	1.56	
5.6	0.368	0.368	40.0	7.06	5.0
14.0	0.368	0.368	40.0	17.5	
1.4	0.368	0.368	50.0	2.56	
5.6	0.368	0.368	50.0	11.8	20.8
14.0	0.368	0.368	50.0	29.5	
1.4	0.368	0.368	60.0	7.41	
2.8	0.368	0.368	60.0	15.8	63.4
5.6	0.368	0.368	60.0	34.3	
1.4	0.368	0.368	69.5	3.68	
2.8	0.368	0.368	69.5	10.0	320.0
5.6	0.368	0.368	69.5	101.0	
1.4	0.736	0.368	30.0	1.88	
1.4	1.840	0.368	30.0	1.11	
1.4	3.680	0.368	30.0	0.72	
1.4	0.368	0.736	30.0	2.89	
1.4	0.368	1.104	30.0	2.91	
1.4	0.368	1.840	30.0	3.10	
1.4	0.368	0.736	50.0	2.74	
1.4	0.368	1.104	50.0	2.03	
1.4	0.368	1.840	50.0	1.45	
1.4	0.736	0.368	50.0	2.69	
1.4	1.104	0.368	50.0	2.19	
1.4	1.840	0.368	50.0	1.58	

Table 2. Ferric Acetylacetonate Catalyzed Reaction of *ortho*-Tolyl Isocyanate with *n*-Butyl Alcohol

Catalyst moles/liter $\times 10^5$	Alcohol moles/liter	Isocyanate moles/liter	Temperature $^{\circ}\text{C}$	$k \times 10^4$ liter mole $^{-1}$ sec $^{-1}$	k_c liter 2 mole $^{-2}$ sec $^{-1}$
1.4	0.368	0.368	20.0	0.31	
1.4	0.368	0.368	30.0	0.52	
2.8	0.368	0.368	30.0	0.59	0.23
8.4	0.368	0.368	30.0	0.80	
14.0	0.368	0.368	30.0	1.20	
1.4	0.368	0.736	30.0	0.65	
1.4	0.368	1.104	30.0	0.97	
1.4	0.368	1.472	30.0	0.96	
1.4	0.736	0.368	30.0	0.56	
1.4	1.104	0.368	30.0	0.44	
1.4	1.472	0.368	30.0	0.41	
1.4	0.368	0.736	50.0	0.66	
1.4	0.368	1.104	50.0	0.43	
1.4	0.368	1.840	50.0	0.31	
2.8	0.736	0.368	50.0	0.93	
2.8	1.104	0.368	50.0	0.66	
2.8	1.840	0.368	50.0	0.58	
1.4	0.368	0.368	50.0	0.72	
2.8	0.368	0.368	50.0	1.90	4.51
8.4	0.368	0.368	50.0	3.40	
14.0	0.368	0.368	50.0	6.80	
1.4	0.368	0.368	60.0	0.76	
1.4	0.368	0.368	70.0	1.25	

Table 3. Ferric Acetylacetonate Catalyzed Reaction of para-Tolyl Isocyanate with n-Butyl Alcohol

Catalyst moles/liter x 10 ⁵	Alcohol moles/liter	Isocyanate moles/liter	Temperature °C	k x 10 ⁴ liter mole ⁻¹ sec ⁻¹	k _c liter ² mole ⁻² sec ⁻¹
1.4	0.368	0.368	20.0	3.56	26.0
1.4	0.368	0.368	30.0	3.89	
2.8	0.368	0.368	30.0	7.59	
8.4	0.368	0.368	30.0	23.9	
14.0	0.368	0.368	30.0	36.8	
1.4	0.368	0.736	30.0	4.86	
1.4	0.368	1.104	30.0	3.69	
1.4	0.368	1.472	30.0	3.23	
1.4	0.736	0.368	30.00	4.81	
1.4	1.104	0.368	30.0	3.66	
1.4	1.472	0.368	30.0	3.26	
0.7	0.368	0.368	50.0	2.71	36.3
2.8	0.368	0.368	50.0	10.1	
8.4	0.368	0.368	50.0	30.6	
0.7	0.368	0.736	50.0	2.97	
0.7	0.368	1.104	50.0	2.08	
0.7	0.368	1.472	50.0	1.74	
0.7	0.736	0.368	50.0	11.8	
0.7	1.104	0.368	50.0	9.67	
0.7	1.840	0.368	50.0	7.69	
1.4	0.368	0.368	60.0	5.61	
1.4	0.368	0.368	70.0	6.67	

distributed between two immiscible solvents, nitromethane and iso-octane, in the presence of varying amounts of ferric acetylacetonate, which was largely in the nitromethane layer. The amount of ferric acetylacetonate present in each layer was determined colorimetrically; isocyanate was determined by the amine-equivalent method (cf. Ref. 9); and alcohol was determined by acetylation (cf. Ref. 10).

Table 4. Exponents of Catalyst, Isocyanate, and Alcohol Concentration

Temperature °C	Catalyst	Isocyanate	Alcohol
α-Naphthyl Isocyanate			
20.0	0.60		
30.0	0.57	0.96	0.96
40.0	0.62		
50.0	0.69	0.98	0.95
60.0	0.61		
69.5	0.57		
ortho-Tolyl Isocyanate			
30.0	0.73	0.93	0.99
50.0	0.81	0.96	1.03
para-Tolyl Isocyanate			
30.0	0.50	1.01	0.93
50.0	0.62	0.95	0.96

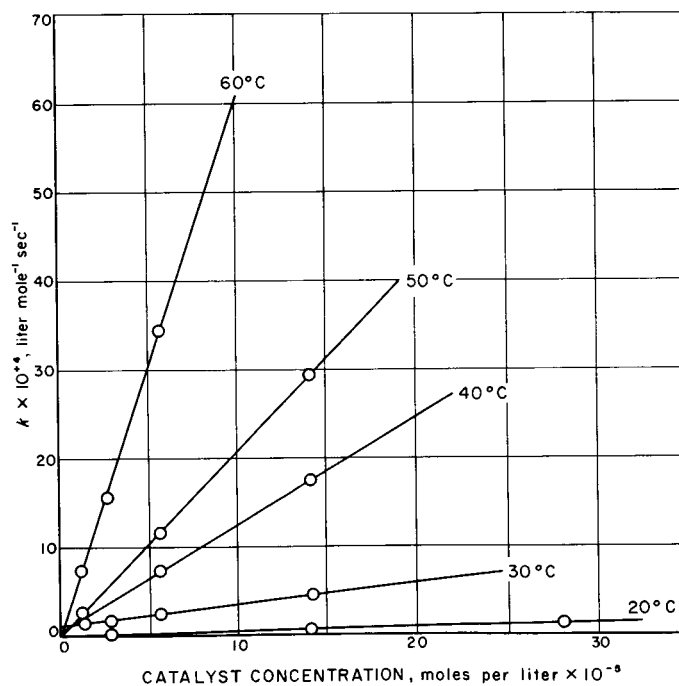


Fig. 5. Evaluation of k, for the Ferric Acetylacetonate Catalyzed Reaction of α-Naphthyl Isocyanate and n-Butyl Alcohol at Several Temperatures

A similar experiment was carried out in which ferric acetylacetonate, ethyl isocyanate, and n-butyl alcohol in iso-octane solution were studied alone and in combination by means of their ultraviolet and infrared absorption spectra. No evidence of interaction between ferric acetyl-

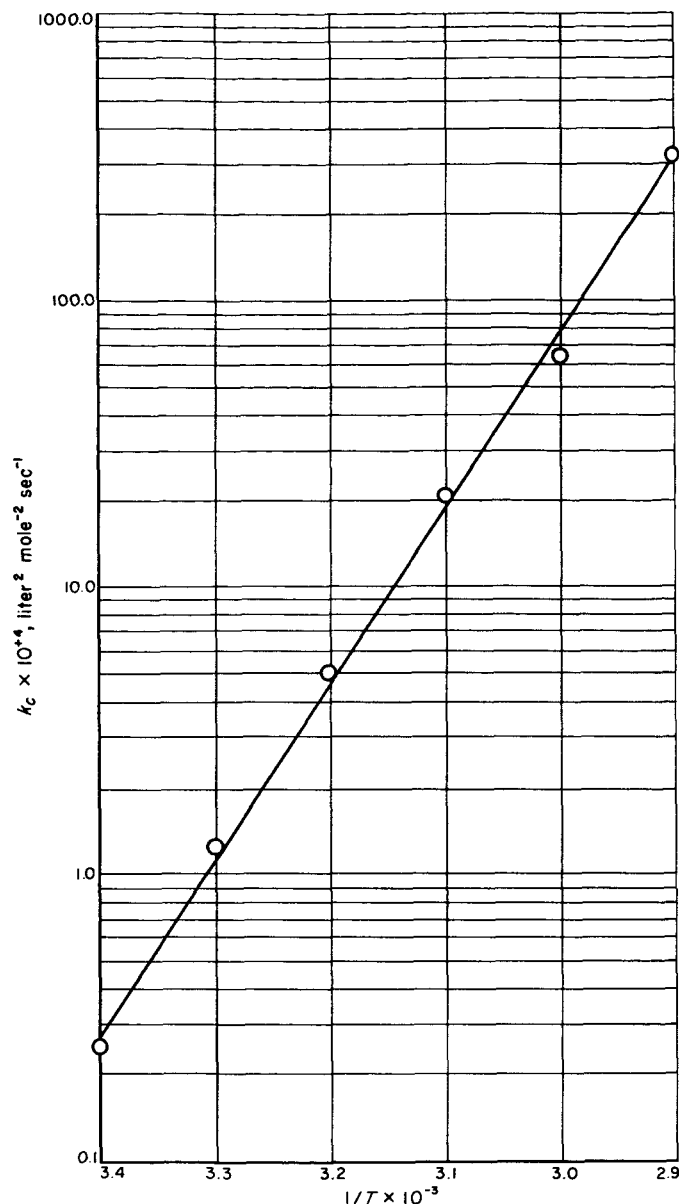


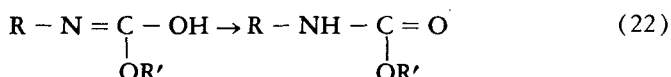
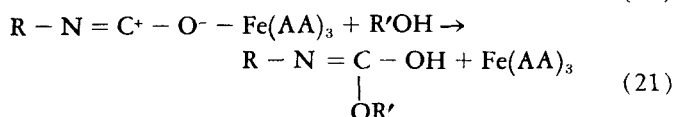
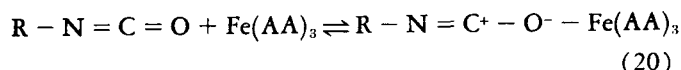
Fig. 6. Temperature Dependence of the Ferric Acetylacetonate Catalyzed Reaction Between α -Naphthyl Isocyanate and *n*-Butyl Alcohol

acetone and the reactants was found in either experiment. Although these experiments were unsuccessful insofar as they did not demonstrate association between reactants and catalyst, they do indicate that if such associations occur it is very slight and that the magnitude of K_{eq} in Eq. (16) must be very small.

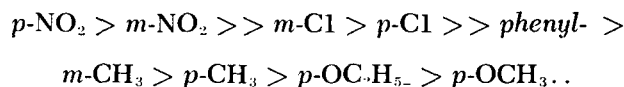
Another possibility which could conceivably contribute to the ferric acetylacetonate catalyzed kinetics of urethane formation was the dimerization of isocyanate in the pres-

ence of ferric acetylacetonate. In separate experiments, dimerization of isocyanate in the presence of ferric acetylacetonate was demonstrated by heating samples of α -naphthyl isocyanate in a 1 wt % solution of ferric acetylacetonate in diethylene glycol diethyl ether overnight at 70°C. A precipitate formed that was identified to be the dimer by elemental analysis and determination of amine equivalent. However, no evidence was found to indicate that dimerization was a significant side reaction in the presence of alcohol since no precipitate insoluble in diethylene glycol diethyl ether was observed.

The kinetic data are consistent with a mechanism analogous to an acid-catalyzed aldol condensation.



Such a mechanism is consistent with the observation that the rate of reaction is increased by introduction of electron-attracting groups into the aromatic ring of the isocyanate. Thus, from Table 6 can be seen that the order of reactivity



decreases in order of decreasing electron-attracting strength. The observation that aliphatic and cyclohexyl isocyanates are less reactive than aromatic isocyanates (cf. Ref. 4), presumably by removing the possibility of conjugation with the isocyanate group, further substantiates the importance of considering resonance concepts in the reaction mechanism.

The lesser dependence of the reaction rate on the nature of electrons-attracting groups of the alcohol (see Table 5) is likewise in agreement with the proposed mechanism. As would be expected, steric effects play a relatively more important role.

In general, the relative reactivity of isocyanates has been found to be considerably less in polar solvents such as nitrobenzene. For example, the second-order rate constant for the reaction of α -naphthyl isocyanate and *n*-butyl alcohol is 1.88×10^{-4} liter mole⁻¹ sec⁻¹ in diethylene glycol diethyl ether as compared with 0.32×10^{-4} for the same

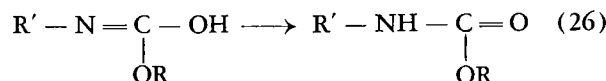
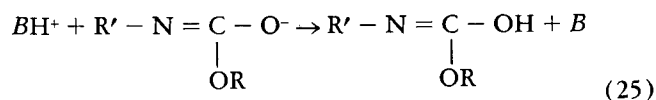
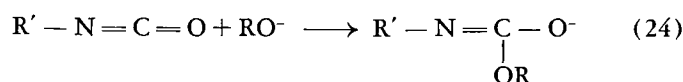
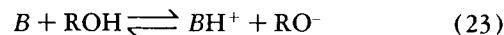
Table 5. Rate of Reaction of Substituted Alcohol with α -Naphthyl Isocyanate*

Alcohol	$k \times 10^4$ liter mole ⁻¹ sec ⁻¹
Methyl	16.20
Ethyl	9.51
<i>n</i> -Butyl	6.50
<i>n</i> -Hexyl	6.23
3-Bromo-1-propanol	1.85
3-Chloro-1-propanol	1.72
2-Bromo-1-ethanol	1.57
2-Chloro-1-ethanol	1.39
Sec-butyl	1.87
Tert-butyl	0.09

*In all experiments the concentrations of isocyanate, alcohol, and ferric acetylacetonate were 0.368, 0.368, 1.4×10^{-5} moles/l, respectively. All reactions were carried out in diethylene glycol diethyl ether solution at 30.0°C.

reaction in nitrobenzene. In both cases the reaction was carried out at 30°C with equal concentrations of alcohol and isocyanate (0.368 mole/liter) and a catalyst concentration of 2.8×10^{-5} moles/liter. This is further indirect evidence for the participation of a polar intermediate in the reaction mechanism.

In the same way, the base-catalyzed reaction between alcohols and isocyanates (cf. Ref. 4 through 7) may be considered as a base-catalyzed aldol condensation. Here the basic (proton-accepting) reagent must function in a different way (cf. Ref. 11) from that in the acid-catalyzed mechanism.



where B is any proton-accepting reagent.

Here the same dependence of reaction rate on the possibility of resonance in the isocyanate molecule should be required, and this was in fact found to be the case by Baker et al. However, the base-catalyzed aldol condensation mechanism differs from the acid-catalyzed mechanism in two important respects. First, it requires that the reaction rate be dependent on the nature of the alcohol, i.e., the acid strength of the alcohol, since the functioning of the basic catalyst depends on the ease with which a H^+ can be donated by the alcohol. As was discussed previously (see Eq. 6), the value of k_1 was very dependent on the nature of the alcohol, although the mechanism proposed by Baker et al did not predict behavior. Furthermore, the deviation was in the order methanol > ethanol > isopropanol which is predicted by decreasing order of acid strength of the alcohols which should be a determining factor in the base-catalyzed aldol condensation. Secondly, Baker et al (cf. Ref. 6) have shown an interaction between the tertiary amine catalyst and alcohol by means of infrared absorption studies, whereas no interaction between amine and isocyanate was demonstrated.

III. DEPENDENCE OF RATE OF URETHANE FORMATION ON STRUCTURE OF REACTANTS

A. Substituted Isocyanates

The data of Baker and Gaunt (cf. Ref. 4) for the base-catalyzed reaction suggested the possibility of correlating the effect of isocyanate substituents on reaction rate by means of the well-known Hammett equation

$$\log \frac{k}{k_0} = \sigma \rho$$

where k and k_0 may be either the rate or equilibrium constants for reactions of the substituted and reference unsubstituted compounds, respectively, σ is the substituent constant which depends on the nature and position of the substituent, and ρ is a constant which depends on the type of reaction.

In this Report, equivalent concentrations of various isocyanates were reacted under identical conditions with *n*-butyl alcohol employing both ferric and vanadous acetylacetonate catalysis. The experimental results are presented in Table 6. The correlation between meta- and para-substituted isocyanates and the observed reaction

Table 6. Rate of Reaction of Substituted Isocyanates with *n*-Butyl Alcohol

Isocyanate	Acetylacetonate Catalyst $k \times 10^4$ liter mole ⁻¹ sec ⁻¹	
	Ferric	Vanadous
Phenyl	39.2	12.9
<i>o</i> -Tolyl	3.31	2.08
<i>m</i> -Tolyl	33.9	9.85
<i>p</i> -Tolyl	10.3	5.83
<i>o</i> -Methoxy	0.26	0.13
<i>p</i> -Methoxy	8.03	3.32
<i>o</i> -Ethoxy	3.26	0.76
<i>p</i> -Ethoxy	9.17	4.21
<i>o</i> -Chloro	29.2	5.76
<i>m</i> -Chloro	119.6	42.9
<i>p</i> -Chloro	100.0	27.2
<i>o</i> -Nitro	45.8	60.0
<i>m</i> -Nitro	583.3	87.6
<i>p</i> -Nitro	709.3	very slow
α -Naphthyl	9.65	118.2
2-Biphenyl	1.46	2.98
4-Biphenyl	0.06	very slow

*In all experiments the concentrations of isocyanate, *n*-butyl alcohol, and catalyst were 0.368, 0.368, and 2.4×10^{-5} moles/l, respectively. All reactions were carried out in diethylene glycol diethyl ether solution at 30.0°C.

rate by means of the Hammett equation is presented in Fig. 7. The slight deviation from linearity obtained in the Hammett plot for the reaction of substituted isocyanates is commonly observed in plots of this type and is of no theoretical significance.

In general, the effect of meta and para substituents on an aromatic ring gives the following order of reactivity, $p\text{-NO}_2 > m\text{-NO}_2 \gg m\text{-Cl} > p\text{-Cl} \gg \text{phenyl} > m\text{-CH}_3 > p\text{-CH}_3 > p\text{-OC}_2\text{H}_5 \cong p\text{-OCH}_3$. This order of reactivity

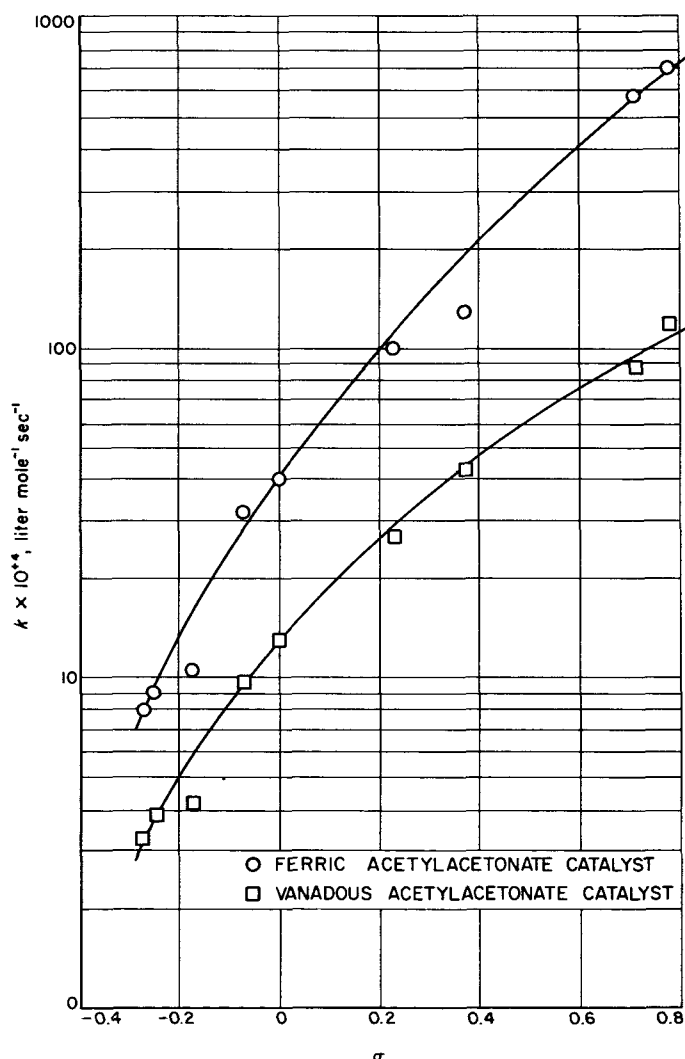


Fig. 7. Hammett Plot for Meta- and Para-Substituted Isocyanates

seems to be independent of the type of catalyst since the same relationship was obtained for both ferric and vanadous acetylacetonate. Furthermore, from the work of Baker and Gaunt (cf. Ref. 4) for the base-catalyzed reaction, it was found that the order of reactivity was $p\text{-NO}_2 \gg \text{phenyl} > p\text{-CH}_3 > p\text{-OCH}_3$ which is also in line with our more extensive order of reactivity.

For the ortho-substituted aromatic isocyanates the order of reactivity is $o\text{-NO}_2 \gg o\text{-Cl} \gg o\text{-OC}_2\text{H}_5 \cong o\text{-CH}_3$ which is similar to that found for the meta and para substituents except for the reversal between $o\text{-CH}_3$ and $o\text{-OCH}_3$ which is probably due to the greater steric hindrance of the methoxyl group. In general, the reactivity order for ortho, meta, and para substituents is meta $>$ para $>$ ortho.

B. Substituted Alcohols

It is interesting to note that Baker and Gaunt (cf. Ref. 5) find an order of reactivity for alcohols in which methyl $>$ ethyl $>$ isopropyl $>$ tertiary butyl for the base-catalyzed reaction, which is identical to that observed for the ferric acetylacetonate catalyzed reaction. This order of reactivity was attributed to the increasing acid strength sequence methyl $>$ ethyl $>$ isopropyl $>$ tertiary butyl alcohol derived from the general inductive effects of alkyl groups.

It is probable that the experimentally observed orders of alcohol reactivity are influenced by both steric and

inductive effects, hence a quantitative correlation was not attempted.

C. Metal Chelate Catalysts

Equivalent concentrations of *n*-butyl alcohol and several isocyanate were reacted under identical conditions with several types of metal catalysts. These data are presented in Table 7.

In general, wide variations in catalytic activity were obtained among the metal chelates tested. The ferric acetylacetonate commonly employed for catalysis of polyurethane polymerization is seen to fall in the intermediate range of activity among the metal chelates tested. Toluene diisocyanate was included in these experiments because of its importance in our polyurethane resin program. For particular applications in which the rate of polymerization is critical, it may be advantageous to have at hand supplementary data from which to choose alternative suitable catalysts.

The catalytic activity of the metal acetylacetonates tested cannot be correlated with any of the simple properties of the metal ion such as radius or charge. It is interesting to note that cyclopentadienyl iron, which is nonionic, shows almost no catalytic activity, making it seem likely that an ionic metal chelate is required for catalytic activity.

Table 7. Rate of Reaction of Isocyanates with *n*-Butyl Alcohol Catalyzed by Various metal Chelates*

Catalyst	2, 4-Toluene Diisocyanate $k \times 10^4 \text{ liter mole}^{-1} \text{ sec}^{-1}$	Hexamethylene Diisocyanate $k \times 10^4 \text{ liter mole}^{-1} \text{ sec}^{-1}$	<i>o</i> -Tolyl $k \times 10^4 \text{ liter mole}^{-1} \text{ sec}^{-1}$	<i>p</i> -Tolyl $k \times 10^4 \text{ liter mole}^{-1} \text{ sec}^{-1}$
Acetylacetonates				
Ferric	8.75	4.83	3.31	10.3
Vanadous	6.38	4.28	2.08	5.83
Cuprous	12.9		7.21	16.5
Cupric	11.9			
Nickelous	12.9		6.3	18.9
Chromic	5.55		2.39	10.6
Plumbous	7.42			
Cobaltic	9.52			
Cobaltous	3.93			
Ferrous	11.9			
8-Quinolinolates				
Ferric	7.73			
Cuprous	7.42			
Naphthenates				
Iron	3.23			
Lead	9.52			
Dicyclopentadienyl Iron	0.34			

*In all experiments the concentrations of isocyanate, *n*-butyl alcohol, and catalyst were 0.368, 0.368, and 2.4×10^{-5} moles/l, respectively. All reactions were carried out in diethylene glycol diethyl ether at 300°C.

IV. CONCLUSIONS

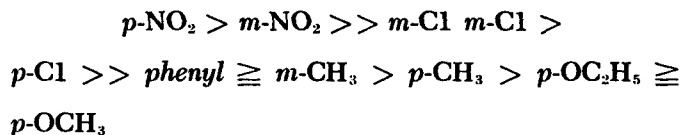
The kinetics of urethane formation are satisfactorily treated by taking into consideration the contribution of the uncatalyzed reaction to the catalyzed reaction. The most likely mechanism for the reaction involves a catalyzed reaction in which catalyst associates with isocyanate to form a reactive intermediate which then reacts with alcohol to form urethane product. The kinetics are complicated by the simultaneous uncatalyzed reaction of isocyanate and alcohol to form urethane.

The differential equation derived from this mechanism which represents the rate of formation of urethane product is

$$\frac{d(\text{product})}{dt} = (k_0 + k_c [\text{Fe}(\text{AA})_3]) [\text{RNCO}] [\text{ROH}]$$

An activation energy of 7.05 kcal/mole calculated from this equation is reasonable and consistent with reported values for similar reactions.

Rates of reaction for meta- and para-substituted aromatic isocyanates are correlated by means of the Hammett equation. It is found that the isocyanates show the following order of reactivity for both ferric and vanadous acetylacetonate catalyzed reactions:



In general, ortho-substituted aromatic isocyanates show a similar order of reactivity but are much slower because of steric effects.

Some data are given showing the influence of alcohol and catalyst on the rate of reaction, but no quantitative correlations were possible.

REFERENCES

1. Magnusson, A. B., Ingham, J. D., and Nichols, P. L., Jr., *Polyurethane Resins as Binders for Composite Propellants*, Progress Report No. 20-64, Jet Propulsion Laboratory, Pasadena, July 15, 1955 (Confidential).
2. Dyer, E., Taylor, H. S., Mason, S. J., and Samson, J., "The Rates of Reaction of Isocyanates with Alcohols. I. Phenyl Isocyanate with 1- and 2-Butanol," *Journal of the American Chemical Society*, 71:4106-4110 (1949).
3. Baker, J. W., and Gaunt, J., "The Mechanism of the Reaction of Aryl Isocyanates with Alcohols and Amines. Part III. The Spontaneous Reaction of Phenyl Isocyanate with Various Alcohols," *Journal of the American Chemical Society*, 19-24 (1949).
4. Baker, J. W., and Holdsworth, J. B., "The Mechanism of Aromatic Side-Chain Reaction with Special Reference to the Polar Effects of Substituents. Part XIII. Kinetic Examination of the Reaction of Aryl Isocyanates with Methyl Alcohol," *Journal of the American Chemical Society*, 713-726 (1947).
5. Baker, J. W., and Gaunt, J., "The Mechanism of the Reaction of Aryl Isocyanates with Alcohols and Amines. Part II. The Base-catalyzed Reaction of Phenyl Isocyanate with Alcohols," *Journal of the American Chemical Society*, 9-18 (1949).
6. Baker, J. W., Davies, M. M., and Gaunt, J., "The Mechanism of the Reaction of Aryl Isocyanates with Alcohols and Amines. Part IV. The Evidence of Infra-red Absorption Spectra Regarding Alcohol-Amine Association in the Base-catalyzed Reaction of Phenyl Isocyanate with Alcohols," *Journal of the American Chemical Society*, 24-27 (1949).
7. Baker, J. W., and Gaunt, J., "The Mechanism of the Reaction of Aryl Isocyanates with Alcohols and Amines. Part V. Kinetic Investigations of the Reaction Between Phenyl Isocyanate and Methyl and Ethyl Alcohols in Benzene Solution," *Journal of the American Chemical Society*, 27-31 (1949).
8. *Handbook of Chemistry and Physics*, 30th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio (1947).
9. Monsanto Technical Bulletin, No. P-125, March, 1953.
10. Siggia, S., *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., New York, 1949.
11. Barnett, E., *Mechanism of Organic Chemical Reactions*, Interscience Publishers, Inc., New York, 1956.